NaY zeolite membrane for the pervaporation separation of methanol–methyl *tert*-butyl ether mixtures

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NaY zeolite membrane grown hydrothermally on the surface of a porous alumina substrate shows a high alcohol selectivity in pervaporation, a membrane-based liquid separation process, of alcohol–benzene, cyclohexane or methyl *tert*-butyl ether.

Pervaporation, a membrane process, has gained widespread acceptance in the chemical industry as an effective process for separation of azeotropic mixtures.[1] The process operates with a liquid feed, which contacts the upstream membrane face, and a vapour permeate under vacuum or a stream of inert gas and has been applied to the dehydration of organic liquids (ethanol, isopropyl alcohol, ethylene glycol, *etc.*) and many fundamental studies have been carried out.[2] Application of pervaporation to separate organic liquid mixtures such as aliphatic–aromatic hydrocarbons or alcohols–ethers, however, are still very limited because of the swelling of polymer membrane. On the other hand, membranes made from inorganic materials are generally superior to organopolymeric materials in thermal and mechanical stability, and chemical resistance. Among inorganic materials, zeolites are promising candidates as high-performance membranes because of the unique characteristics of zeolite crystals such as molecular sieving, ion exchange, selective adsorption and catalysis. Although there are many recent reports[3] on the preparation of zeolite membranes and gas permeation through them, only a limited number of publications[4–6] deal with pervaporation studies. Recently, we have reported a high pervaporation performance of NaA zeolite membrane for the separation of water–organic liquid mixtures.[6,7] Here, we report the synthesis of NaY zeolite membrane and its application to pervaporation.

NaY zeolite membrane was grown hydrothermally on the surface of a porous cylindrical alumina support (Nikkato Corp., 12 mm outer diameter, 1.5 mm thickness, 1.3 μm average pore size). The aluminosilicate gel used in the synthesis of NaY zeolite membrane was prepared by mixing a water-glass solution and alkaline aluminate solution as described in the literature.[8] After formation of the gel, the reaction mixture was stored at ambient temperature for 12 h. The molar composition of the resulting gel was $SiO_2/Al_2O_3 = 10$, $Na_2O/SiO_2 = 1.4$ and $H_2O/Na_2O = 60$. The porous support was coated by a water slurry of seed crystals of NaY zeolite (HSZ-320NAA from Tosoh Co.) and then dried at 60 °C for 12 h. After ageing, the gel was poured into a polypropylene vessel and the support was placed in the gel. After hydrothermal treatment at 100 °C for 5 h, the support was taken out, washed with water and dried under reduced pressure.

The formulation of the NaY zeolite was verified by X-ray diffraction (XRD) with Cu-Kα radiation using a Shimadzu XD-D1 diffractometer. The XRD pattern of the NaY membrane grown on an alumina support consists of strong peaks corresponding to NaY zeolite and weak peaks of the alumina support. The surface of the membrane was examined by scanning electron microscopy (SEM) using a Hitachi S-2300 instrument. The surface of the alumina support was completely covered with randomly oriented, intergrown NaY zeolite crystals, 0.5–1 μm in size. The thickness of the membrane was about 20 μm judging from the cross-sectional view of the SEM image.

Pervaporation experiments were carried out using the apparatus described elsewhere.[6] The feed was introduced to the outer side of the zeolite membrane in a stainless-steel module that was placed in a thermostatted air-bath. Throughout the experiment the flow rate of the feed was held at 30–37 cm³ min⁻¹. The effective membrane area was 47 cm² and the downstream pressure was maintained below 13.3 Pa. The membrane performance was evaluated by the permeation flux (Q/kg m⁻² h⁻¹) and the separation factor (α). The permeation flux was calculated by weighing the permeate collected by a liquid-nitrogen trap. The separation factor was determined as $\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$ where X_A, X_B, Y_A and Y_B denote the mass fraction of components A and B in the feed and the permeate, respectively, where A is the species which is preferentially pervaporated.

Table 1 shows the flux and the separation factor of pervaporation for liquid mixtures through NaY zeolite membrane together with previously reported pervaporation results for water–ethanol mixtures through NaA zeolite membranes.[6,7] The NaA zeolite membrane was highly selective for permeating water preferentially with high permeation flux because of the micropore filling of water in the zeolite pores or the intercrystalline pores between zeolite crystals to afford water-selective permeation through the membrane. NaY zeolite membrane also preferentially permeated water from water–alcohol mixtures. However, both the separation factor and the flux of the NaY zeolite membrane were lower than for the NaA zeolite membrane, probably due to the hydrophobic properties of NaY zeolite. On the other hand, NaY zeolite membrane showed a high alcohol selectivity for several feed mixtures with methanol or ethanol. Especially high separation factors were observed for methanol–methyl *tert*-butyl ether (MTBE) separation. In Fig. 1 pervaporation selectivity expressed as methanol mole fraction in the permeate is shown as a function of methanol mole fraction in the feed mixture. It can be observed that pervaporation through NaY zeolite membrane ensures MTBE enrichment in the feed phase by preferential methanol transfer. The corresponding vapour–liquid equilibrium (VLE) curve[9] is also shown and displays large deviation from ideality. This non-ideal behaviour results in the formation of a vapour–liquid azeotrope of composition 68.5 mol% MTBE at 51.27 °C and

Table 1 Pervaporation performance of NaY zeolite membrane

| Zeolite	Feed solution (A/B) (mass% of A)	T/°C	α(A/B)	Q/kg m⁻² h⁻¹
NaY	Water–Ethanol (10)	75	125	1.59
	Methanol–Benzene (14)	50	1 400	0.62
	Methanol–MTBE (10)	50	7 600	0.32
		40	6 500	0.21
	Ethanol–Benzene (10)	50	740	0.15
	Ethanol–Cyclohexane (14)	50	540	0.19
NaA[a]	Water–Ethanol (10)	75	10 000	2.15

[a] Ref. 6.

atmospheric pressure.[9] It is clear that pervaporation through NaY zeolite membrane can break up the azeotrope and is more selective than distillation (VLE).

Pervaporation flux and separation factors of NaY zeolite membrane for methanol–MTBE mixtures at 50 °C are plotted against the feed composition in Fig. 2. High separation factors
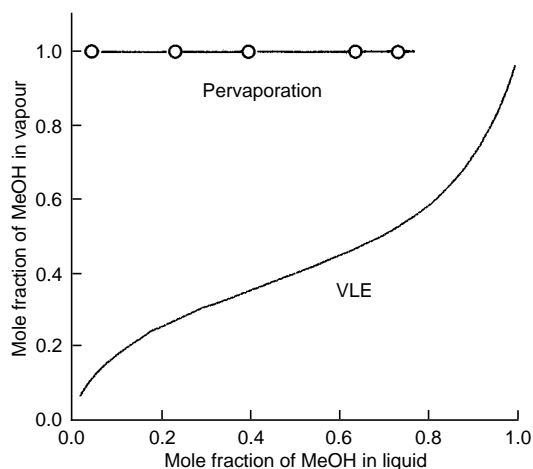
Fig. 1 Pervaporation selectivity at 50 °C through NaY zeolite membrane and vapour–liquid equilibrium (VLE) at 101 kPa in the methanol–MTBE system
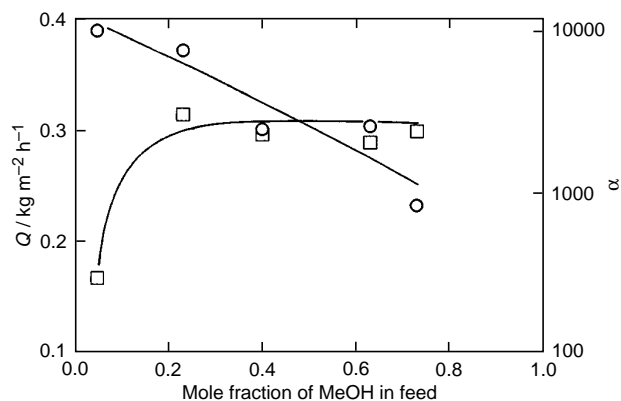
Fig. 2 Flux Q (□) and separation factor α (○) as a function of methanol feed concentration for pervaporation of methanol–MTBE mixtures through NaY zeolite membrane at 50 °C

were obtained over a wide range of feed compositions. The flux increased from 0.17 kg m^{-2} h^{-1} at 5.3 mol% methanol composition to 0.32 kg m^{-2} h^{-1} at 23 mol% composition while it was almost constant over the range 23–73 mol% composition. It is well known that the overall selectivity of a pervaporation process is determined by mobility selectivity and sorption selectivity. For methanol–MTBE mixtures, the kinetic diameters of these two molecules are approximately 0.38 and 0.62 nm, respectively, and are smaller than the intrinsic NaY zeolite pores of 0.74 nm.[8] Therefore, the sorption process presumably determines the pervaporation performance. Methanol sorption into the membrane increases with increasing methanol feed concentration and increasing sorption causes an increase in the pervaporation flux. When the methanol sorption approaches saturation, the flux becomes constant as shown in Fig. 2. Thus, the high selectivity of NaY zeolite membrane may be attributed to the selective sorption of methanol into the membrane.

Footnote

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