Highly selective separation of n-hexane from branched, cyclic and aromatic hydrocarbons using B-ZSM-5 membranes

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Boron-modified ZSM-5 zeolite membranes were effective for separating n-alkanes from 2,2-dimethylbutane, benzene and cyclohexane in binary mixtures, and enhanced selectivity was seen when both benzene and cyclohexane were mixed with n-hexane.

Zeolite membranes have high potential for separations owing to their unique pore structures and adsorption properties, and their superior thermal, mechanical and chemical properties. Zeolite membranes have been prepared with different zeolite structures, but the MFI structure has been studied most extensively. The MFI structure can be modified by isomorphous substitution of Si by trivalent elements into the zeolite framework. The zeolite surface can change from hydrophobic (silicalite) to hydrophilic (Al-ZSM-5) and from non-acidic (silicalite) to strongly acidic (Al-ZSM-5). Recently, we reported that B-ZSM-5 membranes have superior separation properties over silicalite or ZSM-5 with Al, Ge or Fe substitution.[1,2] For example, a B-ZSM-5 membrane had an n-C_4H_{10}/i-C_4H_{10} separation selectivity of 60 at 473 K. Here we report the separation of binary mixtures of n-hexane with branched, cyclic and aromatic hydrocarbon vapors using B-ZSM-5 membranes. The ternary n-hexane–benzene–cyclohexane mixture was also separated.

The B-ZSM-5 membranes used in this study were prepared by *in situ* crystallization from alkali-free gels onto tubular porous supports (stainless steel: 500 nm diameter pores, Mott Metallurgical; α-alumina: 200 nm diameter pores, US Filter). The molar gel composition was 4.44 TPAOH : 19.46 SiO_2 : 1.55 $B(OH)_3$: 500 H_2O, where TPAOH (tetrapropylammonium hydroxide) was used as the template. This corresponds to a Si : B ratio in the gel of 12.5. A previous study[2] has shown that the Si : B ratio in the zeolite is similar to that in the synthesis gel. Details of membrane preparation were reported elsewhere.[1] Membranes prepared for this study were characterized by single gas permeation and n-butane/i-butane ideal selectivity at 473 K. The results were similar to previous membranes that were characterized by SEM and XRD.[1] The SEM photos showed a continuous, intergrown layer that was 85–100 μm thick and was composed of randomly oriented crystals 5–10 μm in diameter. The XRD pattern of the membrane matched the MFI structure. The peak intensities in the patterns of all membranes were high and the background was low indicating a high degree of crystallinity.

Vapor permeation rates were measured in a continuous flow system that was described in detail elsewhere.[3] The hydrocarbon liquid was evaporated into a helium stream that flowed through the inside of the tubular membrane. The membrane was located in a stainless steel module that was heated by heating tapes. The binary hydrocarbon feeds were approximately 50 : 50, and the feed stream was *ca.* 10% hydrocarbon and 90% helium. Both sides of the membrane were at atmospheric pressure, and the He sweep gas provided a driving force across the membrane by removing the permeating components. The permeate stream was analyzed by a GC equipped with a flame ionization detector. A log-mean pressure driving force was used to calculate permeances, and permselectivity was calculated as the ratio of the permeances.

Fig. 1 shows that n-hexane can be separated from 2,2-dimethylbutane (DMB) using B-ZSM-5 membranes on α-alumina and stainless steel supports. The separation selectivities were highest (> 2000) at 373 K and they decreased with increasing temperature. The selectivity may decrease at high temperature because zeolite and non-zeolite pores expand with temperature. Since DMB (0.62 nm kinetic diameter) is larger than the MFI zeolite pore diameter, as measured by XRD (0.53–0.56 nm), its flux is expected to increase more with a slight increase in pore size. Even at 523 K, the stainless steel-supported membrane separated the n-hexane–DMB mixture with selectivity of 72.

The B-ZSM-5 membranes had much higher separation selectivities than a silicalite-1 membrane prepared by the same procedure (Fig. 2). The DMB permeances were lower and the n-hexane permeances were higher in the B-ZSM-5 membrane. The lower DMB permeances may be due to the narrowing of zeolite pores because either B^{3+} is smaller than Si or extra-framework boron deposited in the pores. According to the Pauling rule, B^{3+} cations are less stable in the framework due to their small size and they are partially removed from the framework during calcination. The gel composition for a B-ZSM-5 membrane is different from that for a silicalite-1 membrane and that could also change the quality of the membrane and reduce the number of non-zeolite pores.

Selectivities for n-hexane–DMB of 600–2000 at 360–373 K were reported by Coronas *et al.*[4] and Gump *et al.*,[5] but preferential adsorption of n-hexane rather than molecular sieving was responsible. In contrast, Ginoir-Fendler *et al.*[6] and Flanders *et al.*[3] observed selectivities of 1000 at 363 K and 70–250 at 473 K and separation was not due to preferential adsorption. Vroon *et al.*[7] obtained a selectivity of 600 at 300 K and of 2000 at 473 K. The separation selectivities were only 25–120 at 300 K for other ZSM-5 membranes.[8,9]

Separation of n-alkanes from cyclic and aromatic compounds has been studied less. Funke *et al.*[10] obtained a separation

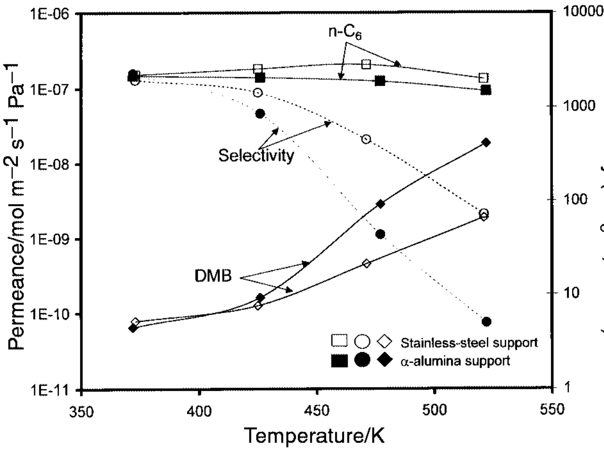

Fig. 1 n-Hexane–2,2-DMB permeances and separation selectivities as a function of temperature for B-ZSM-5 membranes on alumina and stainless steel.

Table 1 Permeances and separation selectivities for 50:50 n-hexane–organic mixtures through supported B-ZSM-5 membranes

	α-Alumina support			Stainless steel support		
	Permeance/mol m^{-2} s^{-1} Pa^{-1} (±15%)		Selectivity (±20%) n-Hexane–organic	Permeance/mol m^{-2} s^{-1} Pa^{-1} (±10%)		Selectivity (±14%) n–Hexane–organic
Organic	n-Hexane × 10^7	Organic × 10^{10}		n-Hexane × 10^7	Organic × 10^{10}	
DMB	1.5	0.65	2280	1.5	0.78	1950
Cyclohexane	2.4	3.3	720	1.3	2.2	570
Benzene	2.4	5.5	440	1.0	2.6	370
Benzene + cyclohexane (50:50)	2.2	2.8	790	1.5	1.8	800

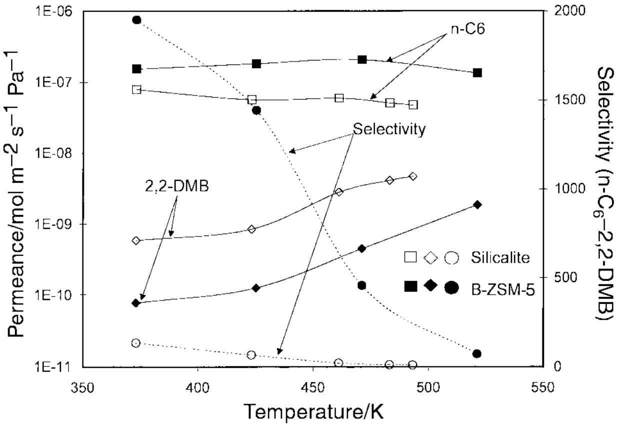

Fig. 2 n-Hexane–2,2-DMB permeances and separation selectivities as a function of temperature for silicalite-1 and B-ZSM-5 membranes on stainless steel.

selectivity of 25 at 373 K for a n-hexane–cyclohexane (50:50) mixture. Our B-ZSM-5 membranes had n-hexane–cyclohexane separation selectivities of 570 and 720 at 373 K (Table 1). Kita *et al.*[11] reported that a Y-type membrane separated n-hexane from benzene with a selectivity of 260 at 373 K. The n-hexane–benzene separation selectivities for B-ZSM-5 at 373 K were 370 on stainless steel and 440 on α-alumina supports. The B-ZSM-5 membrane also separated n-C_5 to n-C_8 alkanes from benzene, and the selectivities changed significantly with carbon number and temperature. At 373 K, the selectivities decreased from 660 to 16 as the carbon number of the alkane increased. In contrast, at 473 K, selectivities increased from 11 to 524 as the carbon number increased. For separations at 373 K, benzene permeances were almost constant but n-alkane permeances decreased as their carbon number increased. Apparently the coverages for all the alkanes were close to saturation at 373 K, so they all effectively inhibited benzene permeances. The benzene permeances in the mixtures were lower than the permeance of pure benzene. The diffusion rate of the alkane decreased with increasing carbon number, probably due to an increase in adsorption strength, and thus the selectivity decreased with carbon number. In contrast, at 473 K, the alkane permeances were almost constant because the permeances of the longer alkanes increased more with temperature. The benzene permeances at 473 K *decreased* as the alkane carbon number increased because the longer alkanes adsorbed more strongly and thus had higher coverages than the shorter alkanes. Thus, the longer alkanes more effectively blocked benzene and therefore the alkane–benzene selectivity was higher for the longer alkanes.

The separation selectivities of the ternary n-hexane–cyclohexane–benzene mixture (50:25:25) were 790–800 at 373 K, which are *significantly higher than those observed for the binary mixtures* (Table 1). The cyclohexane plus benzene permeances were lower than in the binary mixture, whereas the n-hexane permeances were similar. This increase in selectivity in the ternary mixture may be the result of competition for adsorption sites in the zeolite.

In summary, B-ZSM-5 zeolite membranes separated n-alkanes from branched, cyclic and aromatic hydrocarbons with high selectivities at elevated temperatures.

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Notes and references

1 V. A. Tuan, J. L. Falconer and R. D. Noble, *AIChE J.*, 2000, **46**, 1201.
2 V. A. Tuan, R. D. Noble and J. L. Falconer, *Micropor. Mesopor. Mater.*, 2000, **41**, 269.
3 C. L. Flanders, V. A. Tuan, R. D. Noble and J. L. Falconer, *J. Membr. Sci.*, 2000, **176**, 43.
4 J. Coronas, R. D. Noble and J. L. Falconer, *Ind. Eng. Chem. Res.*, 1998, **37**, 166.
5 C. J. Gump, R. D. Noble and J. L. Falconer, *Ind. Eng. Chem. Res.*, 1999, **38**, 2775.
6 A. Ginoir-Fendler, J. Peureux, H. Mozzanega and J. A. Dalmon, *Stud. Surf. Sci. Catal.*, 1996, **101**, 127.
7 Z. A. E. P. Vroon, K. Keizer, M. J. Gilde, J. Verweij and A. J. Burgraaf, *J. Membr. Sci.*, 1996, **113**, 293.
8 T. Matsufuji, K. Watanabe, N. Nishiyama, Y. Egashira, M. Matsukata and K. Ueyama, *Ind. Eng. Chem. Res.*, 2000, **39**, 2434.
9 S. Kallus, P. Langlois, G. E. Romanos, T. Sterioti, E. S. Kikkinides and N. K. Kanellopoulos, *Stud. Surf. Sci. Catal.*, 2000, **128**, 467.
10 H. H. Funke, A. M. Argo, J. L. Falconer and R. D. Noble, *Ind. Eng. Chem. Res.*, 1997, **36**, 137.
11 H. Kita, K. Fuchida, T. Horita, H. Asamura and K. Akamoto, *Proc. 6th International Conference on Inorganic Membranes*, Montpellier, France, 2000, p. 58.