

PERVAPORATION SEPARATION OF ETHANOL/WATER MIXTURES WITH CHLOROSILANE MODIFIED SILICALITE-1/PDMS HYBRID MEMBRANES*

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Abstract Ultra-fine silicalite-1 particles were modified with four kinds of chlorosilanes (dodecyltrichlorosilane, octyltrichlorosilane, hexadecyltrichlorosilane and octadecyltrichlorosilane) and characterized by FI-IR, TGA, contact angle measurements and BET analysis. It was found that the surface hydrophobicity of silicalite-1 particles was improved significantly as the alkyl group was strongly bonded to the particle surface. Modified silicalite-1 particles were incorporated into PDMS (poly(dimethylsiloxanediol)) membranes, which were applied for the pervaporation separation of ethanol/water mixtures. The effect of surface properties, zeolite loading and operation conditions on pervaporation performance of the membranes was investigated. The separation factor of PDMS membranes filled with modified silicalite-1 increased considerably compared with that filled with unmodified ones, and the total flux decreased with increasing zeolite loading. The solution and diffusion selectivity of hybrid membranes were also measured to explain the pervaporation properties of silicalite-1 filled PDMS membranes. It was found that modification of silicalite-1 with dodecyltrichlorosilane effectively improved the solution and diffusion selectivity of silicalite-1 filled PDMS membranes with high zeolite loading. This may be attributed to the high surface hydrophobicity of modified silicalite-1 and its good integration with PDMS membranes. Both the high separation factor and solution selectivity indicated that modification of silicalite-1 with chlorosilanes was an effective method to improve the selectivity of silicalite-1/PDMS hybrid membranes for ethanol.

Keywords: Silicalite-1; PDMS membrane; Modification; Pervaporation.

INTRODUCTION

Extensive work^[1–4] has focused on pervaporation separation of ethanol/water mixtures with zeolite filled silicone membranes, since fuel-grade ethanol was considered to be a promising alternative to fossil fuels in the future, and zeolite particles showed preferable selectivity for ethanol compared with pure silicone membranes. Te Hennepe *et al.*^[5, 6] reported that silicone rubber membranes filled with silicalite-1 showed better selectivity and flux in pervaporation than pure silicone membranes for separation of ethanol from aqueous solutions. Jia *et al.*^[7] prepared ultra-thin zeolite-PDMS composite membranes with selective layer thickness of 3 μm , which showed a selectivity of 34 and total flux of 150 $\text{g}/(\text{m}^2\text{h})$. Vane *et al.*^[8] gave a full comparison of pervaporation performance of zeolite filled silicone membranes prepared under different conditions and also investigated the effect of zeolite and silicone component selection on pervaporation performance. Chen *et al.*^[9] studied the effect of acid and/or steam treatment of silicalite-1 on the pervaporation performance of zeolite filled

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PDMS membranes. Moermans *et al.*^[10] synthesized nano-sized zeolites and treated the zeolites with silane coupling reagent to increase the zeolite loading and dispersion in silicone membranes.

According to the results reported in literatures, the incorporation of zeolite into silicone membranes can effectively improve the selectivity for ethanol compared with pure silicone, since hydrophobic zeolite possessed molecular sieving property for ethanol/water mixtures^[11]. However, the particle size and physical and /or chemical properties of zeolite reported in literatures were of great difference as the synthesis resources and routes were totally different, which may lead to the notable diversity in pervaporation performance of zeolite filled silicone membranes. Despite the disparate pervaporation performance, the following summing-up can be drawn from the literatures: the physical and/or chemical surface properties, the dispersion of zeolite in silicone membranes and integration with matrix polymers were the main factors which determined the pervaporation performance of zeolite filled silicone membranes.

Among the various investigations of PDMS membranes filled with zeolite, few have focused on the effect of surface modification of zeolite particles on the pervaporation performance of Silicalite-1/PDMS hybrid membrane. It was well known that chlorosilane was very effective for tuning physical and chemical properties of organic and inorganic materials^[12–14]. The subject of this article was to provide a surface modification method for zeolite particles with a series of chlorosilanes to improve the surface hydrophobicity of zeolite particles, which was potentially important for the enhancement of separation performance of zeolite filled silicone membranes.

EXPERIMENTAL

Materials

α,ω -Polydimethylsiloxanediol (PDMS) (with kinetic viscosity of 50000 mPa·s) was purchased from Beijing Chemical Reagents Corporation. Silicalite-1 was purchased from Hunan Jianchang Corporation. Octyltrichlorosilane, dodecyltrichlorosilane, hexadecyltrichlorosilane and octadecyltrichlorosilane were purchased from Alfa Aesar. Tetraethoxysilane (TEOS), *n*-hexane, toluene and di-*n*-butyltin dilaurate (DBTOL) were obtained from Beijing Jingyi Chemical Reagents Corporation and were used as received.

Modification of Silicalite-1 with Chlorosilanes

Modification of silicalite-1 particles with chlorosilane reagents was conducted as follows. The zeolite particles were heated at 600°C for 5 h to remove the hydrophilic template and water adsorbed on the surface and inner pores of silicalite-1. The resulting silicalite-1 particles (5 g) were dispersed into toluene (25 g) with vigorous stirring for 30 min. And then chlorosilane (0.9 g, Octyltrichlorosilane, dodecyltrichlorosilane, hexadecyltrichlorosilane and octadecyltrichlorosilane) was added into the suspension with stirring for another 6 h at room temperature. After the treatment, the silicalite-1 particles were filtered and then washed with toluene several times to remove the adhered chlorosilane from particles. And thus obtained silicalite-1 particles were dried at 100°C to remove the residual solvent. The structure of all the obtained silicalite-1 was characterized and verified by FT-IR and TGA. The silicalite-1 particles unmodified and modified with octyltrichlorosilane, dodecyltrichlorosilane, hexadecyltrichlorosilane and octadecyltrichlorosilane were referred as U-silicalite-1, O-silicalite-1, D-silicalite-1, HD-silicalite-1 and OD-silicalite-1 respectively.

Preparation of Silicalite-1 Filled PDMS Membranes

PDMS prepolymer was dissolved in *n*-heptane with magnetic stirring, and then silicalite-1 was dispersed into the solution with vigorous stirring. The obtained suspension was placed in ultrasonic water bath for 30 min and then under magnetic stirring for another 6 h to form uniform suspension. And then TEOS and DBTOL were added into the suspension to initiate prepolymerization of PDMS. The viscosity of the suspension was monitored with a rotating cylinder viscometer (Brookfield, DV-II +Pro). As the viscosity reached around 1000 Pa·s, the suspension was cast onto polyvinylidene fluoride (PVDF) porous substrate (self-made in our lab)^[15] and dried at room temperature for 12 h. And then the membrane was heated at 80°C for another 8 h to complete the cross-linking of PDMS. The weight ratio of PDMS, *n*-hexane, TEOS and DBTOL was 30:70:3:1. The ratio of

silicalite-1 to PDMS varied from 20 wt% to 50 wt%. The thickness of the obtained membranes was controlled in the range of 90–120 μm . The PDMS membranes filled with U-silicalite-1, O-silicalite-1, D-silicalite-1, HD-silicalite-1 and OD-silicalite-1 were referred as U-PDMS, O-PDMS, D-PDMS, HD-PDMS and OD-PDMS respectively.

Characterization

The weight of chlorosilane bonded to silicalite-1 particles was determined by thermogravimetric analysis (TGA) (TA Instruments, TGA-2050). Surface properties of silicalite-1 before and after modification with chlorosilane were characterized by Fourier transform infrared (FT-IR) spectrometer (Nicolet, IR560). The nitrogen adsorption isotherms of silicalite-1 were measured at 77.3 K using an automatic N_2 adsorption apparatus (Quantachrome, Nova 4000). The specific surface area determination of silicalite-1 was performed using nitrogen adsorption based on BET (Brunauer, Emmett and Teller) analysis. The surface hydrophobicity of the silicalite-1 particles was obtained by measuring the contact angle (θ) of a water droplet of 2.4 mm diameter placed on the silicalite-1 wafer using the contact angle meter (Dataphysics, OCA20). The silicalite-1 wafer was obtained on a tablet machine (FW-4 type) under 10 MPa pressure.

The surface and cross-section of D-PDMS membranes was characterized by field emission scanning electron microscope (FESEM, JEOL JSM-7401F).

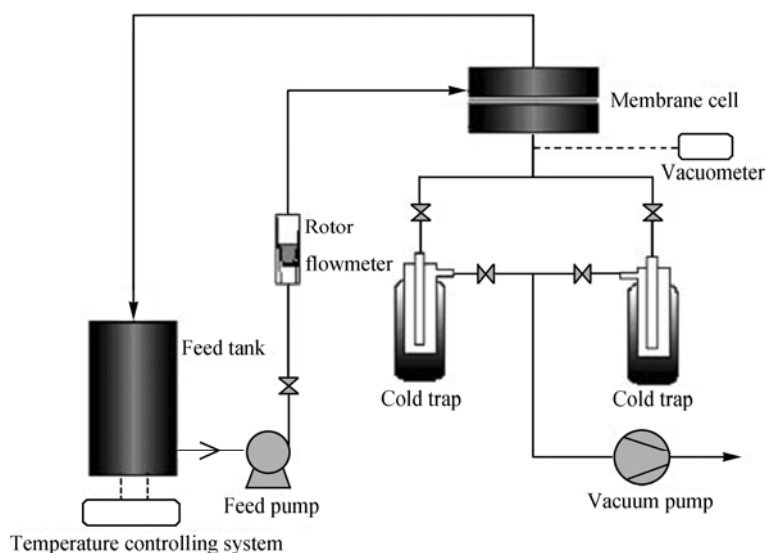


Fig. 1 Schematic diagram of the pervaporation apparatus

Pervaporation Process

The pervaporation experiments were conducted with a standard pervaporation apparatus developed by our own laboratory as shown in Fig. 1^[15]. The permeate was condensed and collected with liquid nitrogen. The composition of the feed and permeate was analyzed by gas chromatography to determine the separation factor. The fluxes were normalized to a membrane thickness of 100 μm assuming an inverse proportionality between the total flux and the membrane thickness. The pervaporation experiments under the same operation conditions were conducted twice to obtain reliable data. The total flux and separation factor are defined as follows:

$$J = \frac{Q}{A \cdot T} \cdot \frac{L}{100 \mu\text{m}} \quad (1)$$

where Q (g) is the total mass of permeate collected in T hours, and A (m^2) denotes the effective area of membrane, and L is the membrane thickness.

$$\alpha = \frac{Y_A \cdot X_B}{X_A \cdot Y_B} \quad (2)$$

Where X_A and X_B represent the ethanol and water concentrations (wt%) in the feed solution respectively, and Y_A and Y_B represent the ethanol and water concentrations (wt%) in the permeate.

Measurement of Solution and Diffusion Selectivity

Dry U-PDMS and D-PDMS membranes were placed in conical flasks filled with 5 wt% ethanol aqueous solution. The conical flasks were sealed and kept in water bath to maintain constant temperature. The membranes were kept in the ethanol aqueous solution for 48 h to maintain adsorption balance. And then the membrane was taken out and wiped with tissue paper to remove the adhered liquid. The wet membrane was immediately put into sealed three-neck flask connected with the standard sorption measurement apparatus developed by our own laboratory as shown in Fig. 2. The solution and diffusion selectivity is defined as follows:

$$\alpha_S = \frac{Y_A \cdot X_B}{Y_B \cdot X_A} \quad (3)$$

$$\alpha_D = \alpha / \alpha_S \quad (4)$$

where X_A and X_B represent the ethanol and water concentrations (wt%) of the initial ethanol solution in conical flask respectively, and Y_A and Y_B represent the ethanol and water concentrations (wt%) in the membranes maintained adsorption balance which was determined by GC (gas chromatography).

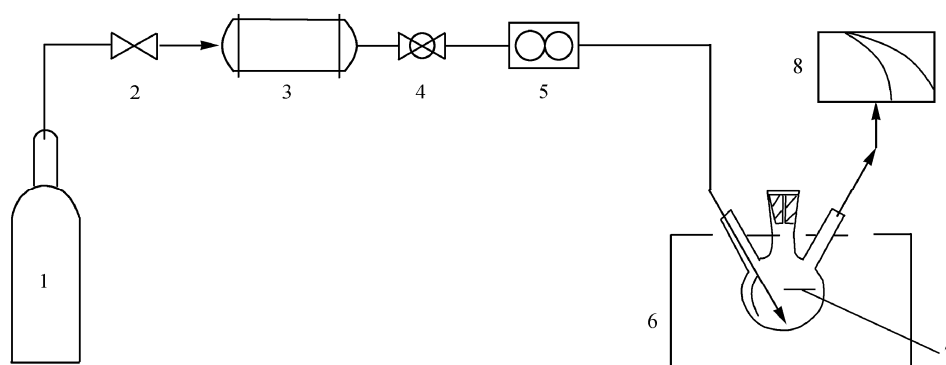


Fig. 2 Schematic diagram of the measurement of sorption selectivity
1) Hydrogen generator; 2) Valve; 3) Desiccating tube; 4) Steady flow valve; 5) Flowmeter;
6) Oil bath with thermocontrol; 7) Membrane; 8) Gas chromatography

RESULTS AND DISCUSSION

Characterization

Figure 3 showed the thermal gravimetric curves of silicalite-1 before and after modification with chlorosilanes. The weight loss near 600°C was attributed to the decomposition of chlorosilanes. The decomposition temperature was notably higher than the boiling point of chlorosilanes (octyltrichlorosilane, 233°C; dodecyltrichlorosilane, 293°C; hexadecyltrichlorosilane, 269°C; octadecyltrichlorosilane, 291°C), which indicated that the chlorosilane was strongly bonded to silicalite-1 particles^[12, 13]. The weight loss of chlorosilane modified silicalite-1 at 600°C was around 3 wt%–6 wt%. The modification of silicalite-1 with dodecyltrichlorosilane was repeated for three times. The weight loss of the modified silicalite-1 particles at 600°C was around (4.0 ± 0.3)%, which indicated that the modification of silicalite-1 with chlorosilane was proved to be a reliable method with good repeatability.

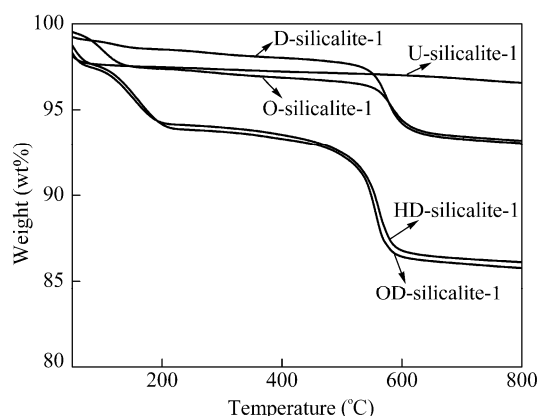


Fig. 3 Thermal gravimetric curves of silicalite-1 before and after modification with chlorosilanes

Comparison of surface properties for silicalite-1 before and after modification with chlorosilane was made based on FT-IR spectra as shown in Fig. 4. In the spectrum of U-silicalite-1, a broad peak near 3450 cm^{-1} was observed which was attributed to the terminal hydroxyl groups and hydrogen-bonding adjacent hydroxyl groups^[16]. The absorption intensity of hydroxyl groups in both of D-silicalite-1 and O-silicalite-1 decreased significantly. In the spectra of O-silicalite-1 and D-silicalite-1, organic C—H peaks in the region of $2850\text{--}3000\text{ cm}^{-1}$ as well as hydroxyl peaks were observed. The difference spectra of (d) and (e) clearly revealed that the hydroxyl groups in the outer surface of silicalite-1 particles reacted with the chlorosilanes.

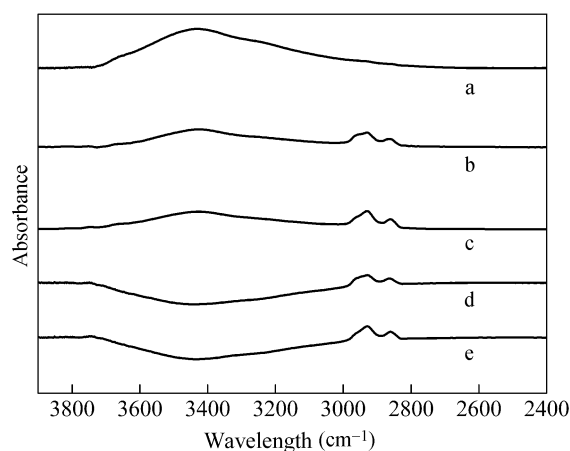


Fig. 4 FT-IR spectra of silicalite-1 before and after modification with chlorosilanes (a) U-silicalite-1, (b) O-silicalite-1, (c) D-silicalite-1, (d) difference spectrum (b-a), (e) difference spectrum (c-a)

The hydrophobicity of silicalite-1 particles was quantitatively studied by contact angle measurements. Figure 5 gives the contact angle measurement results of the U-silicalite-1, O-silicalite-1, D-silicalite-1, HD-silicalite-1 and OD-silicalite-1 respectively. U-silicalite-1 showed good hydrophilicity with a contact angle of 16.4° , and the water droplets spread rapidly on the U-silicalite-1 wafer. And so the images were taken within 10 s after the water droplet touched the wafer surface. The contact angle of pure cross-linked PDMS membrane, O-silicalite-1, D-silicalite-1, HD-silicalite-1 and OD-silicalite-1 was 117.2° , 62.9° , 122.0° , 144.0° and 153.2° respectively and water droplets spread on the modified silicalite-1 very slowly. This indicated that modification of silicalite-1 with chlorosilanes was an effective method to improve its surface hydrophobicity. The longer the alkyl group in chlorosilane, the more hydrophobic silicalite-1 would be obtained.

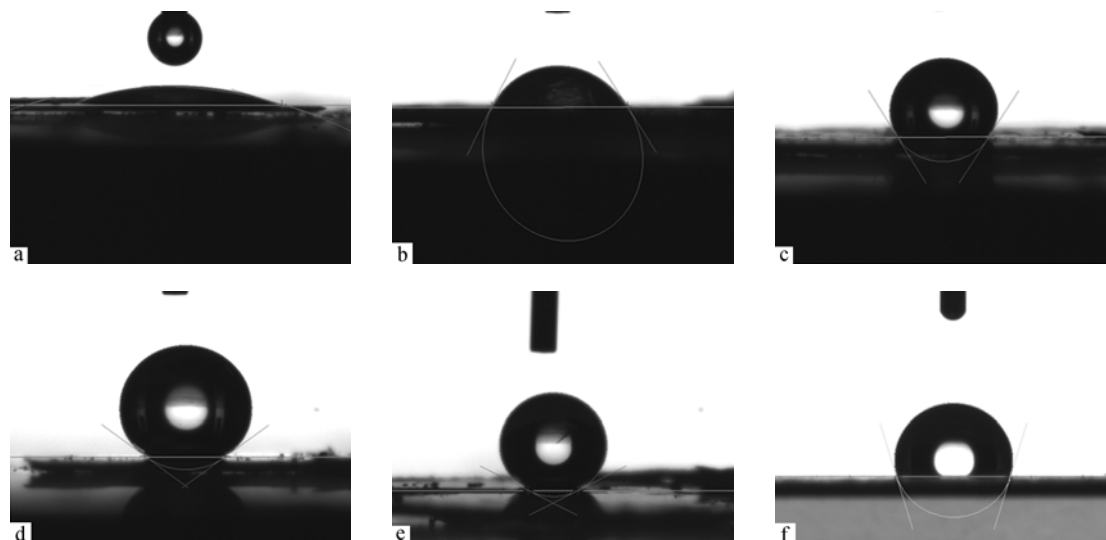


Fig. 5 Contact angle measurements of silicalite-1 wafers

a) U-silicalite-1, 16.4°; b) O-silicalite-1, 62.9°; c) D-silicalite-1, 122.0°; d) HD-silicalite-1, 144.0°; e) OD-silicalite-1, 153.2°; f) Pure cross-linked PDMS, 107.2°

In this study, chlorosilanes with long alkyl groups (octyl-, dodecyl-, hexadecyl, and octadecyl) were applied to alter the surface properties of silicalite-1. The intrinsic pore of silicalite-1 was 0.53×0.56 nm, while the kinetic diameter of octyltrichlorosilane was *ca.* 0.59 nm, which could avoid the intrusion of chlorosilanes into pores of silicalite-1 abstractly. The N_2 adsorption isotherms of silicalite-1 particles before and after modification with chlorosilane are shown in Fig. 6. The specific surface area of silicalite-1 was obtained based on BET analysis. The specific surface area of U-silicalite-1, O-silicalite-1, D-silicalite-1, HD-silicalite-1 and OD-silicalite-1 was 414.1, 283.6, 273.0, 232.8, and 189.8 m^2/g respectively. The maximum adsorption amount of surface modified silicalite-1 was a little lower than that of unmodified ones, and the uptake rate of surface modified silicalite-1 for N_2 was obviously lower than that of unmodified ones. This indicated that the inner pore structures in silicalite-1 were not affected by modification, while the pores in outer surface of silicalite-1 may be partially blocked by modification. And this increased the surface resistance to N_2 molecules^[17]. Moreover, the uptake rate for N_2 decreased as the size of the alkyl group increased, which may be resulted from the increased strength of the surface resistance with increasing the size of the alkyl group in chlorosilanes.

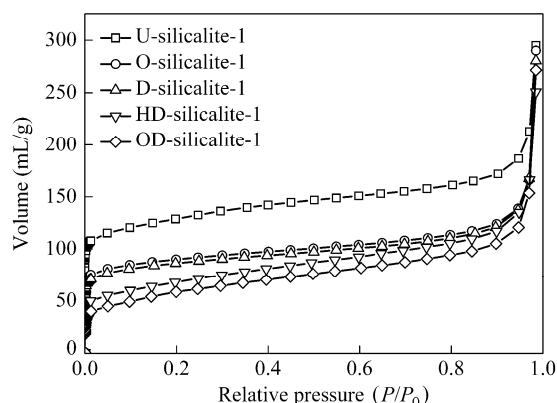


Fig. 6 N_2 adsorption isotherms of modified and unmodified silicalite-1 particles

From the SEM images of D-PDMS and U-PDMS membranes as shown in Fig. 7, it can be seen that the silicalite-1 particles aggregated in the surface and cross-section of U-PDMS membranes, and pinholes appeared in the cross-section due to the particle aggregation. After surface modification, the silicalite-1 particles dispersed uniformly on the whole in D-PDMS membranes, and silicalite-1 particles and PDMS matrix integrated tightly and properly.

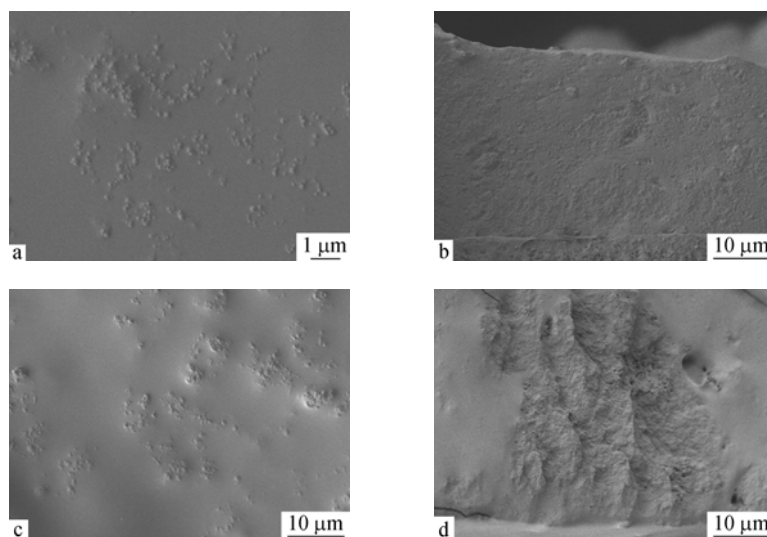


Fig. 7 Surface (a, c) and cross section (b, d) of D-PDMS (a, b) and U-PDMS (c, d) membranes with 50 wt% zeolite loading by SEM

Pervaporation Performance

Effect of chlorosilanes

Pervaporation performance of various silicalite-1/PDMS hybrid membranes with zeolite loading of 50 wt% was measured with 5 wt% ethanol aqueous solution at 40°C, and the results are listed in Table 1. The chlorosilane modified silicalite-1/PDMS hybrid membranes showed much better selectivity for ethanol, and lower total flux than those of U-PDMS. Of all the hybrid membranes, D-PDMS maintained the highest separation factor of 19.9. It was considered that the hydrophobicity and surface energy of D-silicalite-1 and PDMS were close to each other, which was supported by the contact angle results. And the close hydrophobicity and surface energy of D-silicalite-1 and PDMS contributed to the better integration with each other. Both of properly high hydrophobicity of zeolite and better integration with PDMS resulted in the much better selectivity of D-PDMS membranes for ethanol.

Table 1. Pervaporation performance of chlorosilane modified silicalite-1/PDMS hybrid membranes ([EtOH] = 5 wt%, 40°C)

	U-PDMS	O-PDMS	D-PDMS	HD-PDMS	OD-PDMS
Separation factor	8.3	15.7	19.9	15.3	14.9
Total flux (g/(m ² h))	178.9	51.8	66.3	73.6	89.2

Effect of zeolite loading

Pervaporation performance of silicalite-1 filled PDMS membranes with different zeolite loadings at 40°C is shown in Fig. 8. O-PDMS and D-PDMS showed improved pervaporation performance compared with U-PDMS. As the zeolite loading of U-PDMS reached 30 wt%, the separation factor obtained the maximum value of 9.4. The separation factor of D-PDMS increased from 12.7 to 19.9 as the zeolite loading increased from 20 wt% to 50 wt%. U-PDMS showed increased total flux as the zeolite loading increased, while O-PDMS and D-PDMS presented absolutely opposite variation tendency. As shown in Fig. 8(c), water flux of D-PDMS

decreased sharply with the zeolite loading increasing from 20 wt% to 50 wt%, while ethanol flux decreased first and then remained almost unchanged as zeolite loading exceeded 30 wt%. This resulted in the decrease of total flux and improvement of separation factor of D-PDMS with increasing zeolite loading.

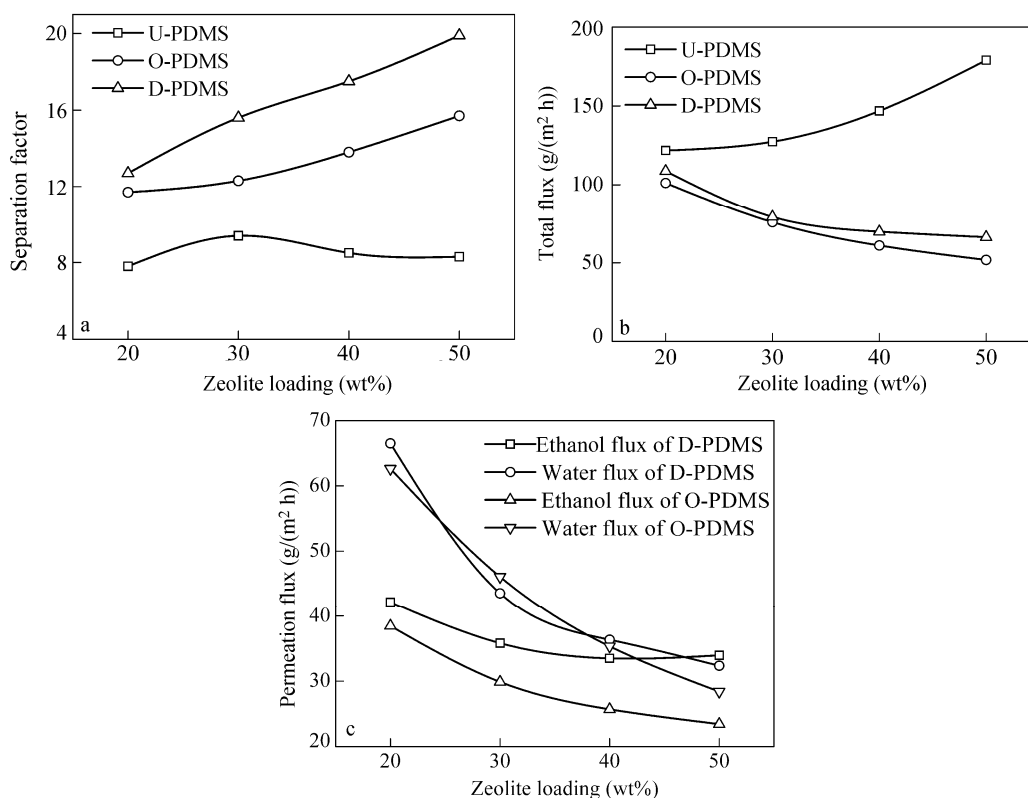


Fig. 8 Effect of zeolite loading on pervaporation performance of U-PDMS, O-PDMS and D-PDMS

a) Separation factor versus zeolite loading; b) Total flux versus zeolite loading; c) Permeation flux versus zeolite loading

The notable increase in total flux of U-PDMS with increasing zeolite loading was considered to be mainly attributed to the surface hydrophilicity of silicalite-1 particles and the pinholes induced by the poor integration of U-silicalite-1 particles with PDMS matrix. Modification of silicalite-1 with chlorosilanes effectively improved the surface hydrophobicity and integration with PDMS matrix, which resulted in the high separation factor of D-PDMS and low water flux with high zeolite loading. The decrease of ethanol flux also reminded that moderate surface modification with chlorosilanes was needed to maintain good integration with PDMS and high permeation properties.

Effect of operation conditions

The pervaporation performance of U-PDMS, O-PDMS and D-PDMS with zeolite loading of 50 wt% ([EtOH] = 5 wt%) at different temperatures is shown in Fig. 9. As operation temperature increased from 40°C to 70°C, the separation factor of O-PDMS and D-PDMS decreased, while the total flux increased exponentially. D-PDMS showed better pervaporation performance than O-PDMS in the whole range of operation temperature. Figure 10 shows the pervaporation performance of D-PDMS at 40°C with zeolite loading of 40 wt%. As the ethanol feed concentration increased from 5 wt% to 50 wt%, the separation factor of D-PDMS decreased sharply from 17.2 to 3.5, the total flux increased from 72.3 g/(m²h) to 236.7 g/(m²h).

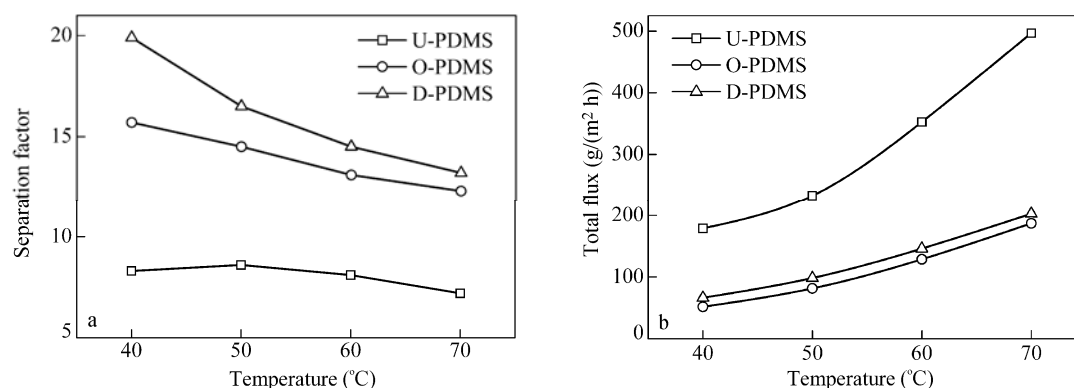


Fig. 9 Effect of operation temperature on pervaporation performance

a) Separation factor versus operation temperature; b) Total flux versus operation temperature

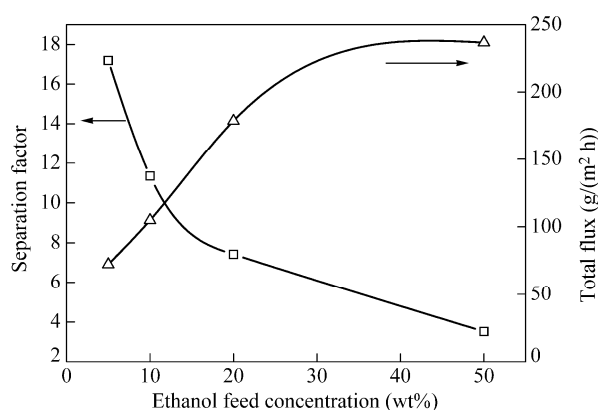


Fig. 10 Effect of ethanol feed concentration on pervaporation performance of D-PDMS with zeolite loading of 40% at 40°C

As operation temperature or ethanol feed concentration increased, the swelling degree of zeolite filled PDMS membranes increased, which was in favor of diffusion of small molecules in membranes. And this resulted in the increase of permeation flux of O-PDMS and D-PDMS. But the increase extent of water permeation flux was larger than that of ethanol as the kinetic diameter of water molecules (0.37 nm) was smaller than that of ethanol molecules (0.52 nm). And so the separation factor decreased as operation temperature or ethanol feed concentration increased^[15, 18].

Solution and Diffusion Selectivity

The solution and diffusion selectivity of U-PDMS and D-PDMS with different zeolite loadings was measured at different temperatures as shown in Fig. 11. As the zeolite loading increased, the solution selectivity of both membranes increased, while the diffusion selectivity decreased. As the temperature increased, the variation tendency of solution and diffusion selectivity followed the reversed order. As for zeolite filled PDMS membranes with higher zeolite loading at low temperature, solution selectivity was higher than diffusion selectivity, which indicated that selective solution was the major contributor to the permeation selectivity. The solution selectivity of D-PDMS was obviously higher than that of U-PDMS in the whole range of zeolite loading tested, which indicated that selective solution of ethanol in D-PDMS was effectively improved by modification of silicalite-1 with dodecyltrichlorosilane. The diffusion selectivity of D-PDMS was lower than that of U-PDMS with lower zeolite loading (less than 30 wt%), while higher with zeolite loading more than 30 wt%. This may be explained as follows. The poor integration of U-silicalite-1 with PDMS in U-PDMS may lead to pinholes with higher zeolite loading, which made the diffusion selectivity drop sharply with increasing

zeolite loading. However, D-silicalite-1 and PDMS matrix achieved good integration, which made the drop of diffusion selectivity with increasing zeolite loading more gently. Both of high solution selectivity and diffusion selectivity of D-PDMS hybrid membranes with high zeolite loading contributed to the high selectivity of D-PDMS.

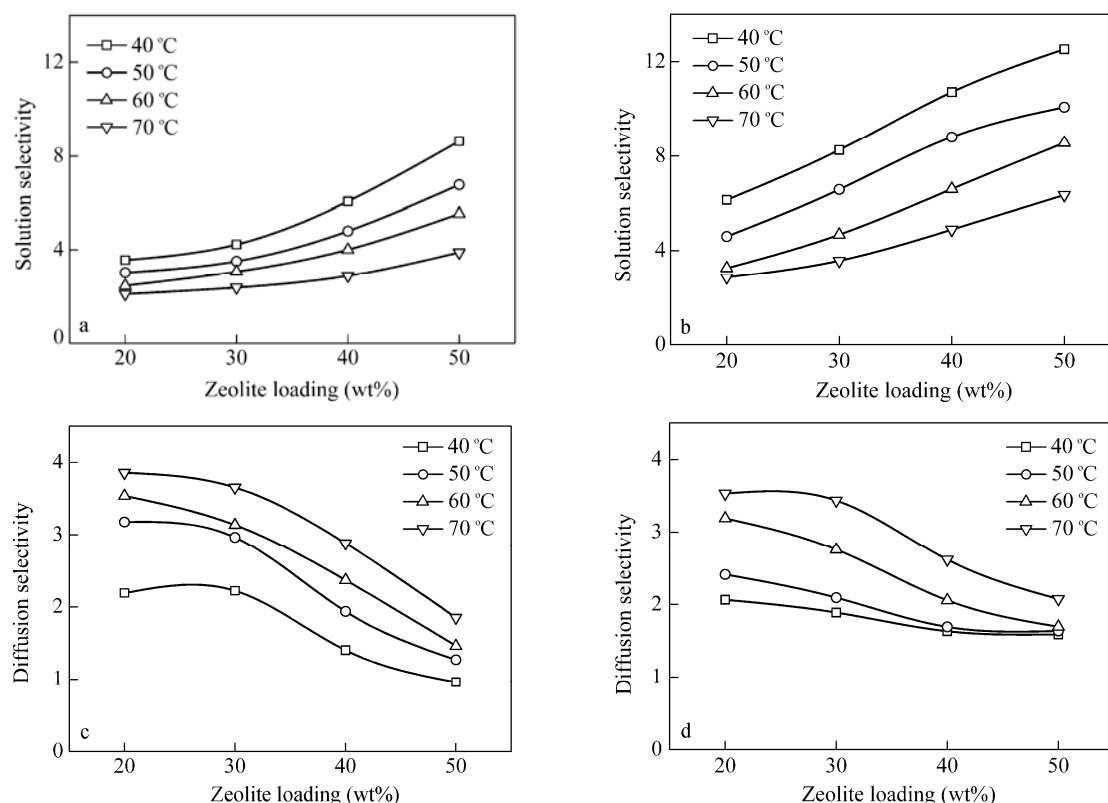


Fig. 11 Solution and diffusion selectivity of U-PDMS and D-PDMS

a) Solution selectivity of U-PDMS; b) Solution selectivity of D-PDMS; c) Diffusion selectivity of U-PDMS; d) Diffusion selectivity of D-PDMS

CONCLUSIONS

In this study, silicalite-1 particles were modified with four kinds of chlorosilanes and the obtained silicalite-1 particles were incorporated into PDMS membranes. It was found that modification of silicalite-1 with chlorosilanes was very effective to increase surface hydrophobicity of zeolite particles and improve integration with PDMS matrix. Of the four kinds of chlorosilane modified silicalite-1/PDMS hybrid membranes, D-PDMS showed the best selectivity for ethanol. The increase of hydrophobicity of D-silicalite-1 by surface modification contributed to the higher solution selectivity of membranes. Better integration of D-silicalite-1 particles and PDMS also led to high diffusion selectivity of D-PDMS with high zeolite loading. Both factors contributed to the best selectivity of D-PDMS with high zeolite loading. It's indicated that modification of silicalite-1 with dodecyltrichlorosilane was an effective method to improve the permeation selectivity of the silicalite-1/ PDMS hybrid membranes, with a little sacrifice of permeation flux.

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