

Separation Properties of Alcohol–Water Mixture through Silicalite-I-Filled Silicone Rubber Membranes by Pervaporation

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ABSTRACT: The structure and the adsorption–desorption properties of zeolite silicalite-I by different treatments after synthesis were studied. The pervaporation properties of the alcohol–water mixture through silicone rubber filled with zeolite silicalite-I by different treatments were also investigated. Treating silicalite-I by acid or/and under steam was found to eliminate the metallic impurities in the zeolite and to perfect the crystalline structure of the zeolite. After treatment, silicalite-I is more selective to alcohol and the desorption of the alcohol from the zeolite is also easier. The silicone rubber membrane filled with treated silicalite-I shows a high performance for alcohol extraction from the dilute aqueous solution by pervaporation. The separation factor of the poly(dimethyl siloxane) (PDMS) membrane filled with silicalite-I treated successively by acid and steam is about 30 when the ethanol content in the feed is 5 wt % at 50°C. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 629–636, 1998

Key words: zeolite silicalite-I; silicone rubber; filled membrane; alcohol–water mixture; pervaporation

INTRODUCTION

Zeolite-filled polymer membranes have recently received much attention in gas separation and in pervaporation.^{1,2} The incorporation of permselective inorganic “fillers” in a polymer membrane were found to improve its separation performance. In our previous articles,^{3,4} the relationships between the properties of zeolite ZSM-5 and its performance in filled silicone rubber membranes in alcohol extraction from dilute aqueous solution by pervaporation were studied. The higher the silica–alumina ratio of zeolite ZSM-5,

the better its affinity with ethanol. Silicalite-I, first synthesized by Flanigen et al., which has the same crystal structure as that of zeolite ZSM-5 and can be considered the Al-free analog,⁵ had the best affinity toward alcohol in our observation. The silicone rubber membrane filled with silicalite-I also showed the best selectivity to alcohol by pervaporation among the series of zeolite ZSM-5.

However, the rough synthetic silicalite-I in our laboratory⁶ contained a trace of metallic impurities such as sodium or aluminum which will introduce some defect in the zeolite crystal and decrease its hydrophobicity, so that the silicone rubber membrane filled with this rough silicalite-I were not very satisfying in separation. Several methods have been adopted to eliminate the metallic impurities in zeolite; among them, treating silicalite-I by acid or under steam was frequently

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used for that purpose. In this article, the crystal-line structure modification and the adsorption–desorption properties of silicalite-I treated by different methods as well as the pervaporation properties of the silicone rubber membranes filled with these rough and treated silicalite-I were studied.

EXPERIMENTAL

Materials

Three room-temperature vulcanizing-type (RTV) silicone rubbers (103, 107, 108), provided by the Shanghai Resin Factory, were used as membrane materials composed of two components: a prepolymer and a crosslinking agent. The main chemical composition of silicone rubber 107, 103, and 108 is poly(dimethyl siloxane) (PDMS), poly(methyl ethoxy siloxane), and poly(methyl phenyl siloxane), respectively.

The silicalite-I samples used in this study were hydrothermally synthesized in the ethylamine– Na_2O – SiO_2 – H_2O system by using water glass as a silicon source.⁶ The molar ratio of the reactant mixtures, i.e., $\text{Na}_2\text{O} : \text{ethylamine} : \text{SiO}_2 : \text{H}_2\text{O}$ was 0.01 : 1.0 : 1.0 : 15.0. The mixture was sealed in a 2 L stainless-steel autoclave, and hydrothermally reacted for 18 h at 180°C without stirring. The as-synthesized product was washed, filtered, dried by an IR lamp, and then calcined in an oven to remove the organic template at about 600°C for 2 h. Therefore, then, *sample S* was obtained. The content of Na_2O in sample S was 0.5 wt % measured by chemical analysis. Sample S was treated with a 0.5 mol/L HCl solution at 95°C for 4 h, then washed, filtered, dried, and calcined at 550°C for 2 h to obtain *sample SA*. After treatment with the HCl solution, the content of Na_2O in sample SA decreased to 0.03 wt %. Samples S and SA were calcined in a quartz tube using an air-saturated water steam at 800°C for 100 h to obtain *samples SH* and *SAH*. The flow rate of the water vapor was controlled at 105 mL/h by a micropump. All samples were stored in a desiccator before use.

Characterization of Silicalite-I

XRD patterns were collected at room temperature using a Regaku D-MAX/II A X-ray powder diffractometer with $\text{CuK}\alpha$ radiation at a scanning speed of $8^\circ(2\theta)/\text{min}$ in the 2θ range of 5° – 45° and at scanning speed of $0.5^\circ(2\theta)/\text{min}$ in the 2θ ranges of 24° – 25° , 29° – 30° , and 48° – 49° . The IR spectra

were run on a Nicolet FTIR-50X IR spectrometer at a scanning range of 400 – 1600 cm^{-1} for a sample of KBr discs and at a scanning range of 3200 – 4000 cm^{-1} for a sample of self-supported discs.

^{29}Si -MAS NMR spectra were recorded at room temperature using a Bruker MSL-300 spectrometer, whose ^{29}Si resonance frequency was 59.595 MHz. The rotor was spun at 3.0 kHz. The radio-frequency field was 37.0 kHz, corresponding to a $\pi/3$ pulse width of $4.5\ \mu\text{s}$; the recycle time was 2 s and Q_8M_8 was used as a second reference for the ^{29}Si chemical shift.

The vapor-adsorption isotherms of ethanol and water were carried out on discs of pressed powder samples in a Sartorius-7012 supermicro electrobalance in a vacuum. The sample was activated *in situ* at 350°C under a vacuum ($<2.7\text{ Pa}$) until complete desorption before starting pure vapor adsorption at 20°C. The adsorption capacity is expressed as the volume gain per 100 g of dry material.

Desorption was performed in a TGA apparatus (DuPont-1090B) on a sample equilibrated with a saturated solvent vapor. The temperature was continuously increased from 30 to 450°C at a rate of $10^\circ\text{C}/\text{min}$. The “desorption temperature” T_d is the value at which half of the sorbed amount was desorbed from the sample and the “desorption fraction” Q_d is calculated as follows:

$$Q_d = (W_1 - W_0)/W_0 \times 100\%$$

where W_1 and W_0 denote the total weight of the sample and the weight of the dry sample, respectively.

Preparation of Silicalite-I-Filled Silicone Rubber Membranes

The silicone prepolymer was first well mixed by stirring with the crosslinking agent. Silicalite-I was previously sieved on the 100 mesh sieve, and the part which was smaller than 100 mesh was added into the silicone liquid mixture with heptane as a diluent. The doped mixture was stilled to degas and then cast onto a polyester plate. After 8 h reaction time at room temperature, the film can be stripped out of the support. Due to the rubbery nature of the polymer matrix, only relatively thick membranes (e.g., $120\ \mu\text{m}$ thick) can be handled. The membranes were put in a vacuum oven at 50°C for more than 24 h before use in order to get rid of the remaining solvent.

Pervaporation Apparatus⁷

A stainless-steel cell with an effective area of a flat membrane of 28 cm² was used. At the downstream side, a pressure below 30 Pa was maintained by using a mechanical pump. The permeate flux was calculated by weighing the permeate condensed in a cold trap. The water contents in the feed and the permeate were analyzed using a chromatograph equipped with a column of Porapak Q. The performance of the membranes in pervaporation was evaluated by the separation factor (α) and the flux (J_d) calculated as follows:

$$\alpha = \frac{c'_E \cdot c_W^0}{c_E^0 \cdot c'_W}$$

$$J_d = \frac{W}{A\Delta t} \cdot \frac{d}{100 \mu\text{m}}$$

where W is the weight of permeate (g); Δt , the permeation time (h); A , the membrane area (m²); d , the membrane thickness (μm), and c'_E , c_E^0 , c'_W , c_W^0 , the ethanol (E) or water (W) content in the permeate or feed, respectively. As can be seen from the definition of the flux J_d , the fluxes were normalized to a membrane thickness of 100 μm .¹

RESULTS AND DISCUSSION

Vapor-Adsorption and -Desorption Behaviors of Silicalite-I

The vapor-adsorption isotherms of ethanol and water of four samples of silicalite-I are presented in Figure 1. The ethanol- and water-adsorption capacity increases in the order of SA > S > SAH > SH. It indicates that the acid treatment improves the vapor-adsorption capacity of silicalite-I whereas the steam treatment results in a decrease. The water-adsorption capacities of samples SH and SAH are even lower than the data published by Olson et al.⁸

Zeolite used as an absorbent is qualified by its high solvent adsorption, which is due to its porous structures and its high specific surface. Generally, the adsorption capacity of zeolite depends on its pore size, pore structure, and pore polarity.^{9,10} As mentioned in the Experimental part, the rough silicalite-I sample (i.e., sample S) prepared in our laboratory contains 0.52% of Na₂O. The sodium species maybe cations or in a state of salts, which cannot enter the zeolite structure but stay in the

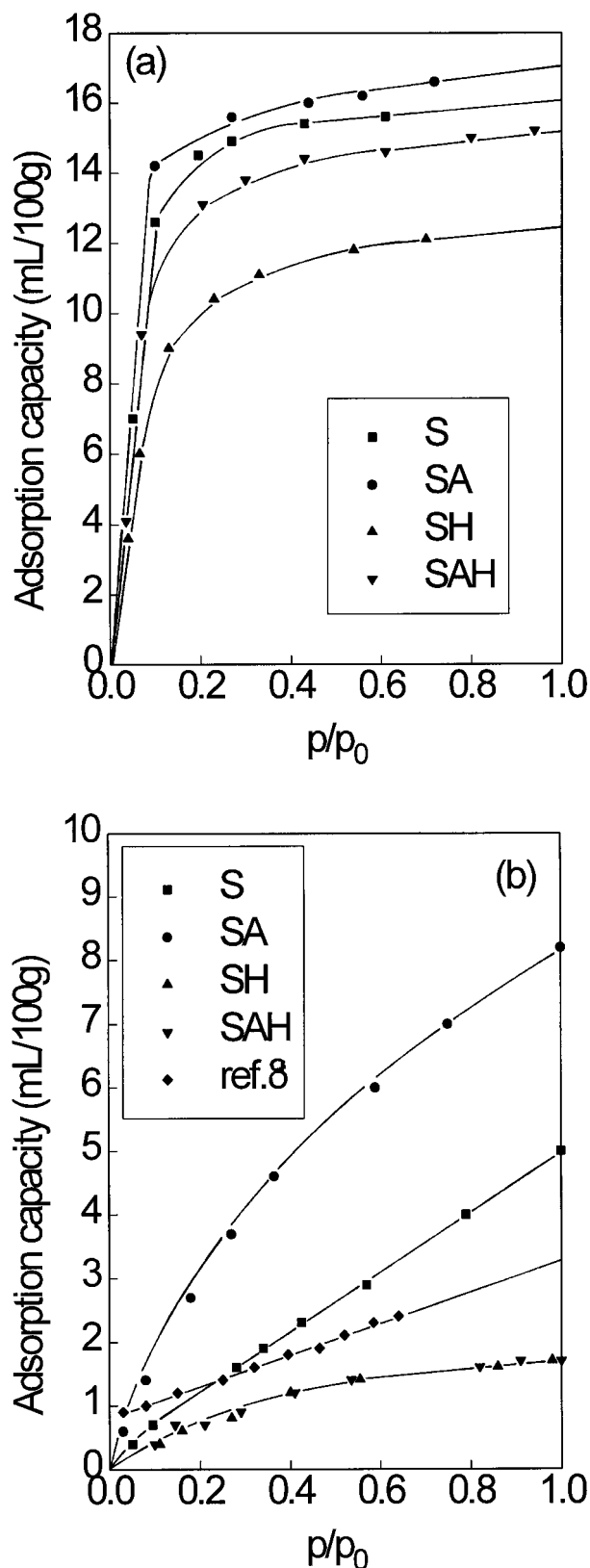


Figure 1 Adsorption of (a) ethanol and (b) water on silicalite-I with different treatments as a function of partial vapor pressure (20°C).

channel and block it. Consequently, the efficient pore volume in the zeolite decreases and its vapor-adsorption capacity is lower. The hydrochloric acid can react with the sodium cations or salts and replace the Na^+ ions by H^+ ions. By treating with acid, the sodium content in silicalite-I is decreased to less than 0.03% measured by chemical analysis, as before. As the H^+ ion is smaller than the Na^+ ion, the acid treatment may make the zeolite channel more open and increase its efficient pore volume. As a result, both ethanol and water adsorption increase in sample SA.

The other impurity in rough silicalite-I is a small amount of aluminum which came from the silica source in the water glass, which can be incorporated into the zeolite framework. Also, there are some silanol groups ($\text{Si}-\text{OH}$) in rough silicalite-I. Both impurities are polar and make the zeolite less hydrophobic. The steam treatment was found to be efficient to remove these impurities. After the steam treatment, it was found by ^{29}Si -MAS NMR spectra that the $\text{Si}-\text{OH}$ peak at -103 ppm and the $\text{Si}(1\text{Al})$ peak at -106 ppm, appearing in the patterns of samples S and SA, disappear in the pattern of samples SH and SAH. The dealuminum and desilanol effect of the steam treatment also can be detected by FTIR spectra, in which a $[\text{TO}_4]$ external asymmetrical stretching vibration at 1226 cm^{-1} and an internal asymmetrical stretching vibration at 1095 cm^{-1} move to higher frequencies, and the vibration of silanol groups at about 3730 and 3450 cm^{-1} disappears. In addition, the silicalite-I samples transit their symmetry from orthorhombic (samples S and SA) to monoclinic (samples SH and SAH) after steam treatment as indicated by measurements of an improved resolution of ^{29}Si resonance.¹¹ As a result, the dealuminum and desilanol effect decreases the polarity and the symmetry transition reduces the cycle diameter or zeolite pore size and the efficient pore volume of silicalite-I. This is the reason why both ethanol- and water-adsorption capacities of silicalite-I decrease after steam treatment. This phenomenon was also observed by other authors when they decreased the alumina content in the ZSM-5 zeolite.⁹

From Figure 1(a), it also can be found that sample SH exhibits the lowest ethanol adsorption in all the samples. As it does not undergo an acid treatment, the Na^+ ions still remained in the zeolite, which distorted the crystalline structure during the steam treatment. According to the intensity of the characteristic peaks in the WAXD and IR spectra, sample SH shows the lowest crystallinity (about 85%) of all the samples and its

Table I Effect of Different Silicalite-I-Treated Methods on the Saturation-Adsorption Capacity^a

Sample	Q_E (mL/100 g)	Q_W (mL/100 g)	Q_E/Q_W
S	0.160	0.050	3.2
SA	0.169	0.082	2.1
SH	0.126	0.017	7.4
SAH	0.153	0.017	9.0

^a Q_E and Q_W denote the saturation-adsorption capacity of ethanol and water, respectively.

crystalline structure is not perfect.¹² Low crystallinity and the imperfection of the crystalline structure bring about the divergence of the pore-size distribution and the decrease of an efficient pore volume—consequently, the lowest ethanol adsorption is in sample SH. However, sample SAH possesses a perfect crystalline structure, whose framework is constructed by $\text{Si}-\text{O}-\text{Si}$ without the $\text{Si}(1\text{Al})$ and $\text{Si}-\text{OH}$ defect, has the highest crystallinity (about 98%) and a good ethanol-adsorption capacity.^{11,12} As a conclusion, removing metallic impurities and perfecting the crystalline structure of the rough silicalite-I by acid and steam treatment is useful and the combination of acid and steam treatment is proposed.

Vapor adsorption is one of the most important characteristics for zeolite; selectivity is another one, which can be represented by the ratio of vapor adsorption between ethanol and water sorbed in the zeolite. According to the saturation adsorption of the samples, the selectivity of silicalite-I to ethanol follows the increasing order of $\text{SA} < \text{S} < \text{SH} < \text{SAH}$ (Table I). The adsorption ratio of ethanol to water in sample SAH is about three times higher than that of sample S, the rough silicalite-I. It is suggested that increase of the selectivity to ethanol of samples SH and SAH depends mainly on the increase of their hydrophobicity (decrease of the polarity) after steam treatment. As it is known that water is more polar than ethanol, the decrease of the zeolite polarity results in a significant reduction of the water-adsorption capacity rather than that of ethanol.

While silicalite-I is used as an adsorbent or as a filler in the membrane, its desorption properties are also important, because if the solvent adsorbed in the zeolite cannot be desorbed in the operation condition, the zeolite does not play any role of separation. So, in a sense, the separation power of the zeolite depends on its desorption property. The desorption properties of four sili-

Table II Ethanol-Desorption Properties of Silicalite-I Treated by Different Methods

	Sample			
	S	SA	SH	SAH
T_d (°C)	102	88	68	65
Q_d (%)	6.8	8.0	5.9	8.2

calite-I samples are listed in Table II. Silicalite-I, which is more selective to ethanol in adsorption, was found to desorb ethanol at a lower temperature. For samples SH and SAH, this is more strong evidence of the decrease of the zeolite polarity by steam treatment: Alcohol is a polar solvent (although its polarity is lower than that of water) and the alcohol molecule will develop interactions with polar centers in silicalite-I (samples S and SA), which will be replaced by weaker van der Waal's interactions when all polar sites are removed from silicalite-I. In addition, for samples SA and SAH, because the zeolite channel becomes more open after acid treatment, it makes the desorption and diffusion of alcohol in the zeolite faster than in samples S and SH, respectively.

Pervaporation Properties of Silicalite-I-Filled Silicone Rubber Membranes

Influence of Zeolite Properties

According to the solution–diffusion mechanism, the membrane selectivity generally depends on the partition of two components between the feed solution and the upstream layer of the membrane and on the difference of their diffusivities across the membrane. Several experiments indicated that the pervaporation selectivity of a dense membrane is principally determined by its preferential adsorption properties.¹³ In the case of zeolite-filled silicone rubber membranes, the selectivity de-

pends mainly on the adsorption selectivity of the zeolite to be filled as discussed in our previous articles.^{3,4}

Table III shows the variation of the separation factor obtained with silicone membranes that were filled with silicalite-I treated by different methods, in the case of the water–ethanol mixture. All filled membranes were found to exhibit a higher selectivity to ethanol than did a pure silicone rubber membrane. Silicalite-I is one of the materials which preferably sorb ethanol to water. The above results clearly indicate that the separation properties of the membrane can be improved by incorporating a selective filler. It shows that the higher the silicalite-I adsorption selectivity the better the membrane selectivity in the pervaporation. The silicalite-I sample SAH shows the best selectivity of all the samples.

The variation of the permeation flux is more interesting (Fig. 2): The water permeation through a silicalite-I-filled membrane corresponds perfectly with the adsorption capacity of silicalite-I to water and follows the same increasing order of adsorption capacity, i.e., SAH < SH < S < SA. However, the ethanol permeation flux of the membrane is not so regular. Sample SAH has not only the best ethanol-adsorption selectivity, but also the best ethanol permeation of its filled membrane among all the membranes. From the ethanol-adsorption data shown in Figure 1(a), the ethanol-adsorption capacity of sample SAH is smaller than that of samples S and SA. So, normally thinking, the ethanol permeation flux of the sample SAH-filled membrane will be lower than that of samples S- and SA-filled membranes because the flux of a component in pervaporation is always determined by its preferential adsorption to the membrane.¹³ So, this “abnormal” phenomenon (the ethanol flux of sample SAH is larger than that of samples S and SA) will be explained by the desorption properties of alcohol from silicalite-I. As indicated in Ta-

Table III Effect of Zeolite-Treated Methods on the Separation Factors of Silicalite-I-Filled PDMS Membranes^a

Content (wt %)	Sample S	Sample SA	Sample SH	Sample SAH
0	5.3	5.3	5.3	5.3
10	7.5	10.9	16.7	29.6
20	9.4	11.4	17.5	25.6
30	10.1	13.2	17.3	21.7
40	11.1	14.4	17.4	26.8
50	12.2	18.2	18.8	29.3

^a Ethanol in feed: about 4.4 wt %, 50°C.

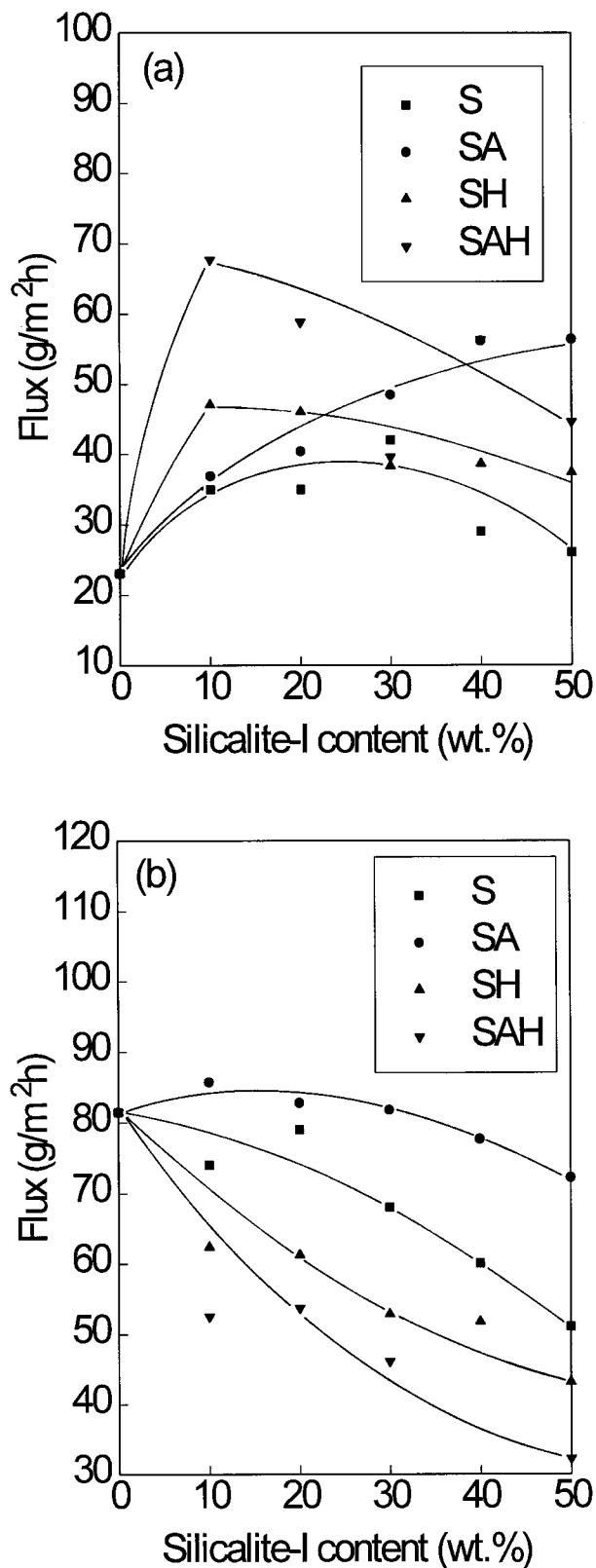


Figure 2 Effect of silicalite-I content on (a) ethanol flux and (b) water flux (ethanol in feed: about 4.4 wt %, 50°C).

Table IV Effect of the Type of Silicone Rubber on Separation Factors of Silicalite-I (Sample SA)-Filled Silicone Rubber Membranes^a

Zeolite Content (wt %)	107	103	108
0	5.3	10.5	11.7
20	11.4	14.4	13.3
30	13.2	15.3	15.3
40	14.4	16.9	19.6

^a Ethanol in feed: 107: 4.4 wt %; 103: 4.4 wt %; 108: 4.1 wt %, 50°C.

ble II, the desorption of ethanol in sample SAH is the easiest among the four samples because it has the lowest desorption temperature, which is the result of the decrease of the zeolite polarity by the steam treatment. So that the desorption of ethanol in the sample SAH-filled silicone rubber membrane is still the easiest and results in the largest ethanol flux which accords with the result that sample SAH has the highest ethanol-desorption capacity (see Table II) although its ethanol-adsorption capacity is not the highest. This means that the desorption properties of the silicalite-I-filled membrane plays a very important role and sometimes determines the diffusion properties through the membrane which express as the permeation flux.

The membrane performance also depends on the silicalite-I content in the membrane (Table III). The table shows that the sample SAH-filled PDMS rubber membrane containing 10 wt % of silicalite-I exhibits the best compromise between the permeability and the selectivity: In the case of 4.4 wt % of ethanol content in feed, the membrane has a good separation factor (ca. 30) and a suitable permeation flux (120 g/m²h).

Influence of Different Silicone Rubber

Three kinds of silicone rubber are used in our research. The separation factor toward the water-ethanol mixture of silicalite-I (sample SA)-filled silicone rubber membranes are listed in Table IV. According to the different chemical structures of silicone rubbers, the membrane performances are different. The larger the separation factor of the pure silicone rubber membrane, the larger the corresponding zeolite-filled membranes. In the meantime, the fluxes of the silicalite-I-filled silicone membranes were also found to be related to the chemical structures of silicone rubbers.^{14,15}

Table V Effect of Electrolyte Addition on Pervaporation Properties of Silicalite-I (Sample SA)-Filled PDMS Membranes

Electrolyte	α	$J_{d(\text{total})}$ (g/m ² h)	$J_{d(\text{ethanol})}$ (g/m ² h)	$J_{d(\text{water})}$ (g/m ² h)
Without electrolyte	13.4	131	46	85
NaCl (0.10 mol/L)	14.6	130	50	80
HCl (0.10 mol/L)	15.3	125	49	76

Ethanol in feed: about 4.0 wt %; 50°C.

Influence of Operation Conditions

It is well known that the separation properties of a membrane depend on the interaction between the solvent to be separated and the membrane matrix. The hydrophilic membranes, such as PVA membranes that can develop a strong hydrogen-bond interaction, are always used in the extraction of the water from the organic solvent by pervaporation. Contrary, the hydrophobic membranes are applied in the extraction of the organic solvent from the dilute aqueous solution. In such cases, the interaction between the organic solvent and the polymer matrix of the membrane is the dispersion force, which is weaker than that between water and ethanol. The hydrogen-bond interaction between water and ethanol leads two solvents to form a cluster, which has the formula $(\text{ROH})_x \cdot y\text{H}_2\text{O}$, so that the separation by the hydrophobic membrane is somewhat difficult due to the relatively large coupling of the diffusion. Adding the electrolyte agent can partly hinder the formation of the clusters and it also decreases the water activity in the feed. Consequently, the water adsorption and water diffusion in the membrane decrease, so that the selectivity of the ethanol-water mixture can be improved. The results in Table V prove that after adding salt (NaCl) or acid (HCl) to the feed the separation factor increases due to increase of the ethanol flux and decrease of the water flux.

The influence of the feed temperature and feed concentration on the pervaporation properties were also studied. Figure 3 shows that both the separation factor and flux increase with the feed temperature. According to the adsorption and desorption data, it seems reasonable to assume that increasing of the temperature favors the desorption of ethanol from the zeolite. Figure 4 shows the performance of the silicalite-I-filled PDMS rubber membrane at different ethanol contents in the feed. With increase of the ethanol content in the feed, the ethanol content in the permeate also increases whereas the separation factor decreases. The ethanol content in the permeate increases dra-

matically at the low feed concentration, and in all feed concentrations, the membrane is ethanol-selective. It can be noted that the ethanol flux increases linearly with the ethanol content in the feed, while the water flux remains practically constant in the range of 0–30 wt % ethanol content. This is similar to the behavior in a propanol-1-water system.^{3,4} The steep increase of ethanol flux at high ethanol content in the feed is due to the swelling of ethanol in the PDMS rubber.

CONCLUSION

The treatment of silicalite-I after synthesis has a great effect on its adsorption and desorption properties. Leached silicalite-I by acid and treated sili-

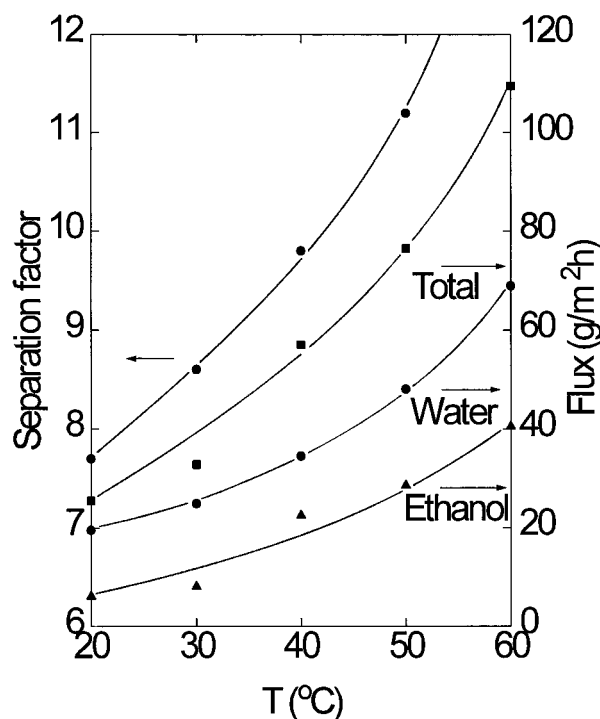


Figure 3 Effect of feed temperature on pervaporation properties (sample S-filled PDMS membrane; zeolite content: 50 wt %; ethanol in feed: about 4.4 wt %).

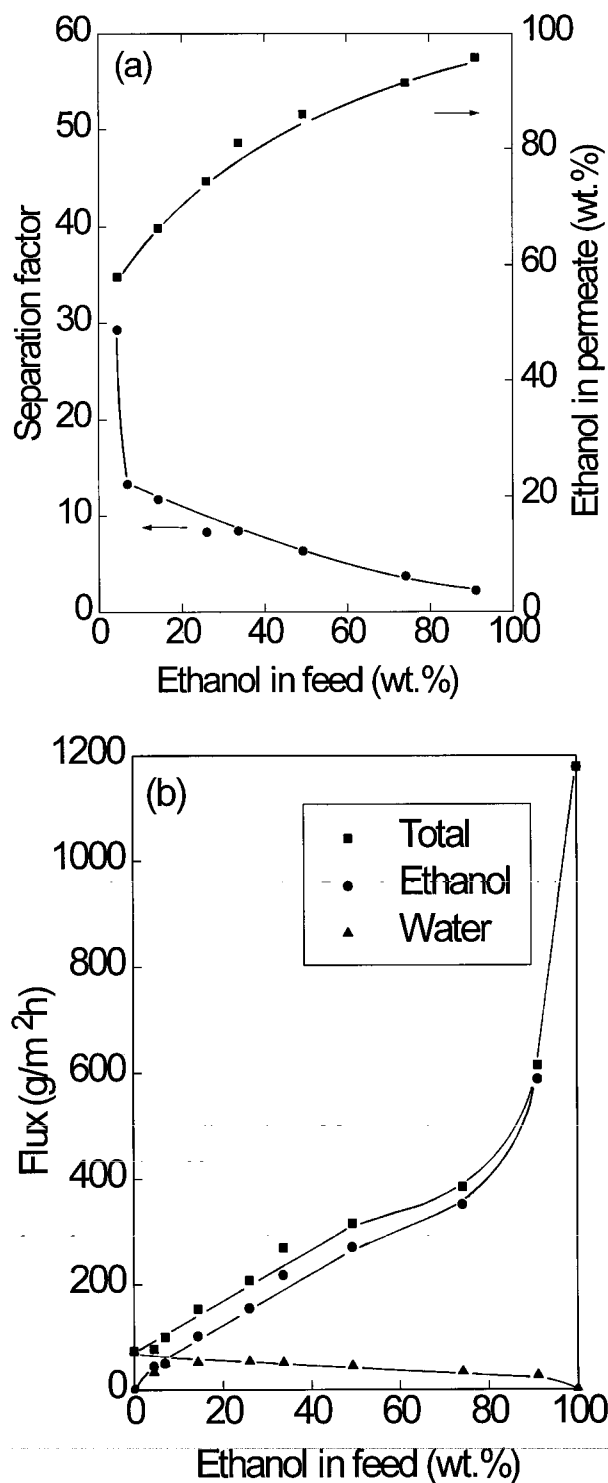


Figure 4 Effect of ethanol in feed on pervaporation properties (sample SAH-filled PDMS membrane; zeolite content: 50 wt %).

calite-I under steam can improve its ethanol-adsorption selectivity and lower its ethanol-desorption temperature. Especially, the sample SAH,

which was treated successively with acid and steam, has the highest ethanol selectivity and the lowest ethanol-desorption temperature, as it relates to the more perfect crystalline structure which can be obtained from WAXD and IR results.

The separation properties of the ethanol-water mixture by pervaporation are also strongly dependent on the treatment of silicalite-I. In accordance with the adsorption and desorption properties, the SAH-filled PDMS rubber membrane has the most outstanding performance, whose separation factor can reach ca. 30 with a flux of 120 g/m²h.

Increase of the feed temperature and the addition of electrolytes such as acid and salt to the feed can improve the separation properties. The separation properties are also significantly influenced by the feed concentration and the structure of silicone rubber as well.

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