

Modified MCM-41 Silica Spheres Filled Polydimethylsiloxane Membrane for Dimethylcarbonate/Methanol Separation via Pervaporation

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ABSTRACT: Inorganic–organic hybrid membrane materials always exhibit high pervaporation performance for organic azeotropic mixtures. Here, MCM-41 silica spheres were modified and embedded into polydimethylsiloxane, and a new filled membrane was obtained. The membrane was used in dimethylcarbonate (DMC) removal from DMC/methanol azeotropic mixture by pervaporation. The effect of membrane preparation parameters including modified MCM-41 silica spheres loading, solvent concentration, and feed temperature on pervaporation properties was systematically studied. The results showed that separation factor and total flux of the filled membranes could be increased simultaneously. Additionally, the sorption and diffusion selectivity of the filled membranes were measured and discussed. The results demonstrated that diffusion selectivity was greatly enhanced by incorporating. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: MCM-41 sphere; polydimethylsiloxane; dimethylcarbonate; methanol; pervaporation

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INTRODUCTION

Dimethylcarbonate (DMC) has been regarded as a green chemical material and represents many attractive practical applications in chemical and petrochemical industries owing to its degradability and nontoxic properties.^{1,2} But during its manufacture, conventional methods of separating DMC from DMC/methanol (MeOH) azeotropic mixture (at a weight ratio of 30 : 70 under normal pressure) require too much capital investment, operation costs, and energy consumption.^{3,4} It is well-known that pervaporation (PV)⁵ is an energy-saving separation technology for such organic azeotropic mixtures because of lower energy demands, less environmental pollution and, most important, no vapor–liquid equilibrium (VLE) limitation.

Separating DMC/MeOH azeotropic mixture by PV can be realized by using either MeOH-permselective membranes or DMC-permselective membranes. So far, several hydrophilic MeOH-permselective membranes such as chitosan,⁶ poly(vinyl alcohol),⁷ and so on have been reported. Their PV performances may be acceptable. However, two problems are horrible especially for industrial application. First, 70 wt % MeOH has to be penetrated and vaporized, and the latent heat of vaporization for MeOH (1073.6 kJ mol⁻¹) is much higher than that for DMC (381.4 kJ mol⁻¹).⁸ These result in severe energy expenditure and depart from the aim of energy saving by PV. Second, swelling degree (SD) was found to be more

than 10 wt % (in DMC/MeOH azeotropic mixture) in most MeOH-permselective membranes,^{6,7,9} which could seriously affect its operation durability. These two aspects make MeOH-permselective membrane difficult to be adopted in industrial application. Compared with MeOH-permselective membrane, DMC-permselective membrane may be difficult to design, but it is more stable and energy saving. However, as far as we know, there are few reports on these kinds of membranes.

In our previous work, hydrophobic silicon dioxide (SiO₂) silica-filled polydimethylsiloxane (PDMS) membrane has been reported for DMC permselective.¹⁰ It was demonstrated that operation durability and selectivity of the membrane could be greatly increased by SiO₂ silica incorporation, but the total flux decreased because SiO₂ silica was nonporous and physical cross-linking was increased. To improve selectivity and total flux simultaneously, maybe we could introduce some porous particles into the membrane to provide preferential channels for DMC permeation.

Many microporous molecular sieves (ZSM-5, silitelite-1, TS-1, and so on) have been commonly used as inorganic porous fillers for alcohol recovery and displayed outstanding PV performances.^{11,12} However, these microporous molecular sieves cannot be used to remove DMC from DMC/MeOH azeotropic mixture because their pore sizes are too small for DMC permeation.

Since 1992, MCM-41 was reported as a new member of M41S ordered mesoporous silica by Kresge et al.¹³ It has become the most popular member of M41S mesoporous silica because of its hexagonal arrangement of uniform mesopores, highly specific surface (up to 1500 m² g⁻¹), adjustable pore diameter (2–10 nm), and varied surface hydroxyl group for modification. Furthermore, Unger's group¹⁴ successfully prepared MCM-41 silica spheres with regular shape and size by modified Stöber method, which make them more competitive in many different fields such as adsorbents, catalysts, and stationary phases in chromatography.^{15–17}

In this study, MCM-41 silica spheres were modified and used as inorganic fillers of PDMS PV membranes, for DMC removal from DMC/MeOH azeotropic mixture. The effect of membrane preparation parameters such as modified mesoporous silica spheres kinds and loadings, solvent concentration, and feed temperature on membrane morphology, structure, and PV performance was systematically investigated. Furthermore, sorption and diffusion selectivity of the filled membranes were measured, and the results were discussed using sorption-diffusion mechanism.

EXPERIMENTAL

Materials

MCM-41 mesoporous silica spheres were synthesized in our laboratory using modified Stöber method.¹⁴ Cetyltrimethylammonium bromide (C₁₆TAB) was used as template, and tetraethoxysilane (TEOS) was hydrolyzed in mixed solutions of ammonia, ethanol, water and C₁₆TAB with a molar composition of 1 TEOS : 0.3 C₁₆TAB : 11 ammonia : 58 ethanol : 144 water. PDMS (RTV 615) was purchased from General Electric Silicones (Fairfield, Connecticut). Chlorotrimethylsilane (CTMS, 98%) and octyltrichlorosilane (OTCS, 97%) were supplied by Alfa Aesar (China). MeOH, ethanol, pyridine, and heptane were obtained from Beijing Chemical Reagents Corporation (China). DMC was received from Tangshan Chaoyang Chemical Reagents Corporation (China). Polyvinylidene fluoride (PVDF) ultrafiltration membrane was prepared in our laboratory.

Silylation of MCM-41 Silica Spheres

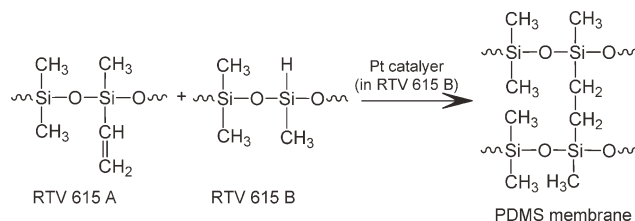
Silylation. In the presence of 10 mL pyridine, 10 g of calcined MCM-41 silica spheres (prepared according to modified Stöber method in our laboratory) and 10 g of chlorosilane reagents (CTMS or OTCS) were dispersed in 100 mL heptanes and stirred for 24 h. To remove the residual chlorosilane, this solution was washed with heptane for several times. Then, the obtained particles were dried overnight at 423 K under nitrogen (N₂) atmosphere. The resulted MCM-41 spheres modified with CTMS and OTCS were referred as M-MCM-41 and O-MCM-41, respectively. The structure of MCM-41, M-MCM-41, and O-MCM-41 spheres and the silylation mechanism were shown in Figure 1.

Characterization. The amount of the chlorosilane modified on MCM-41 silica spheres was evaluated with a thermogravimetric analyzer (Q-500T, TA instruments, New Castle, Delaware). Morphology of calcined and modified MCM-41 spheres were recorded by scanning electron micrographs (SEM; JSM-6301F, JEOL, Japan). The N₂ adsorption isotherms were measured

using an automatic N₂ adsorption apparatus (Nova 4000, Quantachrome Corporation, Boynton Beach, Florida) at 77.3 K.

Membrane Preparation and Properties

Preparation of MCM-41/PDMS Hybrid Membrane. PDMS (RTV 615) is a two-component system. Component A consists of a vinyl-terminated prepolymer with high molecular weight. Component B is a combination of crosslinker (containing several hydride groups on shorter PDMS chains¹⁸) and platinum catalyzer, which could react with component A by Pt-catalyzed hydrosilylation reaction to form dense polymer network. The reaction mechanism was as follows:



The MCM-41/PDMS hybrid membranes were prepared as follows. First, RTV 615 A was dissolved in heptane to make a 60 wt % solution, and then calcined MCM-41 was dispersed with vigorous stirring for 2 h. The obtained solution was placed in ultrasonic water bath for 1 h and then RTV 615 B was added. The weight ratio of RTV 615 A and B was fixed at 10 : 1.1. Then the suspension was stirred for another 2 h till a homogeneous suspension was formed. After degassing under vacuum for 15 min, the suspension was cast on a glass plate to form homogeneous membranes and on PVDF membranes to form composite membranes. These membranes were left at room temperature overnight to evaporate the solvent and then put into an oven at 100°C for 6 h to assure complete crosslinking.

Membrane Characterization. The surface and cross-section morphology of composite membrane were observed by SEM (JSM-6301F, JEOL, Japan). The mechanical property of calcined and modified MCM-41-filled PDMS membranes were measured using an tensile testing machine (AGS-J, Shimadzu Corporation, Japan) with a crosshead speed of 1 cm min⁻¹. The width of the sample was 1 cm, and the length between the jaws was approximately 5 cm.

Swelling Behavior and Sorption Experiments. The homogeneous membrane sample was dried at 60°C until the weight kept constant, carefully weighed, and then immersed into DMC/MeOH azeotropic mixture at 40°C until reaching a constant weight. To measure the swelling behavior of the membrane, the sample was carefully taken out, rapidly wiped, and quickly weighed. Swell degree (SD) of the membrane can be defined as:

$$\text{SD}(\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where W_s and W_d are weights of the swollen and dry membrane samples, respectively.

To measure sorption selectivity of the membrane, the sample was carefully taken out, rapidly wiped, and placed into a 200 mL round-bottom flask, which was kept at about 90°C until the

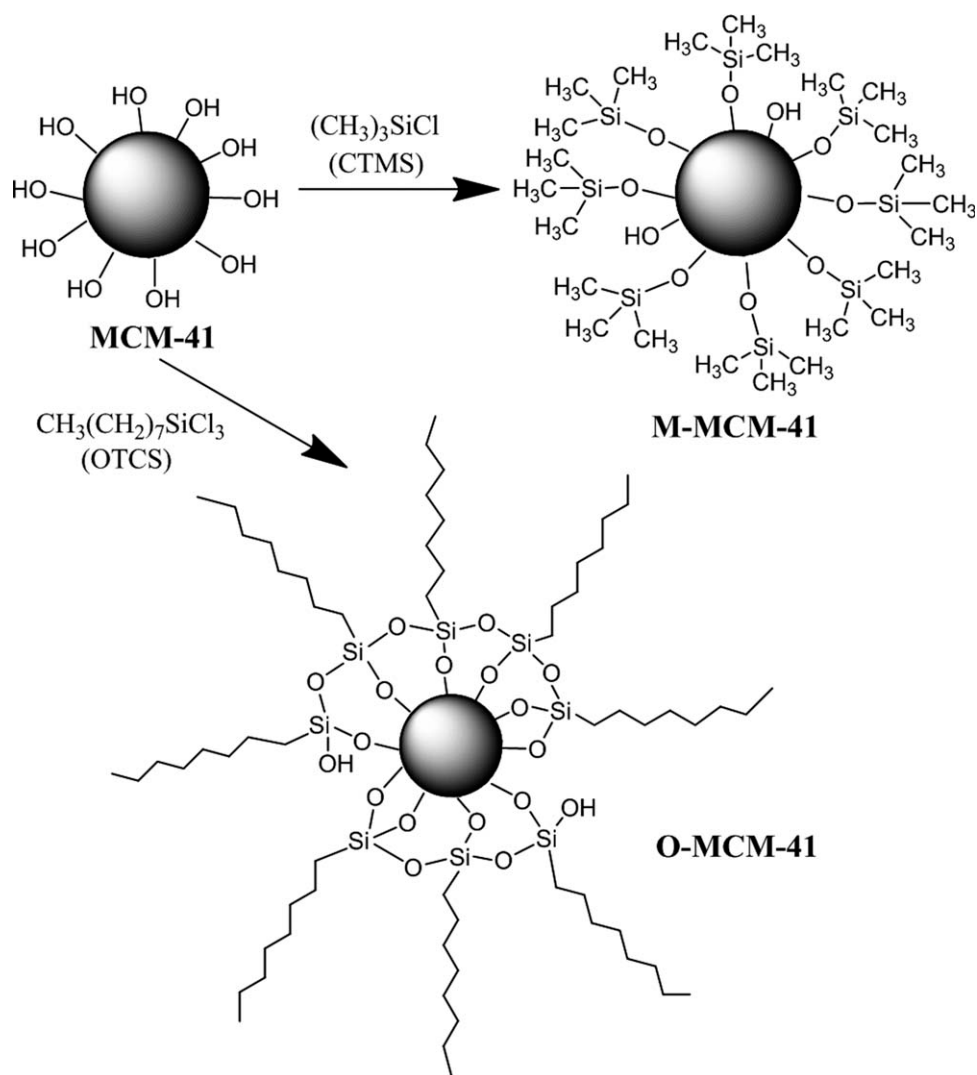


Figure 1. The structure of MCM-41, M-MCM-41, and O-MCM-41 spheres and the silylation mechanism.

absorbed liquid in the membrane was totally removed by a vacuum pump and condensed in a connected liquid nitrogen cold trap. The composition of the liquid was analyzed by gas chromatography (GC-14, Shimadzu Corporation, Japan). Based on the assumption that membrane thickness has nothing to do with its sorption selectivity, the thickness of membranes used in this experiment may exceed 3 mm to minimize the measurement error. All experiments were repeated at least three times, and the errors were less than 5%. Values reported here represent averages. The sorption selectivity α_s was calculated by:

$$\alpha_s = \frac{X_{\text{DMC}}/X_{\text{MeOH}}}{x_{\text{DMC}}/x_{\text{MeOH}}} \quad (2)$$

where x and X are weight fractions in feed and membrane, respectively. Diffusion selectivity (α_d) is calculated from separation factor (α) and sorption selectivity (α_s) using eq. (3), based on the solution-diffusion mechanism.

$$\alpha_d = \alpha/\alpha_s \quad (3)$$

Pervaporation Experiments. PV experiments were carried out using an apparatus developed in our laboratory. The membrane with surface area of 22.4 cm^2 was positioned in a stainless-steel permeation cell. Feed solution was circulated between feed tank and membrane upstream by a pump, and the feed temperature was monitored by a digital thermometer. PV experiments were carried out by maintaining atmospheric pressure on feed side and about 200 Pa using a vacuum pump on permeate side. After about 1 h, a steady state was obtained, and the permeate was collected in the cold trap and condensed by liquid nitrogen. The compositions of the feed and permeate solution were obtained by GC (GC-14, Shimadzu Corporation, Japan). The results were reproducible, and the inherent errors in the PV measurements were less than 2%. PV performances of the membranes can be evaluated on the basis of selectivity and total flux. The separation factor (α) of the membrane is obtained as follows:

$$\alpha = \frac{y_{\text{DMC}}/y_{\text{MeOH}}}{x_{\text{DMC}}/x_{\text{MeOH}}} \quad (4)$$

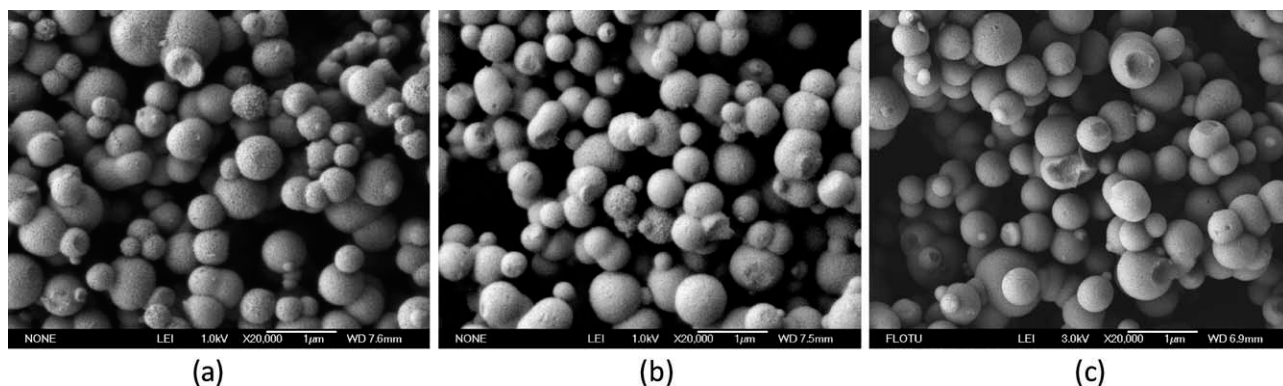


Figure 2. SEM images of (a) calcined MCM-41, (b) M-MCM-41, and (c) O-MCM-41.

where x and y represent the weight fraction of corresponding solute in feed and permeate, respectively. The permeate total flux J was determined by measuring the weight of permeate collected in the cold trap (W) and dividing this by time (t) and the membrane surface area (A) as shown in eq. (5):

$$J = \frac{W}{At} \quad (5)$$

Apparent activation energy (E_{pi}) is calculated using Arrhenius relationship as follows:

$$J_i = J_{0i} \exp\left(\frac{-E_{pi}}{RT}\right) \quad (6)$$

where J_i is the flux of component i , J_{0i} is the permeation rate constant, T is the feed absolute temperature, and R is the molar gas constant.

RESULTS AND DISCUSSION

Characterization of Modified MCM-41 Spheres

In this study, monofunctional chlorosilane (CTMS) and trifunctional chlorosilane with long alkyl (OTCS) were applied to alter

the surface properties of MCM-41 mesoporous silica spheres. It can be seen from the SEM images of calcined and modified MCM-41 spheres (Figure 2) that morphology of the spheres remains unchanged after modification. The amount of chlorosilane modified on MCM-41 spheres was evaluated by the

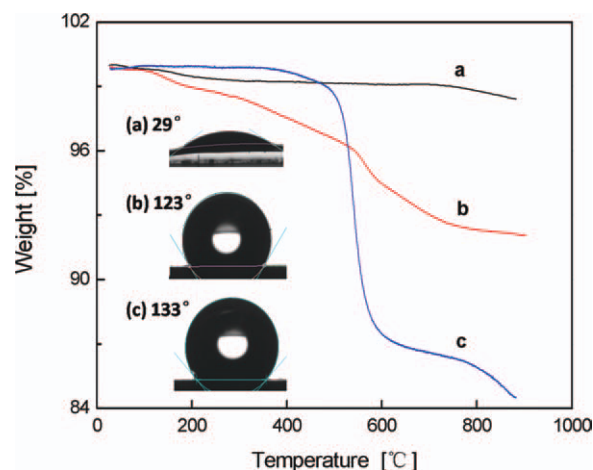


Figure 3. TGA curves and contact angle of (a) calcined MCM-41, (b) M-MCM-41, and (c) O-MCM-41. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

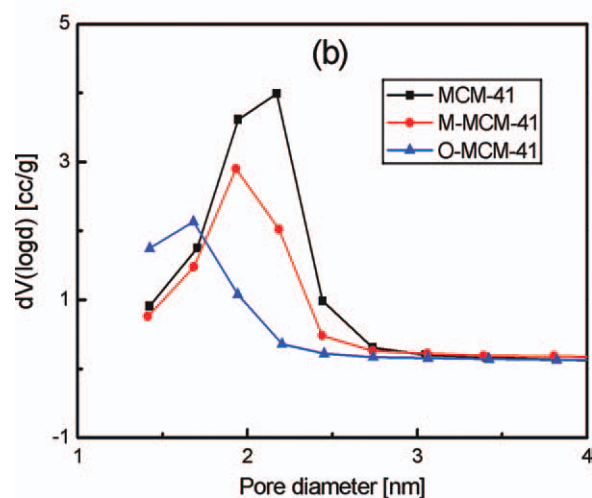
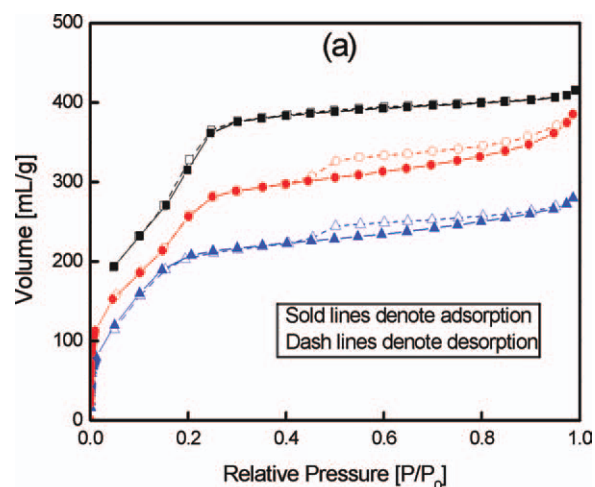


Figure 4. Nitrogen sorption isotherms (a) and BJH pore size distributions (b) for calcined and modified MCM-41 spheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

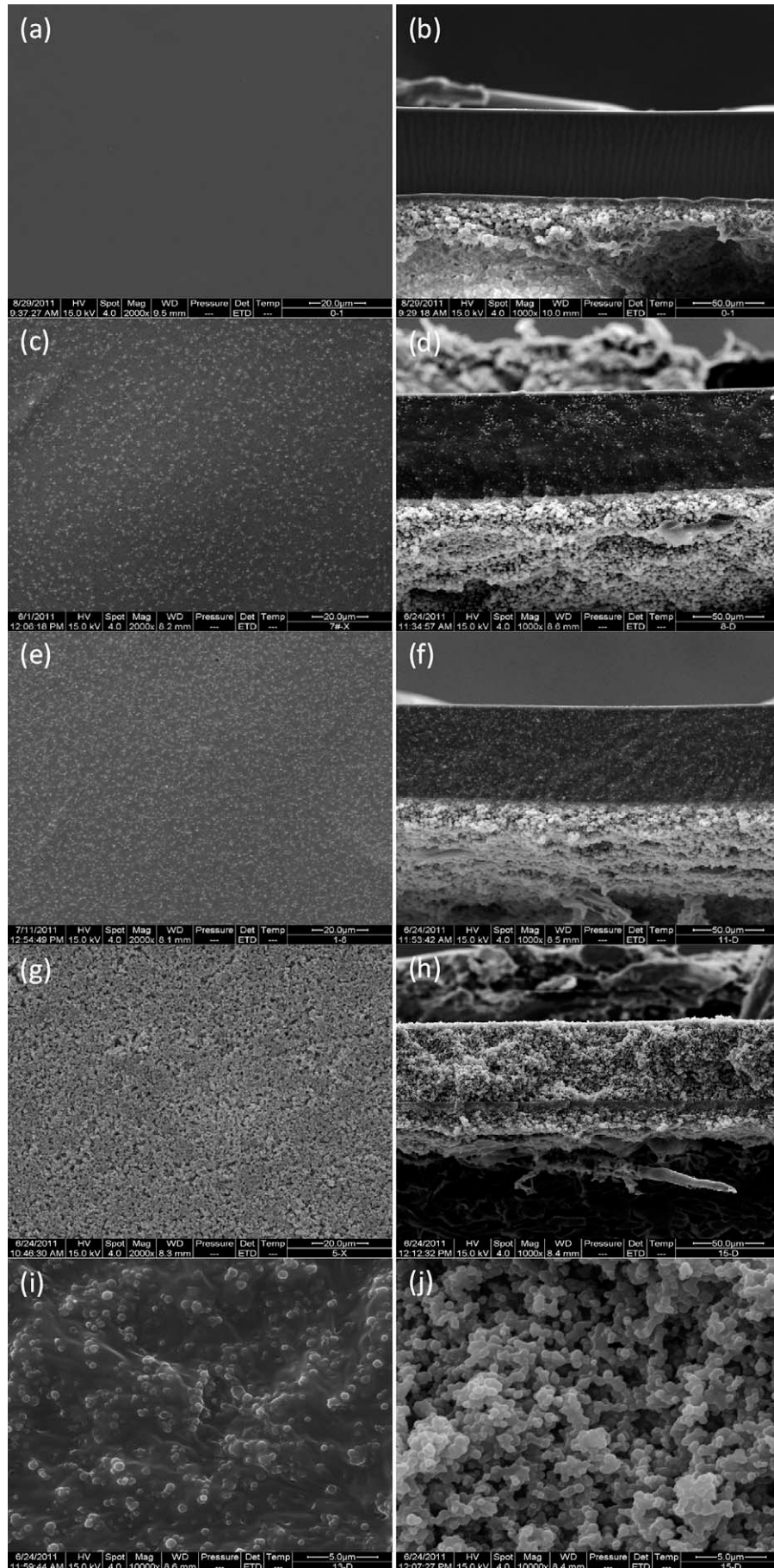


Figure 5. The surface and cross-section morphology of MCM-41/PDMS hybrid membranes with various MCM-41 contents (a, b) 0 wt %, (c, d) O-MCM-41 30 wt %, (e, f) O-MCM-41 50 wt %, (g, h) calcined MCM-41 50 wt %, (i) O-MCM-41 50 wt % (with high magnification), and (j) calcined MCM-41 50 wt % (with high magnification).

thermogravimetric (TGA) curves in Figure 3. The weight losses of O-MCM-41 between 500 and 600°C were attributed to the decomposition of OTCS. This degradation temperature was notably higher than the boiling point of OTCS (233°C), indicating that OTCS was not adsorbed but strongly covalently bonded to MCM-41 spheres.^{19,20} Owing to the monofunctional property of CTMS, its connection with MCM-41 was not as strong as OTCS, so the degradation temperature of M-MCM-41 was much lower and the TGA curve exhibited both adsorption and covalent bonding sections. However, contact angle results (as shown in Figure 3) indicated that a tuning of surface properties from hydrophilicity to hydrophobicity had been achieved by both CTMS and OTCS modification.

The amounts of N₂ adsorbed on MCM-41 spheres before and after silylation were shown in Figure 4. The overall appearance of all the nitrogen adsorption–desorption isotherms [Figure 4(a)] was very similar and exhibited typical type-IV curves,²¹ indicating the retained channel characteristics after modification. The lower adsorption plateau values reflected that BET surface area and pore volume both decreased following the trend of O-MCM-41 < M-MCM-41 < MCM-41, because of the reduced effective pore opening and the enhanced surface resistance to N₂ molecules.²² Similarly, according to the BJH analysis [Figure 4(b)], the pore size decreased with the same trend. All these results could demonstrate that the large pore size of mesoporous MCM-41 spheres enabled grafting both at the outer surface and within the pores. Most important, all these pores were large enough for DMC (6.8 Å) permeation.

However, hysteresis of type H³ could be detected on M-MCM-41 and O-MCM-41 spheres above the relative pressures of 0.4, suggesting the presence of a remained secondary mesoporosity.²³ This phenomenon indicated that not all the channels were full of grafted chlorosilane. In some cases, chlorosilane could only graft near the pore mouth region because of the steric hindrance.

Characterization and Pervaporation of Filled Membranes

Scanning Electron Microscope. Extensive work demonstrates that in preparation of inorganic/organic hybrid membranes, adhesion between inorganic particles and polymer matrix is of primary importance for good membrane performance.^{11,21} Aggregation of inorganic particles may lead to pinholes in the membrane, thus ruin its selectivity. The SEM of surface and cross-section of PDMS membranes with different unmodified MCM-41 or O-MCM-41 loadings are shown in Figure 5. As shown in Figure 5(g,h,i), hybrid membranes filled with unmodified MCM-41 (50 wt %) contained many interfacial voids around MCM-41 spheres. Comparatively, O-MCM-41 particles could disperse uniformly in PDMS membrane matrix even at a high loading of 50 wt % [see Figure 5(e,f,i)]. This was because a very hydrophobic silanized surface layer was formed after silylation and improved the interfacial adhesion of MCM-41 particle and the polymer.^{24,25} Moreover, the flexible PDMS chains could promote good contact with the surface of the inorganic particles. The cross-sectional micrographs clearly showed that the top layers were tightly and properly cast on the top of the PVDF substrate, with the thickness of about 75 ± 7 μm.

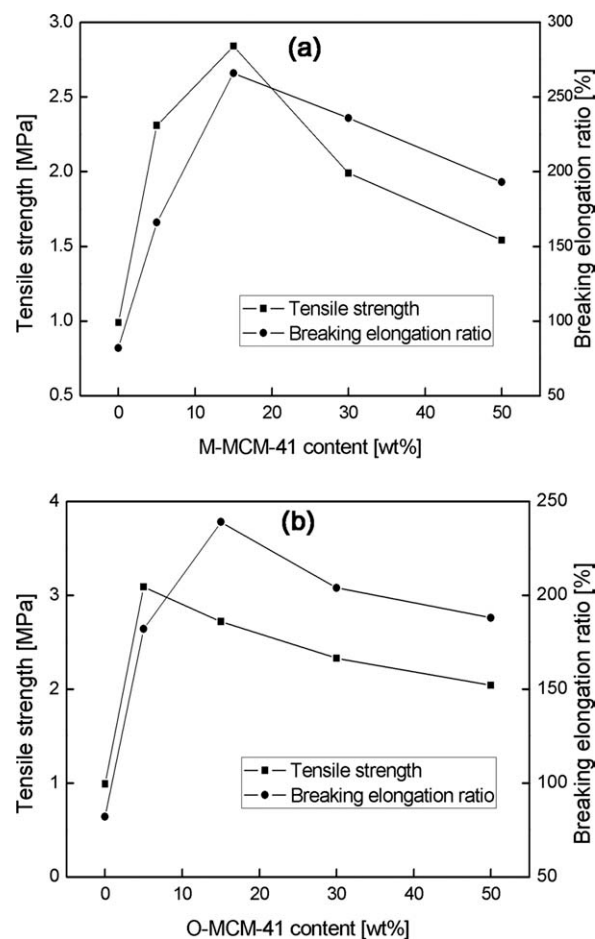


Figure 6. Effect of M-MCM-41 (a) and O-MCM-41 (b) content on the tensile strength and breaking elongation ratio of the filled membranes.

Mechanical Property. The effects of filler loadings on the mechanical properties of M-MCM-41- and O-MCM-41-filled PDMS membranes are shown in Figure 6. It could be seen that with increasing content of modified MCM-41, tensile strength and breaking elongation ratio of the membranes markedly increased at first but then decreased a little. However, the mechanical property of filled membranes is much better than that of pure PDMS membrane.

Membrane Swelling in DMC/MeOH Azeotropic Mixture. The effect of modified MCM-41 loading on membrane swelling behavior was investigated at 40°C in DMC/MeOH azeotropic mixtures. As mentioned above, there were plenty of channels in modified MCM-41 spheres, which were big enough for DMC and MeOH to enter. But it can be seen from Figure 7 that the SD decreased by the incorporation of modified MCM-41 spheres, indicating that the swelling and plasticization in PDMS polymer chains can be effectively suppressed. That was because of the enhanced physical crosslinking between hydrophobic silanized surface layer of MCM-41 spheres and PDMS polymer chains.

Sorption and Diffusion Properties. According to the solution-diffusion mechanism,^{26,25} sorption and diffusion behavior of O-MCM-41-filled PDMS membrane was carefully investigated.

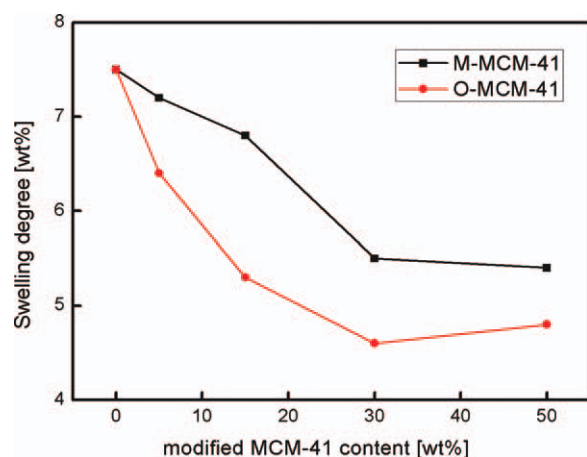


Figure 7. Effect of M-MCM-41 and O-MCM-41 content on SD of the filled membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Based on the assumption²⁸ that the support layer of composite membranes has little effect on membrane sorption, diffusion and PV performance, sorption selectivity was measured using homogeneous membranes instead of composite membranes used in PV. Diffusion selectivity was calculated from separation factor (α) and sorption selectivity (α_s). The sorption and diffusion selectivity data of O-MCM-41 filled PDMS membranes in DMC/MeOH azeotropic mixture are listed in Table I. Diffusion selectivity greatly increased with increasing O-MCM-41 concentration due to the following two aspects: first, the introduction of O-MCM-41 particles increased the physical crosslinking and decreased the plasticization of the membrane, and second, hydrophobic O-MCM-41 silica spheres created a preferential channel for DMC permeation. However, the decrease of sorption selectivity was attributed to the remained hydrophilic groups after hydrophobic silylation treatment. Considering both sorption and diffusion factors, PV selectivity increased somewhat with increasing O-MCM-41 content.

Pervaporation Performance of Modified MCM-41/PDMS Membranes

Effect of modified MCM-41 concentration. Figure 8 shows the effect of M-MCM-41 concentration on separation factor and total flux for DMC/MeOH azeotropic mixtures at 40°C. Both separation factor and total flux increased with increasing M-MCM-41 concentration and attained a maximum with 30%

Table I. Effects of O-MCM-41 Spheres Content on PV, Sorption, and Diffusion Selectivity of O-MCM-41/PDMS Hybrid Membranes for DMC/MeOH Azeotropic Mixtures at 40°C

O-MCM-41 concentration (wt %)	α	α_s	α_d
0%	3.01	4.64	0.65
5%	3.42	4.13	0.83
15%	3.66	2.93	1.25
30%	3.83	2.78	1.37
50%	3.58	1.82	1.97

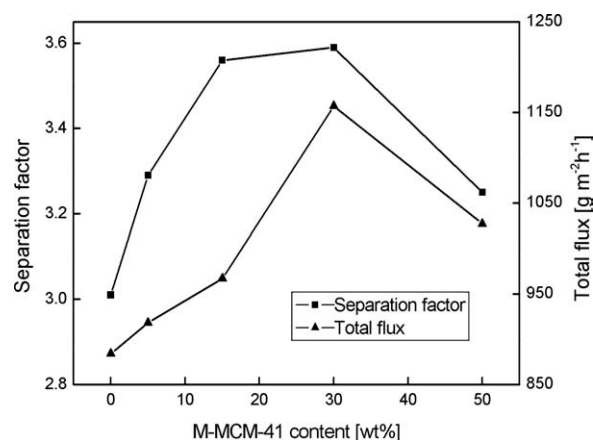


Figure 8. Effect of M-MCM-41 spheres loading on separation factor and permeation flux of M-MCM-41/PDMS hybrid membranes for DMC/MeOH azeotropic mixtures at 40°C.

M-MCM-41 spheres filling. These results agreed well with the desired purpose of M-MCM-41 incorporation in polymer membranes—that the modified MCM-41 particles could create a preferential pathway for DMC permeation due to the following reasons. First, modified MCM-41 spheres with large pore size could provide plenty of channels for both DMC and MeOH molecular to permeate even after modification. Second, the hydrophobic outer surface of the modified MCM-41 spheres guaranteed that DMC preferentially permeate through the channels while MeOH primarily permeate through the polymer rubber phase.²⁹ Third, in the channels of M-MCM-41 spheres, MeOH permeation was further blocked because of the hydrogen-bond force with the remained —OH on the inner surface of the channels. So separation factor and permeation flux could be increased simultaneously by M-MCM-41 spheres incorporation. On the other hand, as more M-MCM-41 spheres were introduced and well dispersed in PDMS polymer, physical crosslinking was enhanced, which could effectively restrict the membrane swelling and plasticization. So the permeation flux

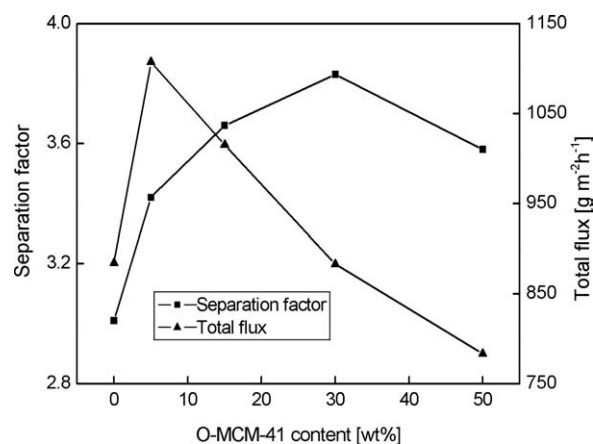


Figure 9. Effect of O-MCM-41 spheres loading on separation factor and permeation flux of O-MCM-41/PDMS hybrid membranes for DMC/MeOH azeotropic mixtures at 40°C.

Table II. Summary of Pervaporation Performance for DMC/MeOH Azeotropic Mixtures

Membrane type	Separation factor, α	Total flux ^a (kg m ⁻² h ⁻¹)	Reference
Addition-cured PDMS	3.21	1.74	8
DNS-2 (15 wt %)/ addition-cured PDMS	3.97	1.05	8
RTV 615	3.01	3.54	This work
M-MCM-41 (30 wt %)/RTV 615	3.59	5.78	This work
O-MCM-41 (30 wt %)/RTV 615	3.83	4.41	This work

^aMembrane thickness base on 20 μm .

decreased when the concentration of M-MCM-41 spheres exceeded 30 wt %.

As shown in Figure 9, the PV performance of O-MCM-41-filled PDMS membranes had the similar trend with M-MCM-41-filled membranes. However, O-MCM-41-filled PDMS membranes dis-

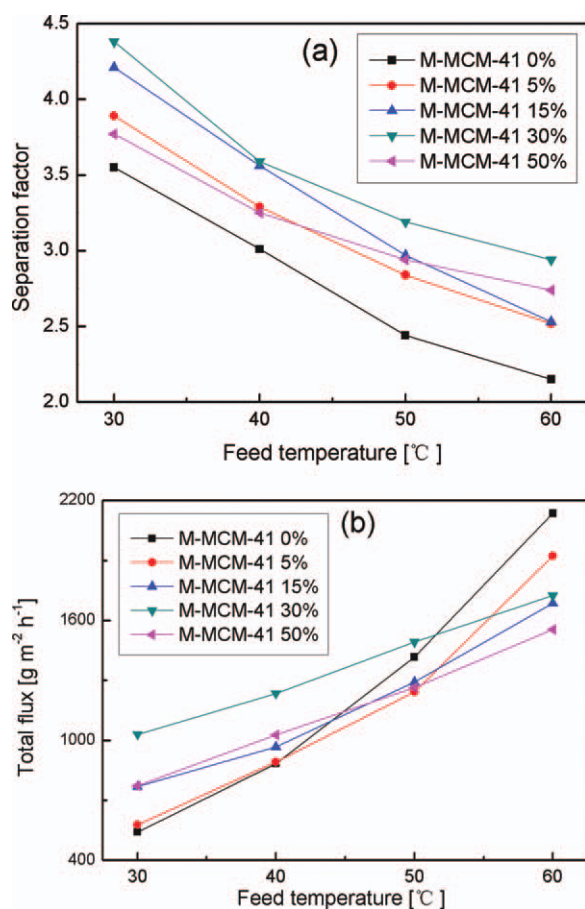


Figure 10. Effect of feed temperature on separation factor (a) and total flux (b) of M-MCM-41/PDMS hybrid membranes with various M-MCM-41 spheres content for DMC/MeOH azeotropic mixtures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

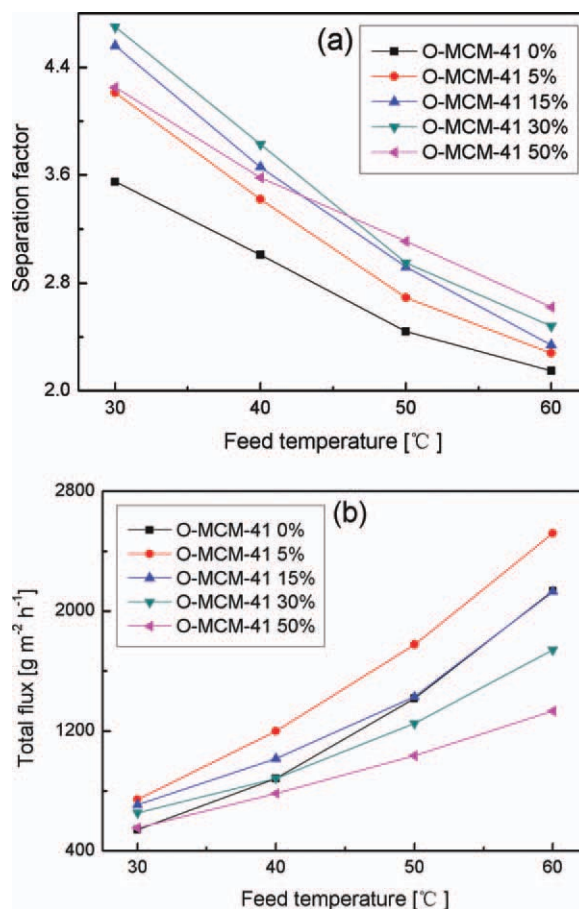


Figure 11. Effect of feed temperature on separation factor (a) and total flux (b) of O-MCM-41/PDMS hybrid membranes with various O-MCM-41 spheres content for DMC/MeOH azeotropic mixtures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

played higher separation factor and lower total flux. Moreover, the flux started to decrease over 5 wt % O-MCM-41 loading. That is owing to more hydrophobic surface and smaller pore size of O-MCM-41 spheres than M-MCM-41 spheres, which is supported by the above contact angle and BET results. Compared with previous report in Table II, membrane prepared in this study has much higher normalized total flux with acceptable separation factor decreasing.

Effect of feed temperature. The studies of operating temperature influence were performed using 30 wt % M-MCM-41- and O-MCM-41-filled PDMS membranes, operated at the DMC/MeOH azeotropic mixture. The results are shown in Figures 10 and 11. As depicted, separation factor decreased while permeation flux increased with increasing temperature, which was consistent with previous report.³⁰ Generally, when the feed temperature was increased, the rubbery PDMS membranes swelled and the mobility and flexibility of polymer segments enhanced, resulting in more free volume of the membranes and faster permeation velocity of small molecules, especially beneficial to the smaller molecules. Moreover, a higher temperature led to an enhanced difference in vapor pressure across the membrane. So

Table III. Apparent Activation Energies of Permeate Molecules in M-MCM-41/PDMS and O-MCM-41/PDMS Hybrid Membranes

M-MCM-41 concentration (wt %)	$E_{p,DMC}$	$E_{p,MeOH}$	O-MCM-41 concentration (wt %)	$E_{p,DMC}$	$E_{p,MeOH}$
0%	29.76	47.39	0%	29.76	47.39
5%	25.47	37.03	5%	25.86	43.51
15%	17.97	32.15	15%	22.76	42.19
30%	10.83	19.6	30%	20.93	39.859
50%	12.57	23.35	50%	17.25	30.79

the driving force increased with increasing temperature, which helped to increase the permeation flux.³¹ As a result, the increasing temperature gave a higher flux, whereas the selectivity decreased.

To have a quantitative estimate of the temperature effect, DMC and MeOH fluxes were plotted against reciprocal of absolute temperature. The data showed good linearity and thus confirmed the Arrhenius relation of temperature on fluxes. Based on these data, permeation activation energies of DMC and MeOH (E_{pi}), calculated from the slope of $\ln(J)$ versus $1/T$ are listed in Table III. Generally, the less permeable species (MeOH) had higher permeation activation energy than the more permeable one (DMC), suggesting that the partial permeate flux of

MeOH is more sensitive to the variation of feed temperature because of its smaller molecular volume. So with increasing operating temperature, MeOH flux increased faster, resulting in the decrease of separation factor. In addition, the pure membrane exhibited higher E_p values than M-MCM-41- and O-MCM-41-incorporated membranes. Obviously, porous silica-incorporated membranes took less energy because of the molecular sieving action due to its straight and sinusoidal channels in the framework.³² So the downward tendency of the permeation activation energy in the filled membrane with the increasing loading of M-MCM-41 and O-MCM-41 silica fillers implied that the filler did involve in and contribute to the separation.

Effect of feed composition. The effects of DMC feed concentration on separation factors and total fluxes using PV at 40°C are shown in Figure 12. It can be seen that the separation factor decreased and total flux increased with increasing DMC concentration. This phenomenon is profitable for the industrial application. The separation efficiency using 30 wt % M-MCM-41- and O-MCM-41-filled PDMS membrane at 40°C is depicted in Figure 13, compared with the VLE data using distillation process.³³ This comparison demonstrates that both membranes are DMC permselective and exhibit attractive potential to break the azeotropic balance of DMC/MeOH azeotropic mixtures.

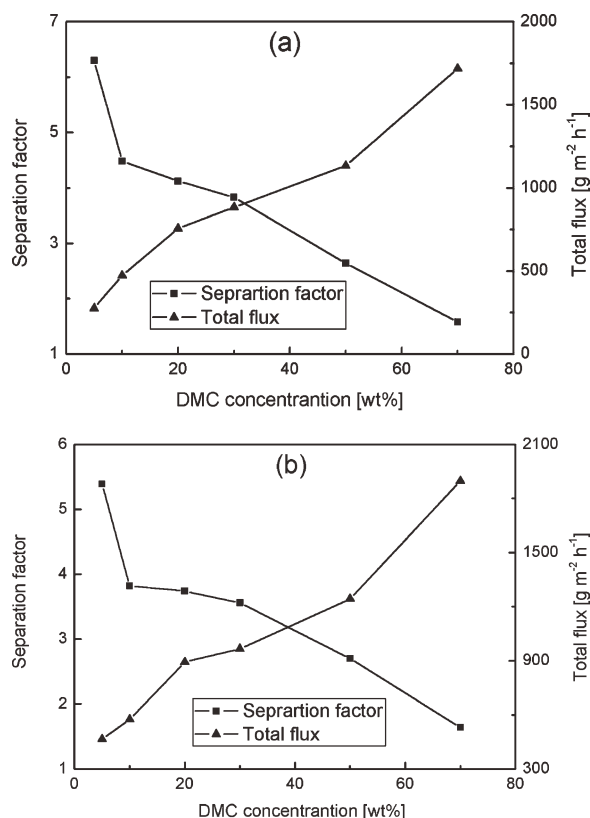


Figure 12. Effect of feed concentration on separation factor and total flux of M-MCM-41/PDMS hybrid membranes (a) and O-MCM-41/PDMS hybrid membranes (b) at 40°C.

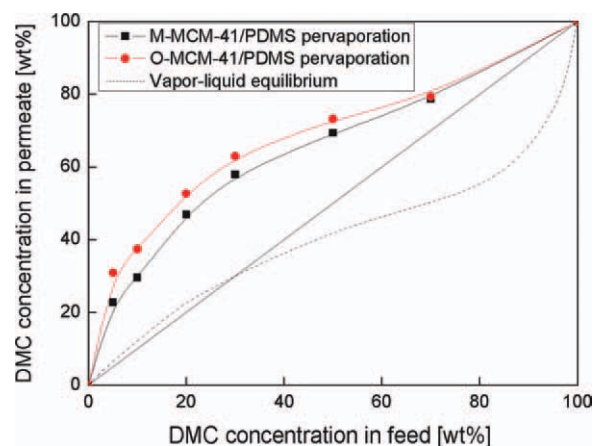


Figure 13. Separation efficiency of DMC/MeOH mixtures on M-MCM-41- and O-MCM-41-filled membranes and VLE data at a constant pressure of 101.3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

In this study, mesoporous MCM-41 spheres were modified with hydrophobic chlorosilanes both at its outer surface and within its channels via strong covalent bond. The modified particles exhibited outstanding hydrophobic surface properties and regular spherical morphology. The modified spheres were filled into PDMS membranes, and the SEM image showed that it could be dispersed uniformly into the membrane. The filled membrane was used for DMC removal from DMC/MeOH azeotropic mixtures. It was found that with increasing M-MCM-41 loading, separation factor and permeation flux increased simultaneously and attained a maximum with 30 wt % M-MCM-41 spheres filling. However, modified MCM-41 spheres filled membranes displayed excellent potential to break the DMC/MeOH azeotropic balance, which could be used in the industrial application.

Additionally, solution-diffusion results indicated that diffusion selectivity was greatly enhanced with modified MCM-41 incorporating, suggesting that modified MCM-41 spheres could create a preferential pathway for DMC molecular, which would be the key reason of simultaneously increased separation factor and total flux.

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