

Effects of Zeolite Membrane Structure on the Separation of 1,3-Propanediol from Glycerol and Glucose by Pervaporation

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Seven types of zeolite membranes were synthesized on the inside surfaces of alumina and stainless steel supports. The medium-pore membranes (MFI, MEL, and a MFI + MEL composite) were prepared by using organic templates, whereas the larger pore membranes (MOR, FAU) were prepared by a template-free method. These membranes were used in pervaporation to separate 1,3-propanediol from glycerol and glucose in an aqueous solution. All membranes had 1,3-propanediol/glycerol selectivities higher than 27, and zeolite pore size did not have a large influence on membrane selectivity, which was mainly due to preferential adsorption of 1,3-propanediol. The 1,3-propanediol/glucose selectivities were higher than 1600 for all membranes because the selectivities were mainly controlled by molecular sieving. Zeolite structure had a significant effect on the pervaporation flux; the larger pore membranes had higher fluxes. At 308 K, the X-type membrane had the largest 1,3-propanediol flux of 62 g/(m² h), with a 1,3-propanediol/glycerol selectivity of 59.

Introduction

Zeolite membranes have the potential to continuously separate mixtures of molecules by both adsorption and molecular sieving because the zeolite pores are of molecular size. Zeolite membranes have advantages over polymer materials, such as better chemical and thermal stability. Since Suzuki¹ patented the first preparation of zeolite membranes in 1987, many types of zeolite membranes have been prepared and used for gas separations and pervaporation. In the current study, a series of membranes with six zeolite structures were prepared and used in pervaporation separations. Most previous studies have focused on silicalite-1 and ZSM-5 membranes,^{2,3} which have the same MFI structure. Silicalite-1 is composed of pure silica, whereas ZSM-5 has aluminum substituted into a small fraction of the silicon sites in the crystal lattice. Silicalite-1 has a higher thermal stability and is more hydrophobic than ZSM-5. These MFI zeolites have a system of straight channels (pore size: 0.53 × 0.56 nm) interconnected by zigzag channels (pore size: 0.51 × 0.55 nm). Cook and Conner⁴ reported, however, that molecules that are significantly larger than these dimensions could fit into the pores, which they calculated to be 0.62 nm in diameter.

The ZSM-11 zeolite pore size is similar to ZSM-5, but it has the MEL structure, which has intersecting

straight channels (pore size: 0.54 × 0.53 nm) only. The pores have 10-membered oxygen rings (Figure 1) like ZSM-5. To our knowledge, the only preparation of a MEL membrane was by Tuan et al.,⁵ who prepared a B-ZSM-11 membrane that had high selectivities and fluxes for pervaporation of MEK/water, 1-propanol/water, and 2-propanol/water mixtures.

Mordenite (MOR, Si/Al = 5) has an ordered distribution of Si and Al in the framework structure. The structure consists of two major channels: one (0.65 × 0.70 nm pores) has 12 oxygen atoms and the other (0.26 × 0.57 nm) has 8 oxygen atoms. Mordenite membranes have been synthesized previously by the vapor-phase transport method of Matsukata et al.⁶

Zeolites X (Si/Al = 1–1.5) and Y (Si/Al = 1.5–3) are isostructures of faujasite (FAU), but differ in their aluminum content. The FAU zeolites are strongly hydrophilic, and their pore diameters are 0.74 nm. Kita et al.⁷ prepared NaX and NaY membranes on porous, cylindrical mullite supports, and these membranes were highly selective for alcohol in pervaporation of alcohol mixed with benzene, cyclohexane, or methyl *tert*-butyl ether (MTBE). In our previous study,⁸ a series of X-type zeolite membranes were prepared by a template-free method on porous supports. The best X-zeolite membrane had one layer of zeolite on a γ -Al₂O₃ support.

The membranes were used in the pervaporation of 1,3-propanediol/glycerol/glucose/water mixture. The 1,3-

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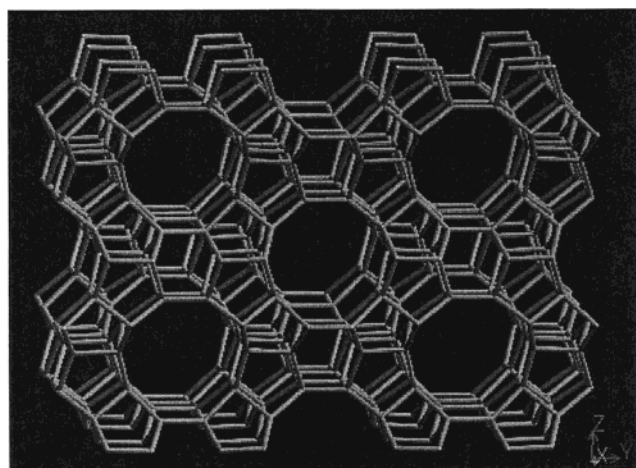
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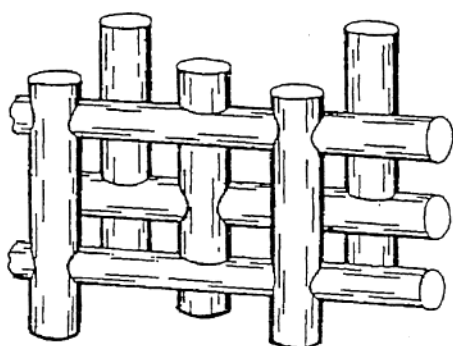
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(a)



(b)

Figure 1. Structures of the ZSM-11 zeolites: (a) framework; (b) channel structure.

propanediol ($C_3H_8O_2$, 3G) molecule is an economical source for the production of 3GT (a polymer of 3G and terephthalic acid), which is a novel polyester with good stretch, recovery, and dyeability.⁹ The 1,3-propanediol molecule is fermented from glycerol ($C_3H_8O_3$) or glucose ($C_6H_{12}O_6$), and thus selective separation methods would be valuable for the recovery of 1,3-propanediol from glycerol and glucose. Distillation can be used to separate 1,3-propanediol from glycerol, but both compounds have high boiling points, and therefore separations require significant energy. Moreover, glucose is thermally sensitive, and thus distillation is neither economical nor suitable. A second approach is to use a packed bed of zeolite that can be used to preferentially adsorb the 1,3-propanediol from the mixture. Ethanol can then be used to remove the 1,3-propanediol from the zeolite.¹⁰ The current study shows that zeolite membranes have both high selectivities and high fluxes for this separation.

Pervaporation has advantages over distillation,¹¹ including reduced energy demand (only a fraction of the liquid is vaporized), and relatively inexpensive equipment (only a small vacuum pump is needed to create a driving force). Pervaporation can also have advantages

over a packed bed. Membrane operation is continuous and does not require an additional separating agent, such as the ethanol used for a packed bed. Eliminating the ethanol also eliminates the distillation step to separate and recycle the ethanol. Pervaporation using zeolite membranes has concentrated on *binary* organic/water feed mixtures: for example, organic-selective silicalite membranes,¹² water-selective A-type membranes,¹³ and water-selective Y-type membranes.^{7,13} Sano et al.¹⁴ separated a methanol/MTBE mixture using a silicalite membrane. Nishiyama et al.^{15,16} reported the separation of benzene/*p*-xylene using a mordenite membrane and the separation of cyclohexane/benzene and benzene/*p*-xylene mixtures using ferrierite membranes.

Pervaporation of feeds containing more than three components has not been studied extensively. In our previous study,¹⁷ Na-ZSM-5 zeolite membranes were used to separate 1,3-propanediol from glycerol and glucose in aqueous solutions. At 308 K, the total flux was 0.21 kg/(m² h). The maximum 1,3-propanediol/glycerol separation selectivity was 54, and the maximum 1,3-propanediol/glucose selectivity was over 2100. Likewise, X-type membranes were used for the same separation.¹⁸ A cell-free aqueous fermentation broth containing 1,3-propanediol, glycerol, and glucose was also used. The total fluxes for the quaternary solution and the broth were 2.1 and 1.2 kg/(m² h), respectively, at 308 K. The corresponding 1,3-propanediol/glycerol selectivities were 59 and 61. The 1,3-propanediol/glucose selectivity for the quaternary solution at 308 K was 1900, and the membrane was stable for at least a week. In contrast, the fermentation broth started to foul the membrane after 60 h, and the membrane was regenerated by calcining at 653 K.

The purpose of the current study was to determine the effect of zeolite structure on pervaporation of a 1,3-propanediol/glycerol/glucose/water mixture. In addition to the ZSM-5 and X-type structures, which are included for comparison, silicalite-1, mordenite, Y-type, ZSM-11, and mixed ZSM-5 and ZSM-11 (designated as ZSM-5+11) membranes were prepared on porous alumina and stainless steel supports. These membranes were characterized by X-ray diffraction, single-gas permeation, and pervaporation of 2,2-dimethylbutane, *o*-xylene, and tri-isopropyl benzene. The silicalite-1 structure was chosen because it is more hydrophobic than ZSM-5, whereas the ZSM-11 structure was chosen because it is more open and was expected to have a higher flux than the ZSM-5. The mordenite structure was used because its pore size is between the ZSM-5 and X-type zeolite pore sizes. The Y-type zeolite was selected because its structure is similar to X-type zeolite but it has a higher Si/Al ratio.

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Experimental Methods

Membrane Preparation. Membranes were prepared by in situ crystallization onto tubular porous supports (γ -Al₂O₃, 5-nm pores, US Filter; α -Al₂O₃, 200-nm pores, US Filter; and stainless steel, 500-nm pores, Mott Company). About 1 cm on each end of the alumina supports was glazed to prevent membrane bypass. Nonporous stainless steel tubes were welded onto each end of the stainless steel supports to provide a sealing surface for the O-rings. The support tubes were then boiled in distilled water for 1 h and dried at 373 K under vacuum for 30 min. The membranes were deposited on the supports by hydrothermal synthesis. One end of the support was sealed with Teflon tape and a Teflon end cap. The support was then filled with the synthesis gel in accordance with the procedure described below for each membrane type. Ludox AS 40 (silica sol) and sodium aluminate (Na₂Al₂O₄) were used as the Si and Al sources, respectively. For the Y-type membrane only, sodium silicate (14 wt % NaOH, 27 wt % SiO₂) was used instead. The top end was taped and capped, and the support was sealed inside a Teflon-lined autoclave and then placed in an oven for synthesis.

Medium-Pore Zeolites. Silicalite-1 and Na-ZSM-5 (Si/Al = 25) membranes were synthesized on the inside of stainless steel tubes. A detailed description of the synthesis procedures was given previously.¹⁷ The following molar gel composition was used for the Na-ZSM-5 membrane: 9.1Na₂O × 1.0Al₂O₃ × 50SiO₂ × 3.0TPAOH × 3213H₂O, where TPAOH (tetrapropylammonium hydroxide) was used as the template. The gel composition for the silicalite-1 membrane was the same as that for Na-ZSM-5 membrane, but it did not contain Na₂O and Al₂O₃. Hydrothermal synthesis was carried out at 458 K for 24 h. Four synthesis layers were required for ZSM-5 and two layers for silicalite-1 membranes. After hydrothermal synthesis, the membrane was washed twice with distilled water, dried in a vacuum oven at 373 K, and then calcined in air at 753 K for 8 h with heating and cooling rates of 0.011 and 0.015 K/s, respectively.

The ZSM-11 membranes were prepared on porous alumina and stainless steel supports using the same procedure as for ZSM-5. The gel composition, the template, and the synthesis conditions were different, however. The molar gel composition was 2.5Na₂O × 1.5TBAOH × 19.46SiO₂ × 0.00162Al₂O₃ × 438H₂O, where TBAOH (tetrabutylammonium hydroxide) was used as a template. One layer was crystallized at 403 K for 24 h and then two layers at 403 K for 72 h. For mixed ZSM-5+11 membranes on stainless steel and alumina supports, the preparation gel and conditions were similar to those used for the ZSM-11 membrane, but the crystallization temperature was 443 K. The number of layers and the times were the same as those for the ZSM-11 membrane.

Large-Pore Zeolites. MOR-type membranes were prepared using the molar gel composition: 3.2Na₂O × 1.0Al₂O₃ × 12SiO₂ × 210H₂O. Two synthesis layers (24 h for each layer) were crystallized at 438 K.

The X-type membranes were prepared by growing one layer onto seed crystals, and details of X-type membrane preparation were reported elsewhere.⁸ The supports were first seeded with zeolite X crystals before the synthesis gel was added. The gel composition was 4.2Na₂O × 3.0SiO₂ × 1.0Al₂O₃ × 150H₂O. Hydrothermal synthesis was carried out at 373 K for 6 h. After synthesis, the membrane was washed five times with distilled water and dried in an oven at 373 K for 15 h to remove water occluded in the zeolite crystals.

Before crystallization of the Y-type zeolite membrane, the alumina tubes were seeded with X-type powder because both X- and Y-type zeolites have the same FAU structure. The seeding process, the preparation procedure, and the conditions were similar to those used for the X-type membrane, except that the gel composition was different. The molar gel composition was 14.0Na₂O × 10.6SiO₂ × 1.0Al₂O₃ × 900H₂O. One synthesis layer was grown at 373 K for 6 h.

Membrane Characterization. Some of the zeolite powders collected from the bottoms of the membrane tubes were analyzed by XRD using a Scintag PAD-V diffractometer with

Cu K α radiation. Some membranes were broken after pervaporation measurements and analyzed by XRD and SEM (ISI-SX-30, operated at 30 kV). The membrane quality was characterized by pervaporation at 300 K of 2,2-dimethylbutane (DMB, 0.62-nm kinetic diameter), *o*-xylene (0.685-nm kinetic diameter), and triisopropylbenzene (TIPB, 0.85-nm kinetic diameter). The fluxes for membrane M4 and M10 were also measured at 330 K. These molecules were chosen because DMB has a kinetic diameter between the XRD pore diameters of the MFI (or MEL) and MOR structures; *o*-xylene has a kinetic diameter between XRD pore diameters of MOR and FAU structures, and TIPB has a larger kinetic diameter than the pore diameter of the zeolites studied. Single-gas permeation rates were measured at 300 and 473 K for H₂, CO₂, N₂, *n*-C₄H₁₀, and *i*-C₄H₁₀ at a feed pressure of 222 kPa and a permeate pressure of 84 kPa.

Pervaporation Measurements. The pervaporation system was similar to that used by Liu et al.¹⁹ The membrane was sealed in a brass module with Viton O-rings, and the liquid feed (250 cm³) flowed through the inside of the membrane at a flow rate of 20 cm³/s. The retentate was recirculated by a centrifugal pump to the feed side of the membrane. The system lines near the membrane module were wrapped with heating tape and insulated so that pervaporation could be carried out at elevated temperatures. The pump raised the solution temperature so that the minimum temperature was 308 K. A thermocouple was placed in the liquid in the center of the membrane and the temperature was controlled by a temperature controller. A mechanical vacuum pump evacuated the permeate side of the membrane to a pressure of approximately 0.2 kPa, and the pump was then valved off during pervaporation measurements. A liquid-nitrogen cold trap condensed the permeate vapor and maintained the vacuum on the permeate side below 0.5 kPa. A permeate sample was collected and weighted every 1–3 h to determine the total flux. The pervaporation experiments were run at 308 K to reach steady state, and then the temperature was increased in increments to 328 K. Permeate concentrations were measured by off-line HPLC (Beckman) equipped with a Beckman 110B solvent delivery module and a Waters 410 differential refractometer. The separation was accomplished using a Shodex HPLC column (SH1011 sugar column, 300 × 8 mm). The mobile phase was 0.005 M H₂SO₄ at 0.6 cm³/min isocratic flow with an operation temperature of 323 K.

The membranes were boiled in a 50 wt % ethanol aqueous solution for 20 min and dried at 373 K under vacuum for 30 min to remove contaminants prior to each run at a given feed composition. The quaternary feed solution was prepared by dissolving 1,3-propanediol (Aldrich, 98% purity), glycerol (Aldrich, 99.5% purity), and glucose (Sigma, 99.5% purity) in distilled water. The concentrations of 1,3-propanediol, glycerol, and glucose were investigated at conditions of industrial interest, which are 100, 5, and 8 g/L, respectively. In addition to the quaternary solution, binary (1,3-propanediol/water, glycerol/water) and ternary (1,3-propanediol/glycerol/water) solutions with the same concentrations were used for the large-pore membranes.

Results

Membrane Preparation and Characterization. The membranes were prepared on alumina and stainless steel supports, and their synthesis properties, including the Si/Al mole ratio in the gels, are listed in Table 1. The XRD pattern of the mordenite membrane M8 showed the presence of both mordenite and α -Al₂O₃ phases (Figure 2). The XRD pattern for mordenite crystals matched that reported by Szostak²⁰ for morden-

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Table 1. Membrane Properties

membrane	type	structure	support	Si/Al ratio in gel	no. of layers	template ^a
M1	silicalite-1	MFI	stainless steel	> 1000	2	TPAOH
M2	ZSM-5	MFI	stainless steel	25	4	TPAOH
M3	ZSM-5	MFI	stainless steel	25	4	TPAOH
M4	ZSM-11	MEL	stainless steel	600	3	TBAOH
M5	ZSM-11	MEL	α -Al ₂ O ₃	600	3	TBAOH
M6	ZSM-5+11	MFI + MEL	stainless steel	600	3	TBAOH
M7	ZSM-5+11	MFI + MEL	α -Al ₂ O ₃	600	3	TBAOH
M8	mordenite	MOR	α -Al ₂ O ₃	6	2	none
M9	X	FAU	α -Al ₂ O ₃	1.5	1	none
M10	X	FAU	γ -Al ₂ O ₃	1.5	1	none
M11	Y	FAU	α -Al ₂ O ₃	5.3	1	none
M12	Y	FAU	γ -Al ₂ O ₃	5.3	1	none

^a TPAOH = tetrapropylammonium hydroxide. TBAOH = tetrabutylammonium hydroxide.

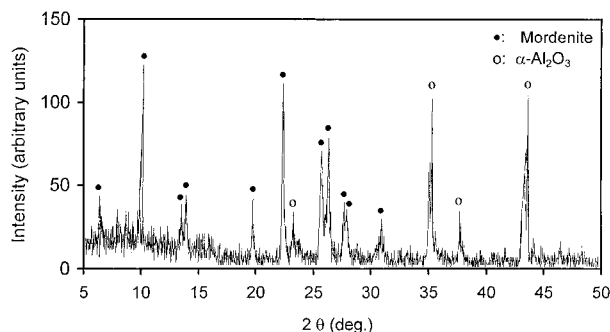


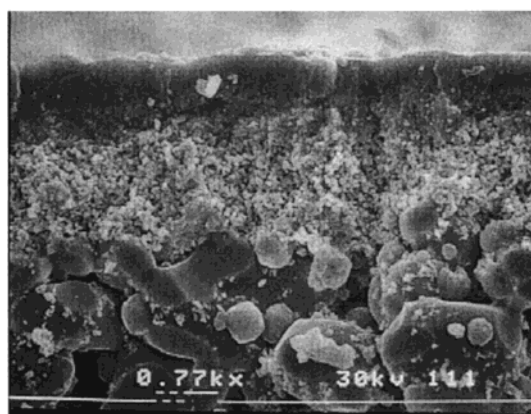
Figure 2. XRD spectrum of mordenite membrane M8 supported on α -Al₂O₃.

ite zeolite, and no additional peaks were observed. The SEM images of membrane M8 are shown in Figure 3. The surface of the mordenite membrane (Figure 3a) had a continuous layer of intergrown crystals 5–20 μ m in diameter. The SEM cross section (Figure 3b) indicates that the zeolite layer was approximately 25- μ m thick. The high intensity of the XRD lines and the crystals shown in SEM micrographs indicate a high degree of crystallinity. The silicalite-1, ZSM-5, ZSM-11, and X- and Y-type membranes also had the XRD patterns expected for these structures. The ZSM-5+11 pattern consisted of both ZSM-5 and ZSM-11 peaks. All membranes had pervaporation fluxes in the order TIPB < *o*-xylene < DMB (Table 2). The TIPB fluxes were 5 g/(m² h) or less for all membranes except for M9 (X-type on α -Al₂O₃). The *o*-xylene fluxes for the ZSM membranes were 2–8 g/(m² h), which is approximately an order of magnitude lower than *o*-xylene fluxes for the large-pore zeolites. At 330 K, the DMB, *o*-xylene, and TIPB fluxes for membranes M4 and M10 were approximately 30% higher than the fluxes at 300 K. Membranes M1, M2, M4, M6, M8, M10, and M12 were used for gas and liquid permeation studies.

Single-Gas Permeation. The single-gas permeances through the medium-pore zeolite membranes (Table 3) decreased as the kinetic diameter increased at both 300 and 473 K. The *n*-C₄H₁₀/*i*-C₄H₁₀ ideal selectivities were in the range of 2–3 at 473 K. These selectivities at 473 K indicate that these membranes are of reasonable quality, but they contain nonzeolite pores because significantly higher *n*-C₄H₁₀/*i*-C₄H₁₀ selectivities have been reported for silicalite-1 and ZSM-5 membranes.^{21,22}



a



b

Figure 3. SEM micrographs: (a) surface and (b) cross section of mordenite membrane M8 on α -Al₂O₃ support.

This is the first report of gas permeances for ZSM-11 membranes. For the large-pore zeolite membranes in Table 3, H₂/N₂ selectivities were similar to Knudsen selectivity, and for mordenite, X- and Y-type membranes, the CO₂, N₂, and butane permeances were all the same. Because these molecules are smaller than the zeolite pores, differences in permeances might not be expected.

Pervaporation of 1,3-Propanediol/Glycerol/Glucose/Water Solution. The liquid-phase concentrations of 1,3-propanediol, glycerol, and glucose were 100, 5, and 8 g/L, respectively. Thus, the main component in the pervaporation feed was water, and water had a higher flux than the other components in the feed. Similar to

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Table 2. Pervaporation Properties

membrane	pervaporation flux at 300 K (g/(m ² h))			pervaporation of 1,3-propanediol/glycerol/glucose/water mixture at 308 K			
	DMB	<i>o</i> -xylene	TIPB	total flux (kg/(m ² h))	1,3-propanediol flux (g/(m ² h))	1,3-propanediol/glycerol selectivity	1,3-propanediol/glucose selectivity
M1	37	8	3	0.11	19	36	>1600
M2	26	6	5	0.20	6	52	1700
M3	8	3	<1	<0.01			
M4	43	6	5	0.24	37	49	>1600
M5	8	2	<1	0.012			
M6	13	5	3	0.080	7	27	>1600
M7	6	3	2	0.016			
M8	310	98	4	1.2	42	69	1600
M9	240	87	16	2.1	58	45	1700
M10	81	78	2	2.1	62	59	1900
M11	64	46	1	0.3	25	65	>1600
M12	65	45	1	0.7	34	60	>1600

Table 3. Single-Gas Permeance

membrane	single-gas permeance ($\times 10^7$ mol/m ² ·s·Pa)									
	H ₂		CO ₂		N ₂		<i>n</i> -C ₄ H ₁₀		<i>i</i> -C ₄ H ₁₀	
	300 K	473 K	300 K	473 K	300 K	473 K	300 K	473 K	300 K	473 K
silicalite-1 (M1)	11	19	6.2	6.2	4.9	5.6	2.1	4.6	1.0	2.2
ZSM-5 (M2)	3.5	5.1	0.80	3.2	0.90	1.5	0.20	1.0	0.04	0.30
ZSM-11 (M4)	3.8	5.5	0.78	3.4	0.76	1.3	0.73	1.0	0.33	0.46
ZSM-5+11 (M6)	3.0	4.5	0.70	2.4	0.45	1.2	0.25	0.52	0.08	0.19
mordenite (M8)	33	30	9.3	6.8	9.5	7.2	9.5	5.7	8.3	5.1
X-type (M10)	35	34	9.2	7.4	10	7.9	8.9	7.2	8.6	6.9
Y-type (M12)	32	23	8.9	6.2	9.3	6.7	8.2	6.5	7.8	6.7

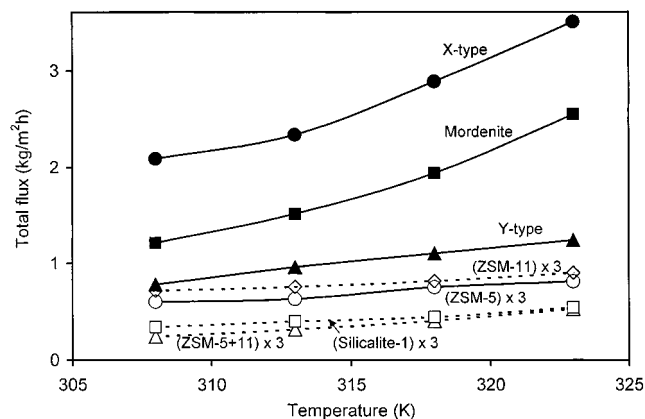


Figure 4. Total flux as a function of temperature for pervaporation of a 1,3-propanediol/glycerol/ glucose/water mixture through the indicated membranes.

ZSM-5¹⁷ and X-type membranes,¹⁸ fluxes for all membranes reached steady state in 6–8 h, and the steady-state results are presented here.

Fluxes and Permeate Concentrations. Figure 4 shows that the steady-state, total pervaporation fluxes increased with temperature for all membranes. The total fluxes were much smaller for the medium-pore size, zeolite membranes, and their fluxes were multiplied by 3 in Figure 4 so they are easier to see. Table 2 lists the total fluxes at 308 K. The highest total flux, obtained for the X-type membranes, was approximately 25 times higher at 308 K than the lowest flux, obtained for the ZSM-5+11 membranes. The fluxes for the X-type and mordenite membranes increased more rapidly with temperature than those for the other membranes.

Figure 5 shows that, for all membranes except ZSM-5, the 1,3-propanediol permeate concentration decreased with increasing temperature. The 1,3-propanediol permeate fluxes increased with temperature for all membranes, as shown in Figure 6, but the water fluxes

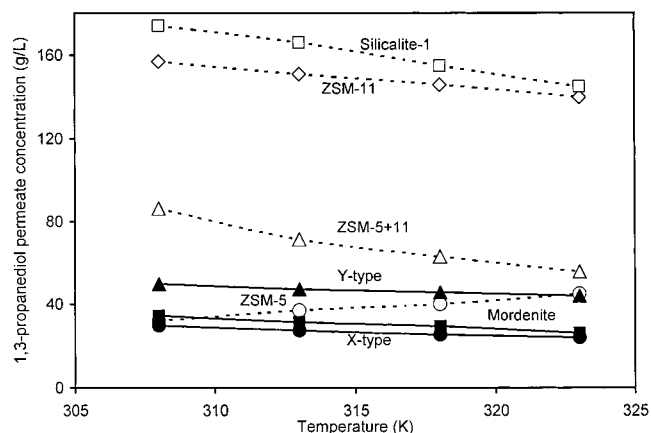


Figure 5. 1,3-Propanediol permeate concentration as a function of temperature for pervaporation of a 1,3-propanediol/glycerol/glucose/water mixture through the indicated membranes.

increased faster. The 1,3-propanediol permeate concentrations were only higher than the feed concentration of 100 g/L for the silicalite-1 and ZSM-11 membranes. Only these two membranes were selective for 1,3-propanediol over water.

Although the X-type membrane had the lowest 1,3-propanediol permeate concentration, it had the highest 1,3-propanediol flux (Figure 6). The 1,3-propanediol fluxes at 308 K are listed in Table 2. Note that the highest 1,3-propanediol flux at 308 K, obtained for the X-type membrane (62 g/(m² h)), was approximately an order of magnitude higher than the lowest 1,3-propanediol flux, obtained for the ZSM-5+11 membrane.

Figure 7 shows that, except for the ZSM-5 membrane, the glycerol permeate concentrations decreased with temperature, as was observed for the 1,3-propanediol permeate concentration. The glycerol permeate concentrations decreased more rapidly with temperature for the medium-pore membranes with high Si/Al ratios

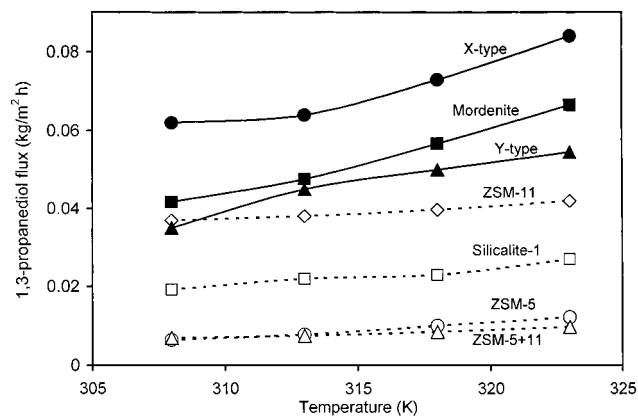


Figure 6. 1,3-Propanediol flux as a function of temperature for pervaporation of a 1,3-propanediol/glycerol/glucose/water mixture through the indicated membranes.

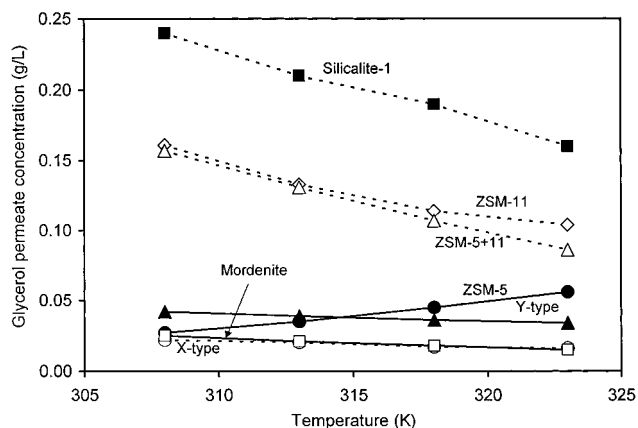


Figure 7. Glycerol permeate concentration as a function of temperature for pervaporation of a 1,3-propanediol/glycerol/glucose/water mixture through the indicated membranes.

(silicalite-1, ZSM-11, and ZSM-5+11). The most hydrophobic membrane, silicalite-1, had the highest glycerol permeate concentration, whereas the most hydrophilic membrane, X-type, had the lowest glycerol permeate concentration. The glycerol concentrations of more hydrophilic structures (low Si/Al ratio membranes such as X, Y, mordenite, and ZSM-5) were more than 2 orders of magnitude lower than the feed concentration of 5 g/L. Even for the more hydrophobic zeolites, the glycerol permeate concentrations were more than an order of magnitude lower than their feed concentrations because 1,3-propanediol blocked glycerol.^{17,18} For most membranes, the glycerol flux increased with temperature (Figure 8). The X-type membrane had the highest glycerol flux, and the ZSM-5 membrane had the lowest. Note in Figure 8 that the glycerol flux is in $\text{g}/(\text{m}^2 \text{ h})$.

The large-pore zeolite membranes were also used for pervaporation of binary (1,3-propanediol/water, glycerol/water) and ternary (1,3-propanediol/glycerol/water) so-

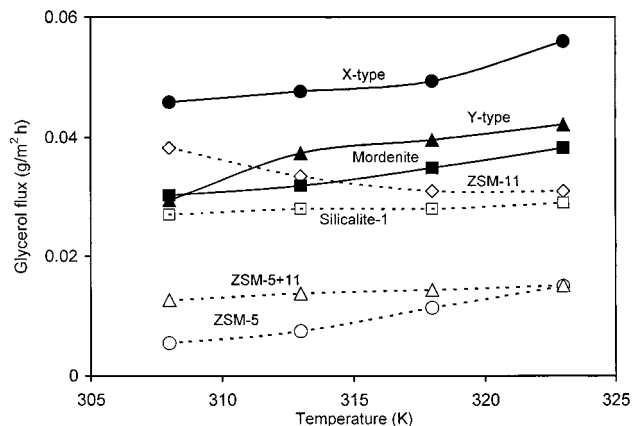


Figure 8. Glycerol flux as a function of temperature for pervaporation of a 1,3-propanediol/glycerol/glucose/water mixture through the indicated membranes.

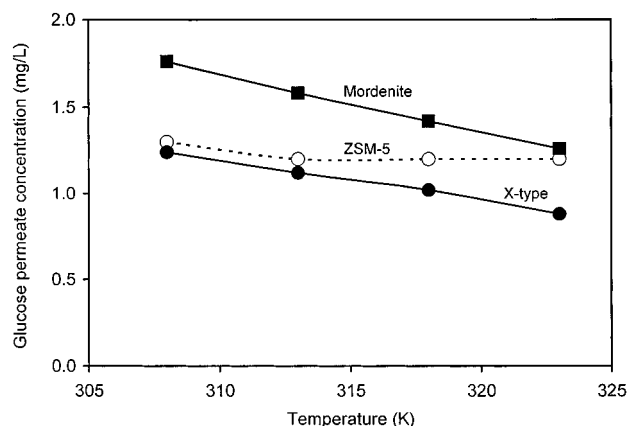


Figure 9. Glucose permeate concentration as a function of temperature for pervaporation of a 1,3-propanediol/glycerol/glucose/water mixture through the indicated membranes.

lutions. Table 4 shows their total fluxes and their 1,3-propanediol and glycerol permeate concentrations. For each membrane, solutions that contained 1,3-propanediol had lower fluxes than solutions without 1,3-propanediol. The 1,3-propanediol permeate concentrations were almost the same for the different feeds. However, the glycerol permeate concentrations for the binary solution were approximately 5 times higher than those of the ternary solution.

For most membranes, the glucose concentration was below the detection limit of the HPLC, and a lower limit on selectivity was estimated. For the ZSM-5, X-type, and mordenite membranes the glucose permeate concentration decreased with temperature, as shown in Figure 9. Note that the glucose concentration is in mg/L. The glucose concentrations for all membranes were more than 3 orders of magnitude lower than the feed concentration of 8 g/L. The glucose fluxes for the three membranes increased with temperature, as shown in

Table 4. Pervaporation through Large-Pore Zeolite Membranes at 308 K

membrane	total flux ($\text{kg}/\text{m}^2 \cdot \text{h}$)			1,3-propanediol permeate concentration (g/L)		glycerol permeate concentration (g/L)		1,3-propanediol/glycerol selectivity	
	binary (1) ^a	binary (2) ^b	ternary ^c	binary (1) ^a	ternary	binary (2) ^b	ternary	ideal	separation
MOR	2.0	2.8	1.7	36	34	0.22	0.036	8.2	47
X-type	2.8	3.6	2.7	30	30	0.20	0.036	7.4	41
Y-type	1.7	2.5	1.6	51	49	0.36	0.058	7.1	42

^a 1,3-Propanediol/water. ^b Glycerol/water. ^c 1,3-Propanediol/glycerol/water.

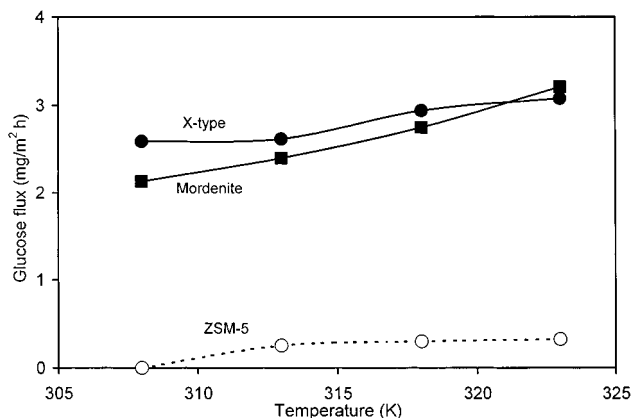


Figure 10. Glucose flux as a function of temperature for pervaporation of a 1,3-propanediol/glycerol/glucose/water mixture through the indicated membranes.

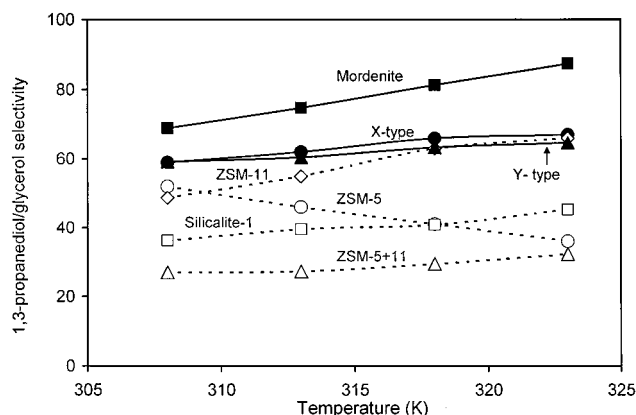


Figure 11. 1,3-Propanediol/glycerol separation selectivity as a function of temperature for pervaporation of a 1,3-propanediol/glycerol/glucose/water mixture through the indicated membranes.

Figure 10. Note in Figure 10 that the glucose fluxes are in $\text{mg}/(\text{m}^2 \text{ h})$ and are more than 4 orders of magnitude lower than the 1,3-propanediol fluxes.

To verify that glucose was sieved by the membranes, a glucose/water solution was used as a feed to a Y-type membrane. After 7 h, the glucose concentration had increased from 8 to 9.9 g/L and the amount of water that permeated gave a good mass balance. Thus, the low concentrations of glucose on the permeate side of the membranes is because glucose permeates slowly through the membranes.

Separation Selectivities. Except for the ZSM-5 membrane, the 1,3-propanediol/glycerol selectivities increased with temperature, and the highest selectivity was obtained for the mordenite membrane, as shown in Figure 11. The 1,3-propanediol/glycerol selectivities increased with temperature for the membranes where glucose could be detected in the permeate (Figure 12). Note that the lowest selectivity, obtained for the mordenite membrane, was 1600. For the membranes where the glucose concentration was below the detection limit, the 1,3-propanediol/glycerol selectivities were higher than 1600.

Discussion

Membrane Preparation and Quality. Most zeolite membranes have been prepared using organic tem-

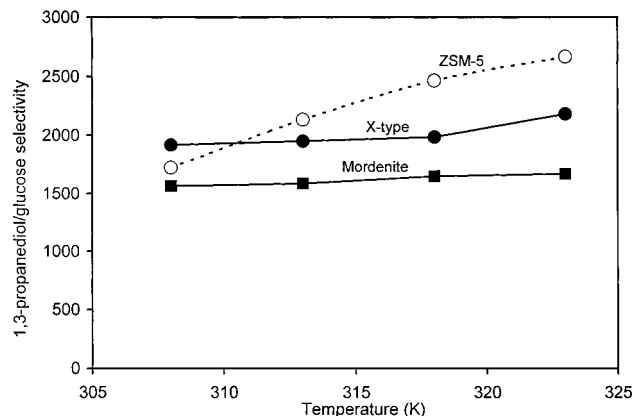


Figure 12. 1,3-Propanediol/glycerol separation selectivity as a function of temperature for pervaporation of a 1,3-propanediol/glycerol/glucose/water mixture through the indicated membranes.

plates,²⁰ and the medium-pore membranes in the current study were prepared with templates. Because of the high Al content in the synthesis gel for ZSM-5 ($\text{Si}/\text{Al} = 25$), crystals did not readily deposit onto the support and four synthesis layers were needed. Silicalite-1, in contrast, only needed two layers. The stainless-steel-supported, medium-pore membranes had higher fluxes than alumina-supported membranes for separation of a 1,3-propanediol/glycerol/glucose/water mixture.

Continuous MFI zeolite film grown on porous supports have been used to separate *n*-hexane from DMB in the vapor phase.^{23,24} These studies indicated that DMB permeates through nonzeolite pores. Burggraaf and co-workers^{25,26} also considered small fluxes of DMB as evidence that few or no defects were present in their membrane. Membranes M1, M2, M4, and M6 had higher DMB fluxes ($13\text{--}43 \text{ g}/(\text{m}^2 \text{ h})$) than membranes M3, M5, and M7 ($<10 \text{ g}/(\text{m}^2 \text{ h})$), indicating that these membranes had more or larger nonzeolite pores. However, their *o*-xylene fluxes are $8 \text{ g}/(\text{m}^2 \text{ h})$ or less, indicating that most of the nonzeolite pores were between 0.62 and 0.68 nm.

The mordenite membrane (M8) had a low TIPB flux ($4 \text{ g}/(\text{m}^2 \text{ h})$) but an *o*-xylene flux of $98 \text{ g}/(\text{m}^2 \text{ h})$, which is higher than those of the FAU structure membranes (M9–M12), which have large pores. Membrane M8 apparently contains some nonzeolite pores with pore sizes between 0.65 and 0.85 nm. Membrane M9 had more nonzeolite pores than the other FAU structure membranes because its TIPB flux is much higher ($16 \text{ g}/(\text{m}^2 \text{ h})$). If DMB, *o*-xylene, and TIPB molecules diffuse at similar rates in the nonzeolite pores, then only a few percent of the DMB or *o*-xylene permeated through the nonzeolite pores, indicating that the FAU membranes M10–M12 were of high quality.

Transport Mechanism. The kinetic diameters of water, 1,3-propanediol, glycerol, and glucose are 0.26, 0.61, 0.63, and 0.86 nm, respectively. During pervapo-

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ration, water permeates through both zeolite and nonzeolite pores because of its small diameter. The 1,3-propanediol molecule adsorbs in the pores of ZSM-5 powders,¹⁰ and this is consistent with calculations that the MFI pores are 0.62 nm in diameter.⁴ The high selectivities reported for *n*-hexane/DMB mixtures indicate that DMB permeates mainly through nonzeolite pores in MFI membranes. The molecular diameter of DMB (0.62 nm) is close to that of 1,3-propanediol (0.61 nm), and DMB fluxes (Table 2) correlated with 1,3-propanediol fluxes. Thus, for medium-pore membranes, 1,3-propanediol probably permeates mainly through nonzeolite pores. The kinetic diameter of glycerol is only slightly larger than that of 1,3-propanediol, and it also diffuses mainly through nonzeolite pores. As reported for the ZSM-5 membrane in our previous study,¹⁷ the 1,3-propanediol/glycerol separation selectivities of these medium-pore membranes are controlled by both preferential adsorption and differences in diffusion rates.

The mordenite membrane has zeolite pores with XRD pore sizes of 0.65×0.70 and 0.26×0.57 nm. Breck²⁷ indicated that neopentane (0.70 nm) could adsorb in mordenite powders. The X- and Y-type zeolites have 0.74-nm pore diameters (XRD measurements). Thus, glycerol should permeate through both zeolite and nonzeolite pores of these membranes. The ideal 1,3-propanediol/glycerol selectivity for the larger pore membranes were calculated from the permeate concentrations in binary 1,3-propanediol/water and glycerol/water. The 1,3-propanediol/glycerol separation selectivities of the ternary 1,3-propanediol/glycerol/water solution were approximately 5 times higher than the ideal selectivities at 308 K, indicating that the primary separation mechanism of 1,3-propanediol/glycerol is preferential adsorption of 1,3-propanediol in these large-pore membranes.

The glucose molecule, however, is significantly larger than the MFI, MEL, and mordenite pores, and all its permeation through these membranes is expected to be through nonzeolite pores. Thus, the high 1,3-propanediol/glucose separation selectivities of these membranes are apparently the result of molecular sieving.

The glucose fluxes through the FAU membranes are almost 3 orders of magnitude lower than the TIPB fluxes, partly because the glucose feed concentration was approximately 2 orders of magnitude lower than the TIPB concentration. Netrabukkana et al.²⁸ found that glucose (0.86 nm) diffused into Y-zeolite, whereas glucitol (0.97 nm) did not. They concluded that either the cyclic ring of glucose deformed and became smaller in one dimension as it interacted with the pore opening, allowing it to permeate into the intracrystalline matrix, or the acidity of the Y-zeolite opened the cyclic ring to form a linear molecule that could pass through the pore. Chang and Lee²⁹ also found that glucose absorbed in Y-zeolite pores during the separation of glucose from fructose. Glucose may diffuse into pores smaller than 0.86 nm, but pass through them slowly because the glucose flux was low through the X-type membrane and below the detection limit through the Y-type membrane.

Table 5. 1,3-Propanediol/Water Separation Selectivities at 308 K

membrane	1,3-propanediol/water selectivity
silicalite-1 (M1)	1.9
ZSM-5 (M2)	0.30
ZSM-11 (M4)	1.7
ZSM-5+11 (M6)	0.85
mordenite (M8)	0.32
X-type (M10)	0.28
Y-type (M12)	0.47

As reported for the X-type membrane in our previous study,¹⁸ the high 1,3-propanediol/glucose selectivities for FAU membranes are due in part to preferential adsorption of 1,3-propanediol, but occur mainly because of the molecular sieving.

The increases in the total pervaporation fluxes (Figure 4) with temperature are mainly due to the increased flux of the smallest molecule, water. As the temperature increases, the 1,3-propanediol, glycerol, and glucose permeate fluxes increased because their diffusion rates increase with temperature (Figures 6, 8, and 10), but their permeate concentrations decreased (Figures 5, 7, and 9) because their diffusion rates increased at a lower rate than the water diffusion rate.

Membrane Comparisons. Although X-type zeolite is the most hydrophilic of the membranes studied and water diffuses rapidly through the X-type membrane, water adsorbs weakly compared to 1,3-propanediol.⁸ All membranes had higher 1,3-propanediol/water separation selectivities (Table 5) than the 1,3-propanediol/water volatility (0.038) at 308 K; these selectivities are due to preferential adsorption of 1,3-propanediol. Only the strongly hydrophobic silicalite-1 ($\text{Si}/\text{Al} > 1000$) and ZSM-11 ($\text{Si}/\text{Al} = 600$) membranes were selective for 1,3-propanediol over water.

Silicalite-1 and ZSM-5. Silicalite-1 and ZSM-5 membrane have the MFI structure. The lower *n*-C₄H₁₀/*i*-C₄H₁₀ selectivity and higher *o*-xylene flux for the silicalite-1 membrane indicates that it has more nonzeolite pores than the ZSM-5 membrane M2. The permeate concentrations of 1,3-propanediol and glycerol were higher for the silicalite-1 membrane than for the ZSM-5 membrane because silicalite-1 is strongly hydrophobic, whereas the ZSM-5 ($\text{Si}/\text{Al} = 25$) membrane is hydrophilic. The glucose flux for the silicalite-1 membrane was below the HPLC detection limit, and thus lower than that of the ZSM-5 membrane, because the silicalite-1 membrane had fewer nonzeolite pores larger than 0.85 nm, as indicated by the TIPB flux. Although the silicalite-1 membrane had more nonzeolite pores, its total flux for pervaporation of the 1,3-propanediol/glycerol/glucose/water solution was lower than that of the ZSM-5 membrane (Figure 4).

ZSM-5, ZSM-11, and ZSM-5+11. Similar to the silicalite-1 membrane, the ZSM-11 membrane ($\text{Si}/\text{Al} = 600$) is hydrophobic, so the fluxes and permeate concentrations of 1,3-propanediol and glycerol were higher for the ZSM-11 than those for the ZSM-5 membrane ($\text{Si}/\text{Al} = 25$) (Figures 6 and 8), which is hydrophilic. The ZSM-5 and ZSM-11 membranes have similar DMB, *o*-xylene, and TIPB fluxes, and similar *n*-C₄H₁₀/*i*-C₄H₁₀ selectivities, so they are of similar quality. The slightly higher total flux for the ZSM-11 membrane may result because ZSM-11 has straight channels, whereas the

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ZSM-5 has both straight and zigzag channels. Both types of zeolites have the same pore diameters, but diffusion rates may be lower for the ZSM-5 than the ZSM-11 membrane because of the straight channels.

The DMB flux through the ZSM-5+11 membrane M6 (13 g/(m² h)) was much lower than that of the ZSM-11 membrane M4 (43 g/(m² h)), but their *o*-xylene fluxes were similar (5–6 g/(m² h)), indicating M6 has fewer nonzeolite pores with sizes between 0.62 and 0.685 nm. As a result, membrane M6 had lower total (Figure 4) and 1,3-propanediol (Figure 6) fluxes than M4 because 1,3-propanediol apparently permeated mainly through nonzeolite pores.

Mordenite, X- and Y-Type. The mordenite and the X- and Y-type pores are larger than 1,3-propanediol and glycerol. As reported for the X-type membrane,¹⁸ in these large-pore membranes, 1,3-propanediol preferentially adsorbs and blocks glycerol permeation. The X-type is the most hydrophilic of all the membranes evaluated so that the 1,3-propanediol permeate concentration was probably the lowest as a result (Figure 5).

Summary

Six types of zeolite membranes were synthesized on the inside surfaces of alumina and stainless steel

supports. The medium-pore membranes (MFI, MEL, and MFI + MEL) were prepared with a template in the synthesis gel and required at least two layers, whereas the larger pore membranes (MOR, FAU) were prepared by a template-free method and only required one layer. The membranes separated 1,3-propanediol from glycerol and glucose in an aqueous mixture by pervaporation. For the medium-pore membranes, 1,3-propanediol and glycerol permeated mainly through nonzeolite pores, whereas for the large-pore membranes, they permeated through both zeolite and nonzeolite pores. Zeolite pore size did not significantly affect the 1,3-propanediol/glycerol selectivity because the selectivities were mainly due to preferential adsorption of 1,3-propanediol. All the membranes had 1,3-propanediol/glucose selectivities greater than 1600. At 308 K, X-type membrane had the largest 1,3-propanediol flux of 62 g/(m² h), with a 1,3-propanediol/glycerol selectivity of 59. The silicalite-1 membrane had the highest 1,3-propanediol permeate concentration.

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