Boron-Substituted ZSM-5 Membranes: Preparation and Separation Performance

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ZSM-5 zeolite membranes with boron substituted into the framework for silicon were prepared on porous stainless-steel and α-alumina tubular supports. These membranes had higher $n\text{-}C_4H_{10}/i\text{-}C_4H_{10}$ separation selectivities, and effectively separated these isomer mixtures to higher temperatures than membranes with aluminum substituted into the framework. Membranes were prepared with Si/B ratios as low as 12, and the best membranes were prepared from alkali-free gels. The highest $n\text{-}C_4H_{10}/i\text{-}C_4H_{10}$ permselectivity at 473 K was 60, and the highest at 527 K was 24. For most alkali-free membranes, the $n\text{-}C_4H_{10}/i\text{-}C_4H_{10}$ permselectivities and separation selectivities increased with boron content, and membranes on α-alumina supports had both higher permeances and separation selectivities. Membranes with the same permeances and selectivities can be reproducibly prepared, and they are stable at elevated temperatures.

Introduction

Inorganic membranes have potential for gas separations owing to their superior thermal, mechanical, chemical, and structural properties compared to polymeric membranes. When the pore size is comparable to the molecular dimensions, separation is possible by molecular sieving, preferential adsorption, and differences in diffusion rates. Zeolites, a class of microporous, crystalline aluminosilicate materials, have extremely narrow pore-size distributions, and they have several advantages when used as membranes. The pore size can be tuned by choosing the appropriate zeolite and by exchanging cations of different diameters. The hydrophilic/hydrophobic nature can be modified by changing the metal (Me) in the framework and the Si/Me ratio. The basic/acidic nature can be modified by exchanging metal cations with H^+. Moreover, catalytic properties of the zeolites can be used for catalytic membrane reactors.

In 1987, Suzuki (1987) patented a preparation of zeolite membranes, and published studies appeared in the early 1990s (Sano et al., 1991; Tsikoyiannis and Haag, 1992). Small-pore (A-type) (Myatt et al., 1992; Yamazaki et al., 1995; Boudreau and Tsapatsis, 1997), medium-pore (MFI and FER-type) (Gues et al., 1993; Dong et al., 1992; Yan et al., 1995a,b; Masuda et al., 1994; Sano et al., 1993; Den Exter, 1996; Nishiyama et al., 1997), and large-pore (MOR and Y-type) (Nishiyama et al., 1995; Kita et al., 1997) zeolite membranes have been made. Membrane preparation was extended to mesoporous materials (MCM-41 and MCM-48) (Koide et al., 1998) and crystalline metal- and silicon aluminophosphates (Me-AIPO and SAPO) membranes (Wu et al., 1996; Sano et al., 1997; Lixiong et al., 1997; Poshusta et al., 1998). However, most studies used MFI-type zeolites, such as silicalite-1 (pure silica) and ZSM-5 (containing Al), which have XRD pore dimensions of 0.53×0.56 nm (Szostak, 1989). Because molecules with different sizes and shapes have different diffusivities, high separation selectivities have been reported for $n\text{-}C_4H_{10}/i\text{-}C_4H_{10}$, and $n\text{-}C_6H_{14}$/3-methyl pentane mixtures (Coronas et al., 1997; Yan et al., 1995; Vroon et al., 1996; Flanders et al., 2000). Likewise high separation selectivities based on molecular sieving were obtained for $CH_4/i\text{-}C_8$, $n\text{-}C_6$/2,2 dimethylbutane, and *p*-/*o*-xylene mixtures (Bakker et al., 1996; Coronas et al., 1998; Keizer et al., 1998). Selectivities are also due to differences in adsorption properties (Poshusta et al., 1998; Coronas et al., 1997; Sano et al., 1997; Liu et al., 1996).

Because MFI-type membranes exhibit high separation selectivities, a significant effort has been made to modify and improve this type of membrane in order to improve separation performance. Yan et al. (1995) reported that the synthesis composition is critical for preparing good-quality membranes. After searching a wide composition range of precur-

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sor gel components (Si, Al, NaOH, and H_2O), they arrived at an optimal composition, producing a membrane with a n-C_4H_{10}/i-C_4H_{10} permselectivity of 31 at 458 K. The choice of synthesis conditions is also important. Vroon et al. (1996) reported MFI membranes with separation selectivities of 50 and 11 at 298 and 473 K, respectively, for a 50/50 mixture of n-C_4H_{10}/i-C_4H_{10}. These membranes were synthesized at 373–393 K, which is much lower than the typical temperature used for MFI membranes (443–453 K). Geus et al. (1992) and Bakker et al. (1993) studied the growth of ZSM-5 membranes on porous alumina, zirconia, clay, and sintered stainless-steel supports. The support surface also played a role in determining the membrane properties.

MFI-type membranes were also prepared with different crystal orientations by modifying supports and preparation conditions. Tsapatsis and coworkers (Tsapatsis, 1998; Xomeritakis and Tsapatsis, 1999; Xomeritakis et al., 1999) reported that changing the crystal orientation affected permeances and selectivities. The n-C_4H_{10} and i-C_4H_{10} permeances changed so that either n-C_4H_{10} or i-C_4H_{10} preferentially permeated. The method of contacting the synthesis solution with the support is also important. Recently, Oh et al. (1997) synthesized MFI membranes by applying pressurized sol gel coatings. Silica sol was forced into the pores of an α-alumina support by pressure, and the outer wall of the tube was contacted with TPAOH solution. Continuous layers of MFI crystals formed on the inner wall.

We recently reported preparation of alkali-free, Al-ZSM-5 membranes on the inner wall and within the pores of porous α-alumina, γ-alumina, and stainless-steel tubular supports (Tuan et al., 1999). *In situ* crystallization was used, but in contrast to previous ZSM-5 membrane preparations, the synthesis gel did not contain NaOH. This approach directly yields acidic H-ZSM-5 membranes. The preparation procedure, crystallization time and temperature, number of synthesis layers, nature of Si source, supports, and gel dilution were studied. The permeation and separation properties of the membranes depended strongly on the preparation procedure. Better membranes were obtained when the synthesis solution permeated into the support pores at room temperature *before* hydrothermal treatment. The highest separation selectivity for n-C_4H_{10}/i-C_4H_{10} was 111, which was obtained at 429 K, and the highest separation selectivity at 473 K was 36. These separations were measured with a pressure drop maintained across the membrane, and no sweep gas was used.

The preparation procedure for the alkali-free, Al-ZSM-5 membranes was used in the current study to prepare ZSM-5 membranes with B incorporated into the framework. Isomorphous substitution has been shown to be an effective method for modifying the MFI structure. The substitution of trivalent elements such as Ga, Fe, and B instead of Al changes the surface properties and the pore structure of MFI zeolites due to changes in the T-O-T angle and T-O length (T = Si, Al, Ga, Fe, B). The surface changes from hydrophobic (silicalite-1) to hydrophilic (Al-ZSM-5) and from nonacidic (silicalite-1) to strongly acidic (Al-ZSM-5). The Bronsted acid strength increases in the following order (Szostak, 1989): silicalite-1 < B-ZSM-5 < Fe-ZSM-5 < Ga-ZSM-5 < Al-ZSM-5.

Since the B^{3+} cation (0.023 nm) is much smaller than other cations (Si^{4+}, 0.042 nm; Al^{3+}, 0.051 nm; Ga^{3+}, 0.062 nm; Fe^{3+}, 0.064 nm), it is less stable in the tetrahedral positions according to the Pauling rule. Cations are stable in the tetrahedral positions when the ratio of cation to oxygen radius is 0.225–0.425. Thus, boron has been reported to be partially removed from the zeolite framework upon calcination to remove the template (Kubelkova et al., 1994). This extra-framework boron, located within the channels and on the external surface of zeolite crystals, could affect membrane properties.

The B-ZSM-5 membranes were prepared on stainless-steel and α-alumina supports by *in situ* crystallization from synthesis gels containing different B concentrations. Some gels contained NaOH and some were alkali-free. The alkali-free gel yields acidic H-B-ZSM-5 membranes, and this is the first preparation of B-ZSM-5 (zeolite powder or membrane) without NaOH. The effects of B-content, preparation method, and support on gas separation were investigated. For comparison, the permeation and separation properties of alkali-free Al-ZSM-5 and silicalite-1 membranes were also investigated. Reproducibility of membrane preparation was studied by making three membranes using the same procedure and measuring their permeation properties, and stability was studied by measuring separations for 48 h.

Experimental Methods

Zeolite membranes containing boron in the structure (B-ZSM-5) were prepared by *in situ* crystallization onto two types of porous supports:

- Asymmetric α-alumina tubes (0.70 cm ID U.S. Filter) with an inner layer that has 200-nm diameter pores.
- Stainless-steel tubes (0.65-cm ID, Mott Metallurgical Co.) with an inner layer that has 500-nm diameter pores.

To avoid bypass during permeance measurements, the ends of 4.7-cm-long alumina supports were sealed with a glazing compound (GL 611A, Duncan), which was calcined at increasing temperature with a final hold at 1,173 K for 30 min. Nonporous, stainless-steel tubes were welded to each end of the porous stainless-steel tubes.

Two types of gels with silica sol (Ludox AS40) as the silicon source and boric acid as the boron source were used for zeolite synthesis. One type of gel was clear and did not contain NaOH, and the second type was not clear and contained NaOH. The template was tetrapropylammonium hydroxide (TPAOH). For comparison, alkali-free Al-ZSM-5 and silicalite-1 membranes were prepared. The gel compositions are in Table 1.

To prepare the membranes, one end of the support tube was wrapped with Teflon tape and plugged with a Teflon cap,

Table 1. Composition of Zeolite Synthesis Gels for Membranes

	Composition (mol)					
Membranes	TPAOH	SiO_2	$B(OH)_3$	H_2O	NaOH	Si/Me
M4, M4a, M4b, M7	1.55	19.46	0.195	438	0	100
M5, M8	2.22	19.46	0.778	500	0	25
M6, M9	4.44	19.46	1.55	500	0	12.5
M1	2.0	19.46	0.39	438	2.0	50
M2	2.0	19.46	0.778	500	2.5	25
M3	2.0	19.46	1.62	500	3.0	12
M10	1.0	19.46	0	438	0	∞
M11, M12	1.0	19.46	0.0162*	438	0	600

*Al_2O_3.

Table 2. Membranes preparation conditions

Membrane	Support	Si/Me	Metal	NaOH	Crystallization Time (h)	No. Layers
M1	Stainless	50	B	Yes	48	4
M2	Stainless	25	B	Yes	24	4
M3	Stainless	12	B	Yes	24	5
M4, M4a, M4b	Stainless	100	B	No	48	2
M5	Stainless	25	B	No	24	4
M6	Stainless	12.5	B	No	24	5
M7	α-Alumina	100	B	No	48	2
M8	α-Alumina	25	B	No	24	4
M9	α-Alumina	12.5	B	No	24	5
M10	Stainless	∞	—	No	48	2
M11	Stainless	600	Al	No	48	2
M12	α-Alumina	600	Al	No	48	2

and the inside of the tubular support was filled with about 2 mL of the synthesis gel. The other end was then plugged with a Teflon cap and left overnight at room temperature. During this time the porous support soaked up almost all the synthesis gel. The tube was again filled with gel, plugged with a Teflon cap, and put into an autoclave to crystallize. The synthesis was conducted over a range of times (24–48 h) at 458 K. The synthesis conditions and supports used are summarized in Table 2.

The synthesis was repeated until an uncalcined membrane, after drying at 373 K, was impermeable to N_2 for a 138-kPa pressure drop at room temperature. Since the TPAOH template filled the zeolite pores during synthesis and thus blocked gas permeation, a membrane without defects should be impermeable, though pores larger than the zeolite pores could also be blocked by the template. After the synthesis was complete, the membranes were washed in distilled water and dried. They were then calcined in air to remove the template using a computer-controlled muffle furnace with heating and cooling rates of 0.6 and 1.1 K/min, respectively. The maximum calcination temperature was 753 K, and the membrane was held there for 8 h and then stored at room temperature under vacuum.

Single-gas permeation rates were measured for H_2, N_2, and CO_2 over a range of temperatures for most membranes, but all were characterized by n-C_4H_{10} and i-C_4H_{10} single-gas and mixture permeances. Single-gas permeation rates were measured by sealing the membrane in a stainless-steel module with silicone O-rings in a dead-end mode. The pressure drop across the membrane was 138 kPa, and the permeate side pressure was 83 kPa. The ratio of single-gas permeances is referred to as the permselectivity. Permeances of single gases measured by the sweep-gas method are lower than those measured by the pressure-drop method because of back permeation of the helium sweep sweep gas (Van de Graaf et al., 1998a). The differences were small, however, when gas permeances were measured at 473 K.

Mixture permeances were measured in a continuous-flow stainless module, using He as a sweep gas. A 50/50 feed mixture of n-C_4H_{10} and i-C_4H_{10}, with a total flow rate of 40 cm^3/min, flowed axially through the inside of the tube, and the permeate diffused radially outward. The pressure was 138 kPa on both sides of the membrane. Silicone O-rings sealed the membrane inside the module. The module was wrapped in heating tape and insulation, and a temperature controller maintained the desired temperature based on a thermocouple placed at the axial outlet of the membrane. The permeate and retentate streams were analyzed by an HP 5890 gas chromatograph with a TC detector and a packed column (1% Alltech AT-1000 on Graph-GC). Each permeance was calculated from an average of four samples taken from the retentate and permeate streams. The calculated concentrations from the four samples at a given set of conditions typically varied less than 2%. The volumetric flow rates of retentate and permeate streams were measured at room temperature and atmospheric pressure using soap-film flowmeters. The n-C_4H_{10}/i-C_4H_{10} separation selectivities are the ratios of permeances, and the log-mean partial pressure were used in the calculation.

Results and Discussion

Preparation of B-ZSM-5 membranes

Membranes M1–M3 were prepared on stainless-steel supports from gels containing NaOH using the same methods used for preparing B-ZSM-5 crystals (Tamaso et al., 1980). Membrane M1 was prepared at conditions used for the preparation of B-ZSM-5 crystals (443–448 K, 48–96 h). After two layers were deposited and the membrane was dried at 373 K, it was impermeable to N_2. However, after calcination it had a low n-C_4H_{10}/i-C_4H_{10} permselectivity, and thus more layers were added. To reduce synthesis time, membranes M2 and M3 were prepared with four and five layers at a higher temperature (458 K). Membranes M2 (Si/B = 25) and M3 (Si/B = 12) contain more boron than M1 (Si/B = 50), and thus higher NaOH concentrations were used. More water was also used because the gels became more viscous as the boron content increased. The lowest Si/Me ratio (Me = trivalent elements) reported for MFI zeolites is 12 (Kosslick et al., 1993), and using Si/B ratios of 5–10 in the gels did not increase the B content in the zeolite (Tamaso et al., 1980).

Alkali-free B-ZSM-5 membranes (M4–M6) with Si/B ratios of 100, 25, 12.5 were prepared on stainless-steel tubes. For membrane M4 (Si/B = 100) after two synthesis layers, the n-C_4H_{10}/i-C_4H_{10} permselectivity was high at 473 K, whereas for membranes M5 and M6, which contain more boron, two or three additional layers were needed after the initial calcination and the membranes were then calcined again. Our attempts to make alkali-free Al-ZSM-5 membranes with high Al content (Si/Al < 100) failed even when high TPAOH concentrations were used. This is apparently due to the large size of TPA cations, which cannot fully compensate the negative charges created by Al incorporation into the framework. However, Al-ZSM-5 zeolites with Si/Al as low as 12 can be prepared in the presence of NaOH. The smaller Na^+ cations compensate the framework negative charges. Interestingly, alkali-free B-ZSM-5 membranes with Si/B = 12.5 could be prepared.

Membranes M7–M9 were prepared *without* NaOH on α-alumina supports with Si/B ratios of 100, 25, and 12.5 under the same conditions used for membranes M4–M6. Although the α-alumina support has smaller pores than the stainless-steel tubes, four or five synthesis layers were also needed to obtain membranes with high B contents. An alkali-free silicalite-1 membrane (M10) was prepared on stainless steel, and

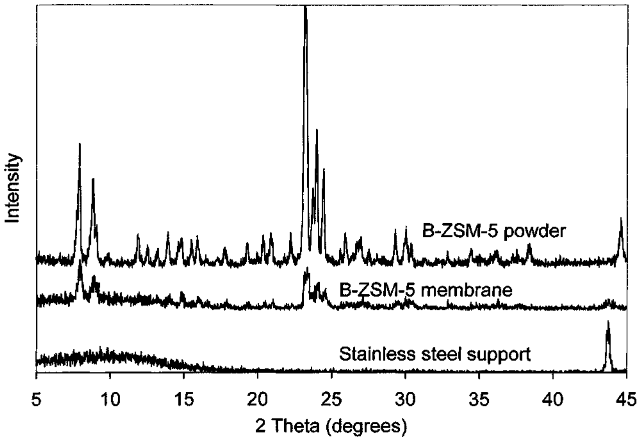

Figure 1. XRD patterns of the stainless-steel support, B-ZSM-5 membrane M4 supported on stainless steel, and B-ZSM-5 crystals formed when membrane M4 was prepared.

alkali-free Al-ZSM-5 membranes were prepared on stainless steel (M11) and α-alumina (M12).

The structures of membrane M4 and of the powders present in the liquids after preparation were checked by XRD. As shown in Figure 1, the boron-containing zeolite membranes have the MFI structure since the positions and intensities of all peaks in the XRD patterns are in agreement with those reported for MFI zeolite (Zsostak, 1989). The B content was checked by inductively coupled plasma by first dissolving the zeolite crystals in HF. The Si/B ratios in the gels were similar to those in the zeolite powders (such as Si/B = 50 in gel, 60 in powder; Si/B = 100 in gel, 125 in powder).

Previous studies (Tuan et al., 1999) using the same preparation procedures for Al-ZSM-5 zeolite membranes showed by electron probe microanalysis that Al was in the zeolite layer. Thus, B is likely to be in the zeolite layer of the current membranes, since it was detected in the zeolite crystals that formed at the same time. The structure of the B-ZSM-5 membranes is also expected to be similar to that of the Al-ZSM-5 membranes, which were characterized by SEM. Another indication that the B is in the membranes is that the B-containing membrane permeation properties were significantly different from membranes prepared without B, as described below. We did not determine how much B was in the tetrahedral positions and how much was extra framework, but B has been reported to be partially removed from the zeolite framework upon calcination (Kubelkova et al., 1994), so both types might be present.

Effect of NaOH on membrane properties

The single-gas permeances of H_2, CO_2, N_2, n-C_4H_{10}, and i-C_4H_{10} *at 473 K* are compared in Table 3 for B-ZSM-5 membranes prepared from gels with and without NaOH. Comparison is made at 473 K because the effects of adsorption are minimized, and high temperatures are a more severe test of membrane properties. The gas permeances roughly decrease with kinetic diameter, but the only large permeance decrease was as the kinetic diameter increased from n-C_4H_{10} to i-C_4H_{10}. The membranes prepared without NaOH (all membranes except M1–M3) have significantly lower i-C_4H_{10} permeances and thus higher n-C_4H_{10}/i-C_4H_{10} permselectivities. The permselectivity of 65 at 473 K for membrane M6 is the highest reported at this temperature for a membrane without post-treatment to block nonzeolite pores.

The n-C_4H_{10}/i-C_4H_{10} separation selectivities at 473 K in Table 3 are quite similar to the permselectivities, except for membrane M6, even thought the permselectivities and mixture selectivities were measured by different methods. The single gas permeances were measured with a pressure drop (no sweep), but the mixture permeances were measured with a helium sweep gas. The separation selectivity was lower than the permselectivity for membrane M6 because the n-C_4H_{10} permeance was lower in the mixture than as a single gas. The membranes with the highest selectivities were those prepared without NaOH. The permselectivities and separation selectivities do not correlate at lower temperatures. Both selectivities were low for membranes prepared with NaOH, whereas those prepared without NaOH have high permselectivities *and* mixture selectivities.

Effect of B-content and support for alkali-free B-ZSM-5 membranes

Single-gas H_2, CO_2, N_2, and n-C_4H_{10} permeances for alkali-free B-ZSM-5 membranes on stainless steel (M4, M5, M6) were about half of those for the alkali-free silicalite-1 membrane (M10), but the i-C_4H_{10} permeances were less than 10% of those for the silicalite-1 membrane. Thus, the n-C_4H_{10}/i-C_4H_{10} permselectivities were significantly higher for the B-ZSM-5 membranes than the silicalite membrane. As shown in Table 3, the n-C_4H_{10}/i-C_4H_{10} permselectivities at 473 K increased with B content for the alkali-free B-ZSM-5 membranes on both stainless-steel and α-alumina supports.

Table 3. Single-Gas Permeances and Selectivities at 473 K for B-ZSM-5 Membranes

		Permeance × 10^{-9} (mol/m^2/s/Pa)					n/i-C_4H_{10} Selectivity	
Membrane	Si/B	H_2	CO_2	N_2	n-C_4H_{10}	i-C_4H_{10}	Perm	Separation
M1	50	48	40	30	30	6.0	5.0	6.0
M2	25	110	89	70	68	23	3.0	3.4
M3	12	180	100	81	80	23	3.5	3.9
M4	100	40	32	20	20	1.0	20	22
M5	25	60	51	24	25	0.78	32	35
M6	12.5	57	53	31	37	0.57	65	27
M7	100	95	88	46	59	2.2	27	39
M8	25	162	162	79	60	2.5	24	27
M9	12.5	195	250	112	162	2.7	60	61
M10	∞	95	77	48	60	11	5.4	5.0

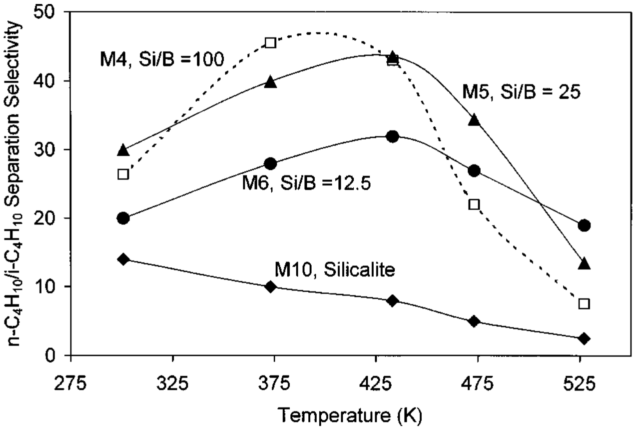

Figure 2. **n-C_4H_{10}/i-C_4H_{10} separation selectivities as a function of temperature for three B-ZSM-5 membranes with different Si/B ratios and a silicalite-1 membrane on stainless-steel supports.**

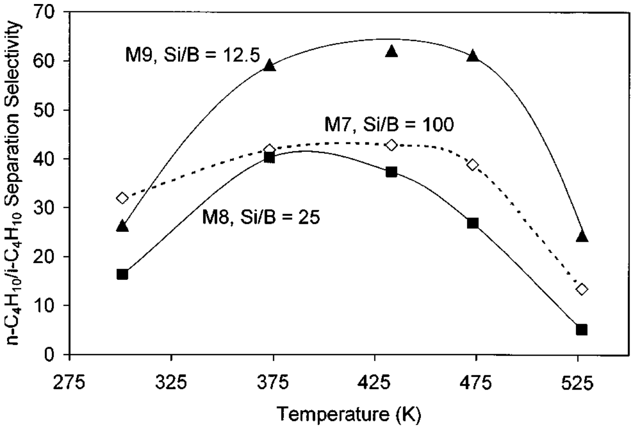

Figure 3. **n-C_4H_{10}/i-C_4H_{10} separation selectivities as a function of temperature for three alkali-free B-ZSM-5 membranes with different Si/B ratios on α alumina supports.**

Interestingly, the permselectivities increased because the i-C_4H_{10} permeances decreased *and* the n-C_4H_{10} permeances increased. Indeed, for alkali-free membranes on a given support, all the permeances but i-C_4H_{10} increased as the B content increased. For the membranes prepared with NaOH, *all* the permeances increased as the B content increased.

The other notable changes in single-gas permeances with B content was an increase in the CO_2/H_2 permselectivity. For membranes with low B contents, H_2 permeated faster than CO_2. As the B content increased, the CO_2 permeance increased faster than H_2 for the alkali-free membranes, but not for membranes M1–M3, which were made with NaOH in the gel. This increase in CO_2/H_2 permselectivity was seen for both stainless-steel and α-alumina supports, and for the membrane on the α-alumina support with a Si/B ratio of 12.5, CO_2 permeated faster than H_2, even at 473 K. Adsorption apparently plays an important role in the permeation of CO_2 *even at 473 K* for the B-ZSM-5 membranes. Similarly, n-C_4H_{10} permeates faster than N_2 at 473 K for membranes M6 and M9, also indicating strong n-C_4H_{10} adsorption on the B-ZSM-5 membranes. The high permeance of n-C_4H_{10} relative to N_2 at 473 K does not indicate a membrane of poor quality since these membranes have high n-C_4H_{10}/i-C_4H_{10} selectivities.

The n-C_4H_{10}/i-C_4H_{10} separation selectivities for stainless-steel-supported membranes are shown in Figure 2 as a function of permeation temperature for alkali-free membranes with different B contents. For silicalite-1, the n-C_4H_{10}/i-C_4H_{10} separation selectivities decreased with increasing temperature. This trend was also found by Vroon et al. (1996) and Moueddeb et al. (1998) for silicalite-1 on porous α-alumina supports. In contrast, n-C_4H_{10}/i-C_4H_{10} separation selectivities for the B-ZSM-5 membranes (M4–M6) had maxima as a function of temperature. Increasing the B content (decreasing the Si/B ratio from 100 to 25), increased n-C_4H_{10}/i-C_4H_{10} separation selectivities at 473–527 K. A further increase in B content to a Si/B ratio of 12.5 (membrane M6) decreased the n-C_4H_{10}/i-C_4H_{10} separation selectivity, except at 535 K (Figure 3), although the n-C_4H_{10}/i-C_4H_{10} permselectivity increased considerably (Table 3).

The support has a significant effect on the membrane properties. Alkali-free B-ZSM-5 membranes on α-alumina have permeances that are 2–5 times higher than permeances for the corresponding membranes on stainless steel (Table 3). In addition, as shown in Figure 3, higher separation selectivities are obtained for membranes on α-alumina supports. For membranes with Si/B = 100 and 12.5, selectivities are higher and the separation selectivity was 60 at 473 K for membrane M9 (Si/B = 12.5). For membranes M8 (Si/B = 25), the separation selectivities are lower than the corresponding stainless-steel supported membrane (M5). The higher n-C_4H_{10}/i-C_4H_{10} separation selectivities for B-ZSM-5 membranes on α-alumina are mainly due to significant increases in n-C_4H_{10} permeances over permeances on the stainless-steel-supported membranes. Figure 4 compares n-C_4H_{10} and i-C_4H_{10} permeances in mixtures for B-ZSM-5 membranes with low B-content (Si/B = 100) on stainless steel (M4) and on α-alumina (M7). The n-C_4H_{10} permeances are approximately twice as high for membrane M7, whereas the i-C_4H_{10} permeances at high temperatures are similar for membranes M4 and M7. Note that the i-C_4H_{10} permeances are multiplied by 5 in Figure 4 to make them easier to see. This trend is more pronounced for membranes M6 and M9, which contain more B (Si/B = 12.5). As shown in Figure 5, the n-C_4H_{10} permeances are approximately 5–7 times higher for membrane M9, whereas the difference in the i-C_4H_{10} permeances is less. Note that a log scale is used for the permeances in Figure 5 to make the comparison easier.

Reproducibility and stability

Van de Graaf et al. (1998) reported that silicalite-1 membrane preparation was difficult to reproduce on stainless-steel supports: only 20% of a group of membranes had n-C_4H_{10}/i-C_4H_{10} permselectivities at 303 K greater than 10. The good membranes were quite stable, however, and could be used for years without loss in properties. Similarly, we observed that not all Al-ZSM-5 membranes were good (Tuan et al.,

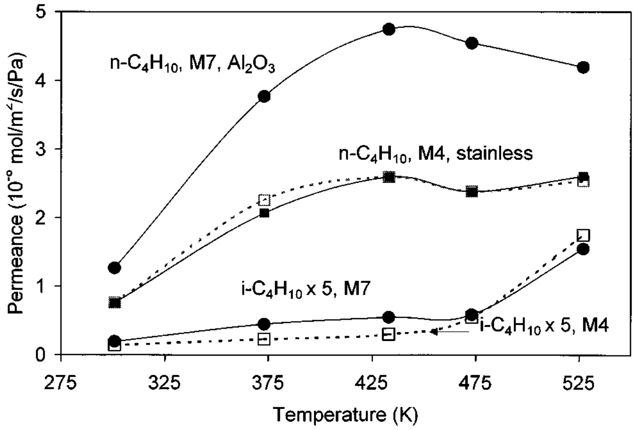

Figure 4. n-C_4H_{10} and i-C_4H_{10} mixture permeances as a function of temperature for two alkali-free B-ZSM-5 membranes.

The membranes have a Si/B ratio of 100 and are on stainless-steel and α-alumina supports as indicated. Repeat measurements are shown for membrane M4, as described in the text.

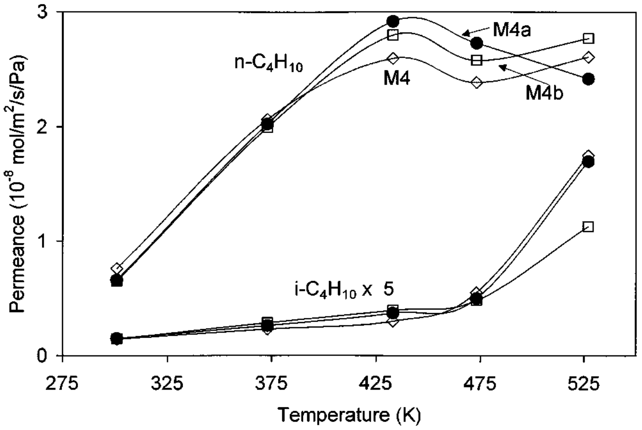

Figure 6. n-C_4H_{10} and i-C_4H_{10} mixture permeances as a function of temperature for three alkali-free B-ZSM-5 membranes prepared under identical conditions.

The membranes have a Si/B ratio of 100 and are on stainless-steel supports.

1999). Reproducibility for B-ZSM-5 membranes prepared on stainless steel appears to be excellent, however. Three alkali-free, B-ZSM-5 membranes (M4, M4a, M4b) were prepared using the same gel composition (Si/B = 100) and synthesis conditions. As shown in Figure 6, these membranes had n-C_4H_{10} mixture permeances that differed by less than 15%. The differences were even less at low temperature. Figure 6 clearly demonstrates that B-ZSM-5 membranes with high selectivities can be reproducibly prepared. The i-C_4H_{10} permeances are also similar at each temperature for the three membranes, and thus the separation selectivities were similar.

To study membrane stability, n-C_4H_{10}/i-C_4H_{10} mixture permeances were measured for membrane M4 at 473 K, then at 527, 433, 373 and 300 K. Permeances were then measured at 373, 433, 473, and 527 K. The measurements took 48 h. The permeances after this sequence, plotted as a dashed line in Figure 4, were almost the same as before, indicating that the membrane is stable at elevated temperatures.

The n-C_4H_{10}/i-C_4H_{10} mixture permeances for membrane M9, which had the best separation permeance, were measured at 473 K for 48 h, as shown in Figure 7. The i-C_4H_{10} permeance decreased approximately 2% in 48 h, whereas the n-C_4H_{10} permeance decreased by 10% during first 24 h and was almost constant during the next 24 h. The separation selectivity decreased from 59 to 56 after 48 h, so the membrane appears to be stable at elevated temperatures, and there was no evidence of butane decomposition.

Comparison to Al-ZSM-5 membranes

To our knowledge, preparation of B-ZSM-5 membranes has not been reported in the literature, nor have alkali-free B-

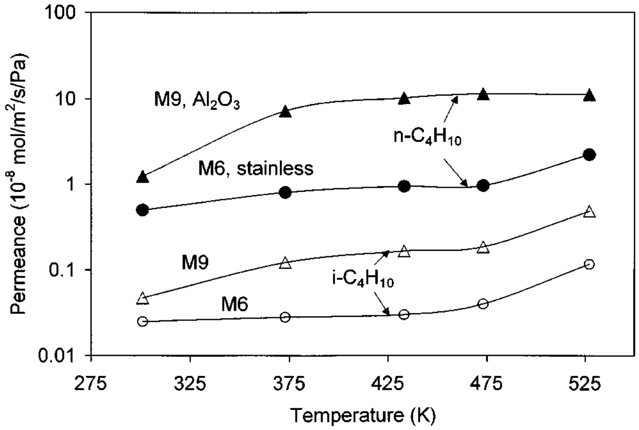

Figure 5. n-C_4H_{10} and i-C_4H_{10} mixture permeances as a function of temperature for two alkali-free-B-ZSM-5 membranes.

The membranes have a Si/B ratio of 12.5 and are on stainless-steel and α-alumina, as indicated.

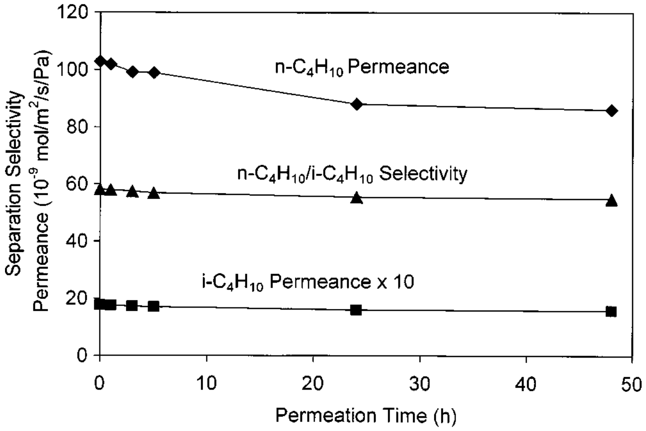

Figure 7. Butane mixture permeances at 473 K and n-C_4H_{10}/i-C_4H_{10} separation selectivity vs. permeation time K for membrane M9, which is supported on α-alumina and has a Si/B ratio of 12.5.

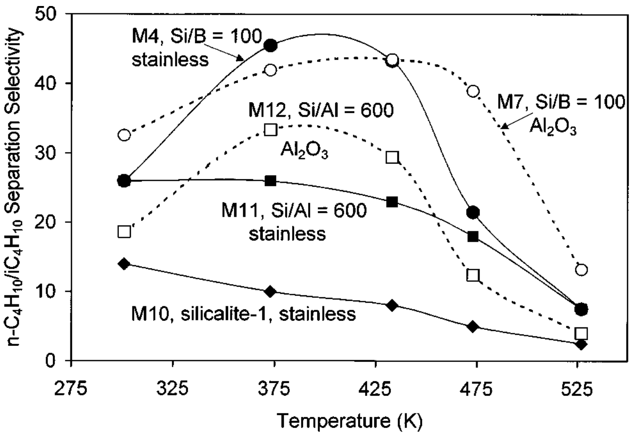

Figure 8. n-C_4H_{10}/i-C_4H_{10} separation selectivities as a function of temperature for B-ZSM-5, Al-ZSM-5, and silicalite membranes.

The Si/B and Si/Al ratios are indicated. The membranes were prepared without NaOH on the indicated supports.

ZSM-5 zeolites been prepared previously. Separation selectivities for two B-ZSM-5 membranes (M4, M7) prepared with low B contents (Si/B = 100) on stainless-steel and α-alumina supports are compared to two Al-ZSM-5 membranes (M11, M12) and a silicalite-1 membrane (M10) in Figure 8. Aluminum incorporation into the silicalite-1 framework enhances gas separation, and B incorporation enhances selectivity more. Membrane M7, which is B-ZSM-5 on α-alumina, exhibits higher n-C_4H_{10}/i-C_4H_{10} separation selectivities and higher n-C_4H_{10} permeances than the silicalite and Al-ZSM-5 membranes.

Single-gas permeances are often used to evaluate membrane quality. Van de Graaf et al. (1998) used n-C_4H_{10}/i-C_4H_{10} permselectivity measured at room temperature as an indicator of membrane quality. They considered an n-C_4H_{10}/i-C_4H_{10} permselectivity of 10 an indication of a good membrane. However, some of our MFI membranes showed n-C_4H_{10}/i-C_4H_{10} permselectivities higher than 10, but they had low n-C_4H_{10}/i-C_4H_{10} permselectivities at 475–527 K and did not separate binary mixtures at higher temperatures. At low temperature, adsorbed coverages are high, and defects (nonzeolite pores) can be blocked by adsorbed gases. Therefore, n-C_4H_{10}/i-C_4H_{10} permselectivities at high temperature, where adsorbed coverages are low, may be a better indication of membrane quality. Thus, at 473–550 K, n-C_4H_{10}/i-C_4H_{10} permselectivities correlate with n-C_4H_{10}/i-C_4H_{10} separation selectivities in the results obtained by Vroon et al. (1996), Moueddeb et al. (1998), Van de Graaf et al. (1998), and ourselves.

Conclusions

- B-ZSM-5 membranes were synthesized for the first time.
- B-ZSM-5 membranes were prepared on α-alumina and stainless-steel tubular supports, and the best membranes were obtained for α-alumina supports and alkali-free gels.
- Substitution of Si by B in the MFI framework increases n-C_4H_{10}/i-C_4H_{10} separation selectivities. For most alkali-free B-ZSM-5 membranes, n-C_4H_{10}/i-C_4H_{10} permselectivities and separation selectivities increase with increasing B-content, and the permselectivities and separation selectivities are similar at elevated temperatures.
- n-C_4H_{10}/i-C_4H_{10} separation selectivities as high as 60 were obtained *at 473 K* for a B-ZSM-5 membrane.
- B-ZSM-5 membrane preparation is reproducible and the membranes are stable at elevated temperatures.

Acknowledgments

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