Preparation and pervaporation properties of a MEL-type zeolite membrane

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A boron-substituted ZSM-11 (Si/B = 100, MEL structure) membrane was prepared and shown to selectively permeate methyl ethyl ketone, propan-1-ol, and propan-2-ol from aqueous solutions.

Zeolite membranes have the potential to continuously separate mixtures by both adsorption and molecular sieving because the zeolite pores are of molecular size. Most previous studies of zeolite membranes have focused on MFI (silicalite-1 and ZSM-5) membranes.[1,2] The 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). Isomorphous substitution has been shown to be an effective method for modifying the MFI structure, and membranes with B substituted into the MFI framework membranes had higher n-C_4H_{10}/i-C_4H_{10} gas-phase selectivities than Al-ZSM-5 membranes.[3] In the current study, a B-ZSM-11 membrane was prepared that exhibited better pervaporation properties for organic/water mixtures than obtained for ZSM-5 membranes that were prepared by the same procedures. The ZSM-11 zeolite pore size is similar to that for ZSM-5, but it has intersecting straight channels (pore size: 0.54 × 0.53 nm).

The B-ZSM-11 membrane was prepared by *in situ* crystallization onto a tubular porous stainless steel support (500 nm pore size, Mott Corporation). The MEL structure can be hydrothermally synthesized from gels containing NaOH. den Exter[4] claimed that the MEL structure could not be synthesized as a pure phase, however, and they obtained a mixture of MFI and MEL structures.[4] Sano[5] prepared Al-ZSM-11 films on nonporous Teflon slabs, but did not show that these films were continuous membranes; no separations were reported for these films.

We prepared an alkali-free, ZSM-11 membrane that contained boron in the structure (Si/B = 100), and XRD of powder collected from the bottom of the tube indicated a MEL structure (Fig. 1). All peaks match those reported by Szostak[6] for MEL crystals, and no additional peaks were observed.

The synthesis was similar to alkali-free, MFI zeolite membranes, which showed higher separation selectivities than MFI membranes prepared from synthesis gels containing NaOH.[3] The molar composition of the gel was: 2.5 TBAOH : 0.195 $B(OH)_3$: 19.5 SiO_2 : 450 H_2O, where TBAOH (tetrabutylammonium hydroxide) was used as template, and silica sol (Ludox-AS40) was the Si source. Hydrothermal synthesis was carried out at 403 K for 72 h, and two synthesis layers were required. After synthesis, the membrane was washed, dried, and calcined at 753 K for 8 h with heating and cooling rates of 0.015 and 0.018 K s^{-1}, respectively.

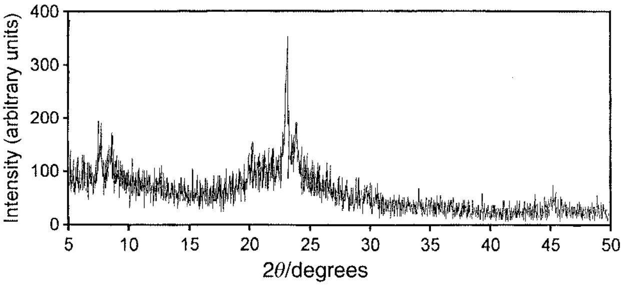

Fig. 1 XRD spectrum of the powder collected from the bottom of a B-ZSM-11 zeolite membrane.

The B-ZSM-11 membrane was used for separation of organic/water mixtures by pervaporation, using an apparatus described previously.[7] The membrane was calcined at 673 K for 3 h prior to each run at a given liquid feed composition in order to ensure that no species remained from previous experiments. The feed concentrations were 5 wt% organic. The permeate vapor was condensed by a liquid-nitrogen trap, and the downstream pressure was maintained below 0.5 kPa. The flux was measured by weighing the permeate, and permeate concentrations were measured by off-line GC.

Fig. 2 shows the steady-state total flux and the MEK/water separation selectivity as a function of temperature. A maximum flux of 0.69 kg m^{-2} h^{-1} and a maximum separation selectivity of 224 were obtained at 333 K. As the temperature increased, the fluxes increased because the diffusion rates increased, and the MEK diffusion rate increased slightly faster than the water diffusion rate. Since pure water permeated faster than pure MEK (Fig. 2), and the ideal MEK/water selectivity was *ca.* 0.8; the high MEK/water selectivity was due to the preferential adsorption of MEK. The separation selectivity was higher than the vapor–liquid equilibrium selectivity, which was 90 at 333 K.

Smetana *et al.*[8] separated a MEK/water mixture using a silicalite membrane and obtained a maximum MEK/water selectivity of 146 at 307 K with a MEK flux of 0.25 kg m^{-2} h for a 5 wt% MEK feed. Their results were similar to those measured for a silicalite-filled silicone composite membrane reported by Devine *et al.*[9] The ZSM-11 membrane has a similar flux and a higher selectivity.

Table 1 shows the pervaporation results for separation of propan-1-ol and propan-2-ol from aqueous solutions through the B-ZSM-11 membrane at 333 K. For comparison, fluxes and

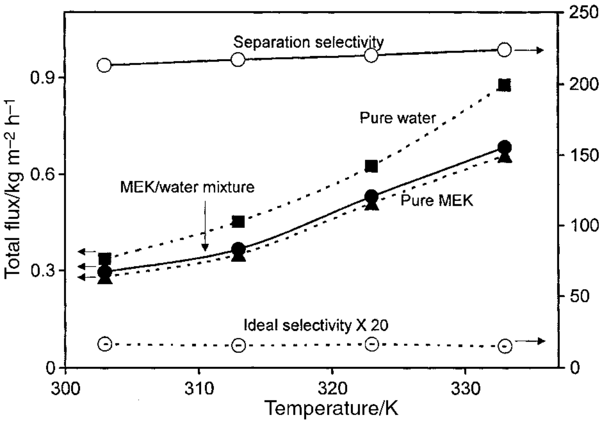

Fig. 2 Total flux and MEK/water selectivity as a function of temperature for pervaporation of a 5 wt% MEK aqueous solution through a B-ZSM-11 membrane. The flux of pure water and pure MEK are also shown. The ideal selectivity is the ratio of the fluxes.

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Table 1 Comparison of pervaporation results through B-ZSM-11 and B-ZSM-5 membranes for propanol/water mixtures at 333 K

Feed solution	Membrane	Total flux/ kg m^{-2} h^{-1}	Separation selectivity
Propan-1-ol/water	B-ZSM-11	0.25	25
	B-ZSM-5	0.072	7.8
Propan-2-ol/water	B-ZSM-11	0.31	16
	B-ZSM-5	0.068	7.0

selectivities are presented for a B-ZSM-5 membrane.[3] Both membranes had two zeolite layers prepared by similar procedures, but the fluxes and separation selectivities for the B-ZSM-11 membrane are approximately three times higher. Both propan-1-ol/water and propan-2-ol/water separation selectivities are higher than their ideal selectivities (0.21 and 0.18, respectively), and this indicates separations is due to preferential adsorption.

For MFI zeolites, the surface changes from hydrophobic (silicalite-1) to hydrophilic (Al-ZSM-5) when Si is replaced by Al in the framework. However, the substitution of B instead of Al in both MFI and MEL frameworks apparently does not make the membrane hydrophilic since high organic/water selectivities were obtained for the boron-substituted membranes, and the separations were due to preferential adsorption.

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