

Separations of C₄ and C₆ Isomers in ZSM-5 Tubular Membranes

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Mixtures of linear and branched hydrocarbon isomers were separated in continuous flow experiments with ZSM-5 zeolite membranes. The method of membrane preparation has a dramatic effect on the selectivity. Changing the preparation procedure apparently changes the amount of the non-zeolitic pores that are in parallel with the zeolite pores and/or the length of the permeation pathways. The highest *n*-hexane/2,2-dimethylbutane separation selectivity is 2580. The *n*-hexane permeance and the *n*-hexane/2,2-dimethylbutane selectivity slowly decreased with time, but the membrane could be regenerated by calcination at 723 K. The highest *n*-butane/isobutane separation selectivity of 57 was obtained at 498 K, and the *n*-butane/isobutane selectivity correlated with the *n*-hexane/2,2-dimethylbutane selectivity but not with the N₂/SF₆ ideal selectivity measured at room temperature. Separations of organic vapors in our membranes are not due to molecular sieving. The separation selectivities are much higher than the ideal selectivities; the *n*-alkane effectively blocks the permeance of the branched-chain hydrocarbon.

Introduction

Zeolites are inorganic crystalline structures with pores of the same size as small molecules, and thus zeolite membranes have the potential to selectively separate mixtures of molecules, including mixtures of organic isomers. Zeolites have the additional advantages that they can operate at high temperatures and are resistant to chemical degradation. Recent studies show high separation selectivities for a variety of organic mixtures (Tsikoyiannis and Haag, 1992; Masuda et al., 1994; Noack et al., 1994; Kapteijn et al., 1995; Nishiyama et al., 1995; Vroon et al., 1996; Funke et al., 1996a,b,c, 1997a; Giroir-Fendler et al., 1996; Bakker et al., 1996; Kusakabe et al., 1996). The most-studied zeolite membranes use MFI-type zeolites such as silicalite and ZSM-5. These zeolites have straight channels of approximately 0.54 × 0.56 nm and sinusoidal channels of approximately 0.51 × 0.54 nm, as measured by X-ray diffraction (Flanigen et al., 1978). Adsorption studies with molecules of different sizes and shapes have yielded larger effective pore sizes of 0.7 × 0.55 nm (Wu et al., 1986), and adsorption of these larger molecules may result because pore sizes can be a function of temperature and can be changed by adsorption (Den Exter, 1996). If one molecule in a mixture is too large to enter the pores, then separation can be obtained by molecular sieving. If both components in the feed solution can permeate, then separation can be obtained due to differences in sorption rates, diffusion rates, and the ability of one molecule to inhibit or block the other from entering the pores.

Coronas et al. (1997) reported that ZSM-5 membranes with high *n*-butane/isobutane separation selectivities could be formed on tubular alumina supports by in-situ synthesis and that the method of synthesis had a significant effect on the membrane properties. Zeolite

layers could be grown as a continuous layer on the inside surface of α - and γ -alumina tubes when synthesis gel was only placed inside the tube during synthesis and the ends of the tube were sealed. When larger amounts of gel were used, and the ends were not sealed so that all the gel was accessible to the inside of α -alumina tubes, a continuous layer of zeolite crystals was not formed, but the zeolite crystals grew inside the alumina pores. The different location of the zeolite crystals for the different preparation methods resulted in dramatic differences in the membrane properties. Membranes prepared by the first method had high ideal selectivities at room temperature (N₂/SF₆ = 140–300, H₂/*n*-butane = 200–2800), but *pure isobutane permeated faster than n-butane* above 350 K. That is, the larger, branched chain hydrocarbon permeated faster, indicating that molecular sieving was not the dominant mechanism determining transport. Even though isobutane permeated faster as a single gas, these membranes had *n*-butane/isobutane separation selectivities as large as 33, with *n-butane being the faster permeating species in the mixture*. In addition, the permeance of isobutane in the mixture increased 2–3 orders of magnitude between 350 and 550 K, so that no separations were obtained above 450 K. In contrast, membranes prepared by the second procedure had low ideal selectivities at room temperature (N₂/SF₆ = 15, H₂/*n*-butane = 15–30), *pure n-butane permeated faster than isobutane*, and isobutane permeance increased only a factor of 2–3 between 350 and 550 K. However, these membranes also separated mixtures of *n*-butane and isobutane, and though the separation selectivities were lower, separation was obtained to significantly higher temperatures.

Because of these large differences in membrane properties as a result of different preparation methods, we compare the separation properties of these membranes for other organic molecules to determine if these differences based on membrane preparation are general. We also compare membranes prepared by other methods and on other supports. An isomer mixture (*n*-hexane/2,2-dimethylbutane) is used here for comparison to our previous studies on silicalite (Funke et al., 1996a, 1997a). To allow comparison to our previous studies on

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ZSM-5 membranes (Coronas et al., 1997), since the identical membranes are not used, *n*-butane/isobutane mixtures were also separated.

For zeolite membranes to be useful for separations of industrial mixtures of organics, the permeances and selectivities must be maintained over long time periods. Membrane stability has not been studied much to date, however, and this is an important aspect of the current study. The separation properties were studied as a function of time on stream for several membranes, and slow degradation in the permeances and selectivities was observed. The degraded membranes could be readily regenerated by calcination at elevated temperature to obtain their original permeances and selectivities. In addition, the effect of water on *n*-butane/isobutane separations was studied to determine how impurities might cause changes in membrane separations.

Experimental Methods

Zeolite Membrane Preparation. Zeolite ZSM-5 membranes were prepared by in-situ synthesis from gels onto two types of asymmetric porous alumina tubes and on porous stainless steel supports, and detailed preparation procedures are presented elsewhere (Coronas et al., 1997). One type of alumina support had an inner layer of γ -alumina with 5 nm diameter pores and 0.70 cm i.d. (US Filter). The other type had an inner layer of α -alumina with 200 nm diameter pores and 0.65 cm i.d. (Golden Technologies). To avoid bypass during permeance measurements, approximately 1 cm on each end of 4.7 cm long tubular supports was sealed with a glazing compound (GL 611A, Duncan), which was calcined at increasing temperatures with a final hold at 1000 K for approximately 2 h. This high temperature may have increased the pore size of the γ -alumina support. The stainless steel supports were obtained from Mott Metallurgical Corp. and had an average pore diameter of 500 nm. Nonporous stainless steel tubes were welded onto each end of a 2 cm length porous stainless tube so that the membrane could be sealed in modules for gas separations.

Two gels were used for ZSM-5 synthesis. A clear gel, which was prepared by the procedure of Yan et al. (1995), had a Si/Al atomic ratio of 600. Its molar composition was $\text{TPAOH}:\text{SiO}_2:\text{H}_2\text{O}:\text{NaOH}:\text{Al}_2\text{O}_3 = 1:6:571:4:0.005$, where TPAOH is tetrapropylammonium hydroxide. The pH of the gel was 11.6. The silica and alumina sources were tetraethylorthosilicate (TEOS) and Al foil, respectively. The second gel, with a Si/Al ratio of 100, was a modification of the silicalite gel of Grose and Flanigen (1977). The modified gel's molar composition was $\text{TPAOH}:\text{SiO}_2:\text{H}_2\text{O}:\text{NaOH}:\text{Na}_2\text{Al}_2\text{O}_4 \cdot 3\text{H}_2\text{O} = 1:21:987:3:0.105$.

Four procedures were used to synthesize ZSM-5 membranes:

(1) One end of the wet support tube was wrapped with Teflon tape and plugged with a Teflon cap, and about 2 mL of the synthesis gel was used to fill the inside of the tubular support (Jia et al., 1994). The other end was then wrapped with tape and plugged with a Teflon cap. The tube was placed vertically in a Teflon-lined autoclave. Approximately 1 mL of water was also placed in the autoclave. As shown previously by scanning electron microscopy (SEM) and ion microprobe measurements (Coronas et al., 1997), this procedure

forms a continuous layer of intergrown zeolite crystals on the inside surface of the tube.

(2) The outer wall of the dry tube was wrapped with four layers of commercial Teflon tape, the tube was placed vertically in the autoclave, and Teflon spacers held the tube in place. About 10–12 mL of the synthesis gel was poured over the tube. The ends of the tube were not plugged, and the top of the gel was approximately 2–3 mm above the top of the tube.

(3) This was the same as procedure (2) except that the autoclave was turned horizontal and rotated in the oven during the synthesis. As shown previously by SEM and ion microprobe (Coronas et al., 1997), procedures 2 and 3 produced zeolite crystals dispersed in the pores of the α -alumina support.

(4) This was the same as procedure 2 except that the tube was not wrapped with Teflon tape.

Procedures 1, 3, and 4 used the gel with a Si/Al ratio of 100. Procedure 2 used the gel with a Si/Al ratio of 100 with stainless steel supports and the gel with a Si/Al ratio of 600 with alumina supports. All syntheses were conducted at 443 K, and the synthesis times were 15–24 h for the first layer, 8–17 h for the second layer, and 15–17 h for the third layer (if needed). The synthesis was repeated until an uncalcined membrane, after drying at 440 K, was impermeable to N_2 for a 138 kPa pressure drop at room temperature. Since the template (TPAOH) filled the zeolite pores during synthesis and thus blocked gas permeation, a membrane with no defects should be impermeable. Normally, the membranes were impermeable after the second synthesis for γ -alumina supports and after the second or third synthesis for α -alumina. The membrane was wrapped with Teflon tape in procedures 2 and 3 to avoid zeolite growth on the outer surface of the support. This tape also protected the glazing on the outside surface, since it could dissolve in the highly basic solution ($\text{pH} > 11$).

After the zeolite synthesis was complete, the membranes were calcined in air to remove the TPAOH template from the pores. The calcination procedure was carried out in a computer-controlled muffle furnace with heating and cooling rates of 0.01 and 0.05 K/s, respectively. The membranes were held at a maximum temperature of 753 K for 8 h and then stored at room temperature under vacuum.

Permeation Measurements. The N_2 and SF_6 single gas permeation rates at room temperature were used as an initial indication of the membrane quality. The membrane was sealed in a stainless steel module by silicone O-rings (Funke et al., 1996a; Bai et al., 1995), and the pressure drop from feed to permeate side was 138 kPa. This is a dead-end system with no outlet for the feed except through the membrane. The ratio of permeances of two single gases is referred to as the ideal selectivity.

A similar module was used for separations of *n*-butane/isobutane mixtures, but the feed flowed through the inside of the tube at steady state (Coronas et al., 1997). Gas flow rates were controlled by Tylan mass flow controllers, and the pressure drop was 138 kPa or less. No sweep gas was used. The permeate and the retentate were analyzed on-line by a HP 5890 gas chromatograph with a TC detector and a packed column. The separation selectivities for the mixtures are the ratios of permeances, and the log-mean, partial pressure drops were used in the permeance calculations.

Table 1. Preparation Procedures and Properties of Zeolite Membranes

membrane/support	preparation procedure	no. of layers	weight gain (mg/g of zeolite)	N ₂ permeance $\times 10^7$ at 300 K (mol s ⁻¹ m ⁻² Pa)
M1/ γ -Al ₂ O ₃	1	2	12	9.3
M2/ γ -Al ₂ O ₃	1	2	14	6.6
M3/ α -Al ₂ O ₃	2	3	23	0.4
M4/ α -Al ₂ O ₃	3	4	27	3.9
M5/stainless steel	1	3	12	1.3
M6/stainless steel	4	2	21	1.0
M7/stainless steel	2	3	12	2.5

The 50/50 *n*-butane/isobutane mixtures were fed at total rates of 39–41 cm³/min at standard conditions.

The *n*-hexane/2,2-dimethylbutane separations were measured in another continuous flow system because a liquid feed system was needed for these organics. This system is described in detail elsewhere (Funke et al., 1996a). The stainless-steel membrane module was designed with custom-made graphite gaskets to allow permeation experiments at higher temperatures. The organic feed was pumped into the system by a syringe pump that allowed slow, constant flow rates. The feed liquid was mixed with a preheated He carrier stream (50 cm³/min at standard conditions) and vaporized while passing through a heated zone at a temperature well above its boiling point. A He stream (50 cm³/min at standard conditions) was used to remove the permeating compounds from the sweep side. Both the feed and the permeate were analyzed on-line by a HP gas chromatograph 5790A with a flame ionization detector and an Alltech packed column. A 10-port Valco valve with two sample loops switched between the feed and the permeate streams. A feed bypass line allowed analysis of the feed before entering the module, and mass balances based on the feed composition and flow rate were within 5%. The feed concentrations for the mixtures were about 2.5% *n*-hexane (99+%) and 2.5% 2,2-dimethylbutane (99%). For the single-gas permeance measurements, the *n*-hexane or 2,2-dimethylbutane concentration was 5%. Before an experiment, membranes were calcined in air at 753 K for 8 h. Before the organic or organic mixture was changed, the system was flushed until no organic was detected by the flame ionization detector and in many cases the membrane was calcined again. The pressures of the feed and permeate sides were adjusted separately by two back-pressure regulators. All experiments were carried out at zero pressure difference to minimize effects of leakage through seals. The temperature was monitored with thermocouples at several locations to avoid cold spots and condensation of the organic compounds.

The permeation of organic compounds led to concentration gradients from feed inlet to retentate outlet and from the sweep inlet to permeate outlet. The flow patterns and the concentration profiles in the modules in each system were unknown, and a mathematical analysis of the gradients across the membrane was not possible. Therefore, the partial pressures of the organic compounds in the feed inlet, the feed exit, and the permeate exit were used to calculate the log-mean partial pressure drops and the permeances.

For both flow systems, steady-state conditions were obtained by waiting until the concentrations in the permeate side were constant upon repeat measurements spaced 16 min apart. For the *n*-hexane/2,2-dimethylbutane system, around 3 h was required to reach steady state at temperatures under 400 K and approximately 2 h at higher temperatures. Permeances were calcu-

Table 2. Gas Permeation Properties of Zeolite Membranes

membrane	N ₂ /SF ₆ ideal selectivity at 300 K	max <i>n</i> -isobutane separation selectivity (<i>T</i> _{max})	<i>n</i> -isobutane separation selectivity at high temp
M1	196	16 (379 K)	1.3 (491 K)
M2	173	54 (394 K)	1.3 (487 K)
M3	6	11 (408 K)	5.7 (514 K)
M4	20	6.2 (408 K)	2.0 (512 K)
M5	17	4.1 (379 K)	1.3 (517 K)
M6	6.6	2.6 (410 K)	1.4 (515 K)
M7	5.8	1.7 (407 K)	1.3 (513 K)

lated from the last three gas chromatography analyses whose areas differed by less than 1–2%.

Results

Seven membranes, prepared by various procedures and on different supports, were used in these studies. Table 1 lists the support, the preparation procedure, the number of layers, the weight gain due to the zeolite formation, and the N₂ permeance at 300 K. Table 2 presents the N₂/SF₆ ideal selectivities, which differ widely with preparation method. As reported previously (Coronas et al., 1997), procedure 1 yields membranes with high N₂/SF₆ selectivities on alumina supports. This procedure also yields membranes with reproducible N₂ permeances and N₂/SF₆ selectivities. The selectivities are much lower for procedures 2 and 3. The ideal selectivities are low for the membranes prepared on stainless-steel supports, but the highest selectivity is for the membrane prepared by procedure 1.

***n*-Butane/Isobutane Separations.** Membrane M2 was able to separate 50/50 *n*-butane/isobutane mixtures over a range of temperature, with *n*-butane being the faster permeating species. This is similar to other membranes prepared by procedure 1 on γ -alumina supports (Coronas et al., 1997). As shown in Figure 1, which plots permeances in the mixture on a log scale, *n*-butane permeance increased about an order of magnitude between 335 and 485 K. The isobutane permeance was almost constant from 335 to 410 K and then it increased by more than 2 orders of magnitude between 410 and 485 K. Thus, as shown in Figure 2, the separation selectivity went through a maximum of 55 near 390 K, but selectivity decreased almost to 1 by 486 K. Though this is similar to behavior that we reported previously (Coronas et al., 1997), the selectivity is higher, and the temperature range for separation is somewhat wider. Membrane M1, which was prepared by the same procedure and has similar N₂ permeance and N₂/SF₆ ideal selectivity (Tables 1 and 2), exhibited similar behavior but with lower selectivities (Table 2).

The permeation and separation behavior are significantly different for membranes prepared by procedures 2 and 3 on α -alumina supports, as has been reported previously (Coronas et al., 1997). Figure 3 shows *n*-butane/isobutane permeances as a function of tem-

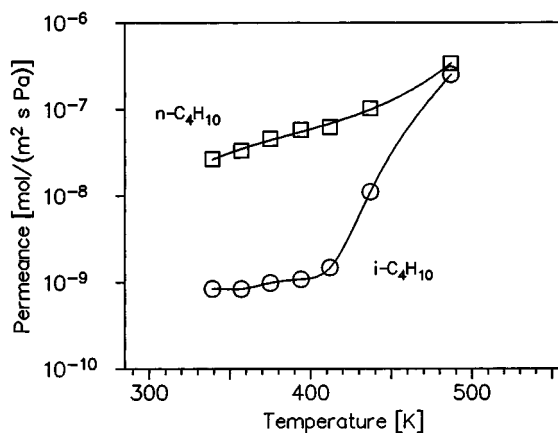


Figure 1. *n*-Butane and isobutane permeances for membrane M2 as a function of temperature. A 50/50 mixture was on the feed side at a pressure of 222 kPa, and the permeate pressure was 84 kPa.

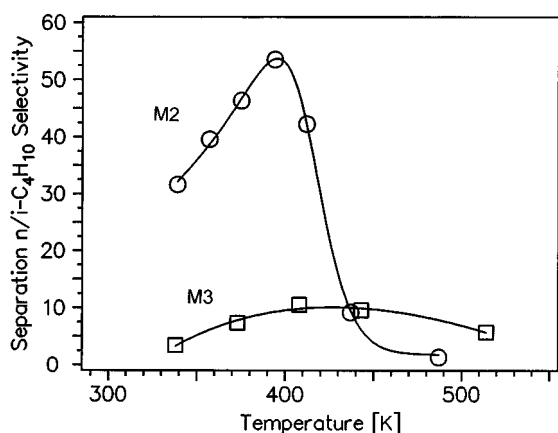


Figure 2. Separation selectivity for 50/50 *n*-butane/isobutane as a function of temperature for membranes M2 and M3.

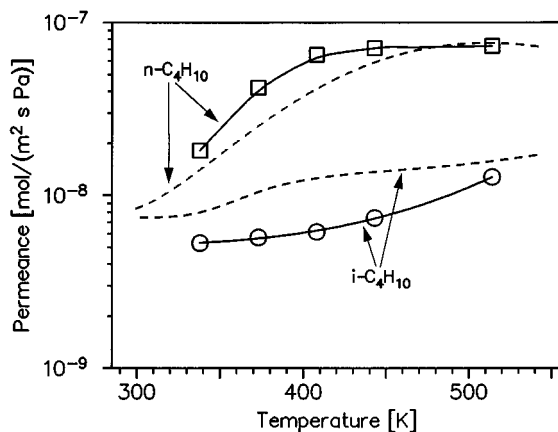


Figure 3. *n*-Butane and isobutane permeances for membrane M3 as a function of temperature. A 50/50 mixture was on the feed side at a pressure of 222 kPa and the permeate pressure was 84 kPa. Dashed lines denote single gas permeances.

perature for membrane M3, which was prepared by procedure 2 on α -alumina. The solid lines are the permeances in the mixture and the dashed lines are the pure gas permeances. These results were reported previously (Coronas et al., 1997), but are important for comparison to the other membranes and for the other isomer mixture. For the mixture, the isobutane permeance increased less than a factor of 5 between 330 and 510 K for membrane M3, but the *n*-butane permeance increased faster than the isobutane permeance

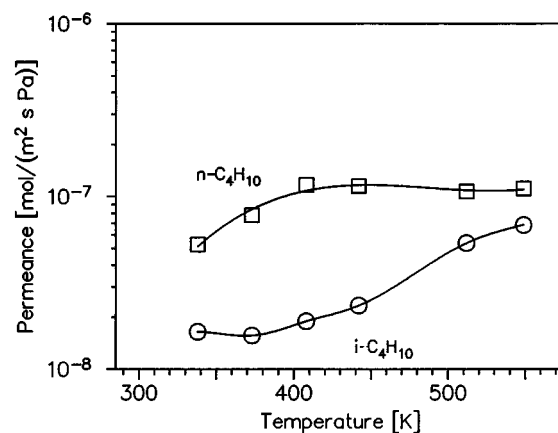


Figure 4. *n*-Butane and isobutane permeances for membrane M4 as a function of temperature. A 50/50 mixture was on the feed side at a pressure of 222 kPa and the permeate pressure was 84 kPa.

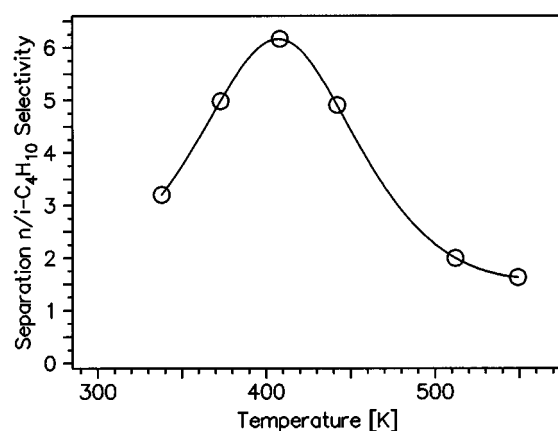


Figure 5. Separation selectivity for 50/50 *n*-butane/isobutane as a function of temperature for membrane M4

at low temperature, so the selectivity increased with temperature. Since the *n*-butane permeance was essentially constant above 440 K, the selectivity decreased at higher temperature, but this membrane still had a selectivity of 5.7 at 514 K, as shown in Figure 2. Note that isobutane permeated slower in the mixture than as a pure component, and the *n*-butane permeance was somewhat higher in the mixture than for the pure component.

For membrane M4, which is also on α -alumina and was prepared by procedure 3, the temperature dependence of the permeances, shown in Figure 4, is similar to that of membrane M3. The isobutane permeance increased a factor of 4 as the temperature increased from 338 to 549 K, and this membrane also has a significant *n*-butane/isobutane selectivity above 500 K. The selectivity is plotted versus temperature in Figure 5.

The three membranes supported on porous stainless steel tubes were less effective in separating *n*-butane/isobutane mixtures. The same general trends were observed in permeances, as shown in Figure 6 for membrane M5, with the *n*-butane permeance increasing faster than that of the isobutane at low temperature, and the permeances becoming similar at higher temperatures. The separation selectivities are smaller for the stainless-steel supported membranes than for the α - or γ -alumina supported membranes prepared by procedure 1. As shown in Figure 7 and Table 2, the highest selectivity for the stainless supported mem-

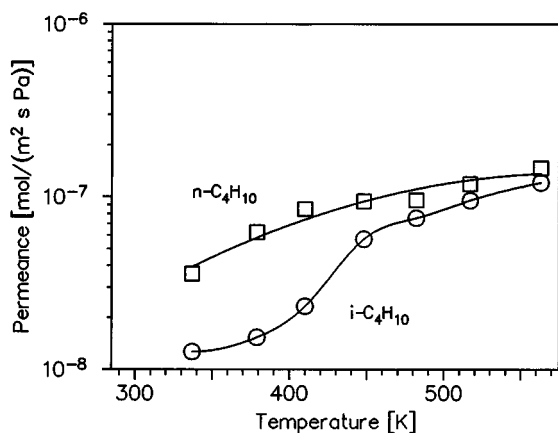


Figure 6. *n*-Butane and isobutane permeances for membrane M5 supported on a stainless steel tube as a function of temperature. A 50/50 mixture was on the feed side at a pressure of 222 kPa and the permeate pressure was 84 kPa.

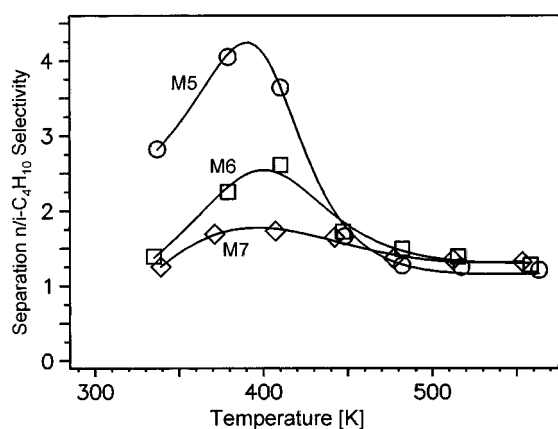


Figure 7. Separation selectivities for ZSM-5 membranes M5, M6, and M7 supported on porous stainless steel.

branes was only 4.1, and the same trends in selectivity are seen as in Figure 2 for membrane M2, with the selectivities having a maximum at 400 K or lower and then decreasing to close to 1.

Change in *n*-Butane/Isobutane Separations with Time. The permeances of a 50/50 mixture of *n*-butane/isobutane were measured as a function of time for membrane M2, and the permeances were also measured after exposure to water vapor. Figure 8 shows the permeances and the *n*-butane/isobutane selectivity versus time at 373 K for membrane M2. Note that the permeances are multiplied by 10^9 so they can be displayed on the same scale as the selectivity, and the isobutane permeance is multiplied by an additional factor of 10 so that its changes can be seen. The butane permeances quickly reached steady state and then slowly decreased over 5 h. The selectivity continued to increase over this time as the isobutane decreased faster than the *n*-butane. After 5 h, the permeance measurements were stopped for about 15 h and the membrane sat at 373 K without any gas flow. When the permeances were measured again, the *n*-butane permeance was lower, and both permeances continued to decrease with time. The selectivity was also lower after 15 h without any flow, but it increased for 3 h until it was close to its previous value.

To determine if water adsorption by the ZSM-5 might be responsible for the changes in butane permeances with time, the membrane was exposed to excess water. The membrane was removed from the module and

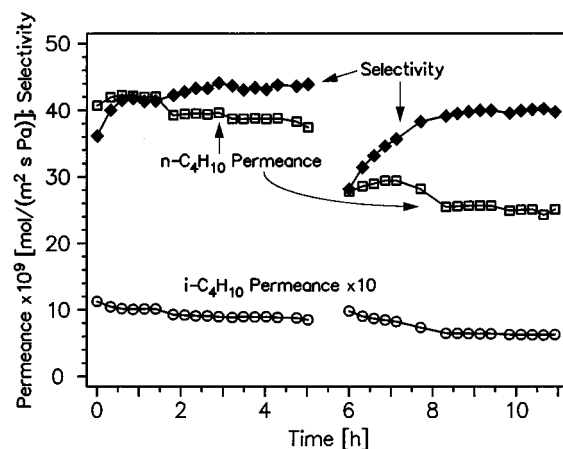


Figure 8. *n*-Butane and isobutane permeances and *n*-butane/isobutane separation selectivity as a function of time for membrane M2 at 373 K for a 50/50 *n*-butane/isobutane mixture. After 5 h of measurements, the membrane was cooled to room temperature overnight and then heated to 373 K and the measurements were continued for an additional 5 h.

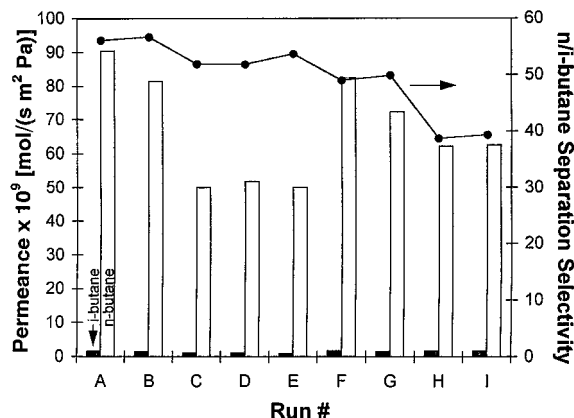


Figure 9. Bar graph: *n*-butane and isobutane permeances at 398 K in membrane M2. The *n*-butane/isobutane selectivity is presented at the top of the figure. The run notation corresponds to various heat treatments and exposure to water, as described in the text.

soaked in distilled water at room temperature for 30 min. It was then dried with a paper towel and placed back in the module. The membrane was held at 373 K for 7 h with a *n*-butane/isobutane mixture on the feed side at 222 kPa and the permeate side at 84 kPa. No permeation was detected over this time period, with the minimum detectable total permeance (*n*-butane + isobutane) estimated to be 10^{-9} mol/(s m² Pa). When the temperature was raised to 468 K, some permeation was detected and, after keeping the membrane for about 15 h at 468 K without any flow, the *n*-butane and isobutane permeances at 473 K were $(1.0 \text{ and } 0.88) \times 10^{-7}$ mol/(s m² Pa), respectively. Thus, water was not removed at 373 K, but it was effectively removed at 468 K.

Additional exposures to water vapor under various conditions were also carried out for membrane M2 at 398 K, and the resulting *n*-butane and isobutane permeances are presented in a bar graph in Figure 9. The *n*-butane/isobutane separation selectivities are also plotted in Figure 9. The treatments that took place prior to each permeance measurement, which required approximately 16 min, are as follows: A, calcination for 2 h at 753 K in air; B, exposure to water vapor in N₂ flow (80 cm³/min) for 10 min at 398 K; C, run *n*-butane/isobutane separations at various temperatures for 2

Table 3. Single-Gas Permeances and Ideal Selectivities as a Function of Temperature for Membranes M2 and M3

membrane/ support	temp (K)	permeance $\times 10^9$ (mol s ⁻¹ m ⁻² Pa)		<i>n</i> -C ₆ H ₁₄ / 2,2-DMB ideal selectivity
		<i>n</i> -C ₆ H ₁₄	2,2-DMB	
M2/ γ -Al ₂ O ₃	374	155	75	2.1
	462	314	210	1.5
	374 ^a	43	97	0.44
M3/ α -Al ₂ O ₃	374	118	7.0	17
	460	176	12	15
	374 ^a	47	8.2	5.7
	374 ^b	51	3.6	14

(after 2,2-DMB) (after *n*-C₆H₁₄)

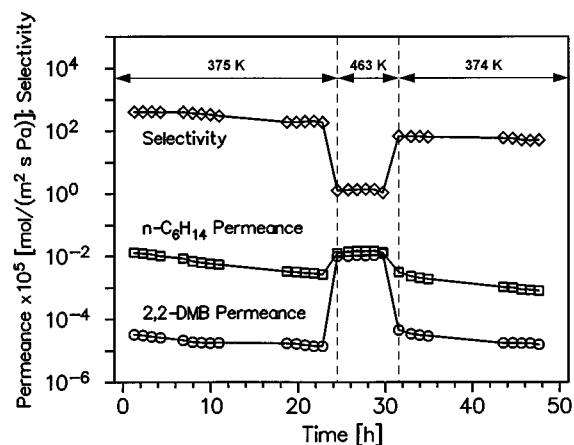
^a Permeance measured after the membrane was held at 460–462 K in the same gas for approximately 5 h and then cooled to 374 K. ^b Permeance measured after the membrane was held at 374–460 K in the other isomer for approximately 10 h and then cooled to 374 K before switching feed gas.

days and then hold the membrane overnight at 398 K without any flow; D, exposure to water vapor in N₂ flow (80 cm³/min) for 30 min at 398 K; E, hold overnight in N₂ flow (75 cm³/min) followed by 30 min exposure to water vapor in N₂ flow (80 cm³/min); F, calcination for 2 h at 753 K in air then expose to water vapor in N₂ flow (80 cm³/min) for 30 min; G, hold overnight in dry N₂ flow (75 cm³/min); H, inject 100 μ L of liquid water into the *n*-butane/isobutane flow, upstream of the module; I, inject 200 μ L of liquid water into the *n*-butane/isobutane flow, upstream de module.

Though some of these treatments decreased the permeances, the membrane returned almost to its original permeances after 2 h in air at 753 K (steps A and F). The selectivity appears to slowly decrease with time in Figure 9 (these experiments took a total of about 35 h with the membrane exposed to butanes), and the biggest decrease is due to liquid water injection. Note, however, that the water vapor did not cause large changes in the permeances.

Hexane/2,2-Dimethylbutane Single Gas Permeances. Table 3 lists single gas permeances for *n*-hexane and 2,2-dimethylbutane at two temperatures for membranes M2 and M3. Each permeation measurement took about 3–5 h. In each membrane, both permeances increase with temperature, and larger increases were seen for membrane M2. Note the ideal selectivities for membrane M2 are small (1.5–2.1), but the 2,2-dimethylbutane permeances are significantly lower for membrane M3, and thus the ideal selectivities are larger (15–17). A hysteresis effect was observed when the membrane was cooled to 373 K after measurements were made at 460–462 K. The 2,2-dimethylbutane permeances at 374 K in both membranes were 15 to 30% higher than those observed prior to the measurements at 460–462 K. In contrast, for both membranes the *n*-hexane permeance was a factor of 3 to 4 lower after the measurements at 460–462 K. Thus, the ideal selectivities decreased after the high-temperature treatments. Note that the ideal selectivity is less than 1 for membrane M2; the larger 2,2-dimethylbutane permeated faster.

The last row in Table 3 lists single gas permeances measured after the membrane was held in the other gas at 374 and 460 K. That is, the *n*-hexane permeance was measured at 374 K, then at 460 K, and then at 374 K (for a total of approximately 10 h) before the *n*-hexane was flushed from the system at 374 K and 2,2-dimethylbutane was introduced to measure its permeance. Thus, the 2,2-dimethylbutane permeance of 3.6×10^{-9} mol/(s m² Pa) was measured after the *n*-hexane per-

**Figure 10.** *n*-Hexane and 2,2-dimethylbutane permeances and *n*-hexane/2,2-dimethylbutane separation selectivity as a function of time for membrane M1 at different temperatures for a 50/50 *n*-hexane/2,2-dimethylbutane mixture.

meance of 47×10^{-9} mol/(s m² Pa) was measured. The membrane was then calcined and the 2,2-dimethylbutane single gas permeances were measured at 374, 460, and 374 K before the 2,2-dimethylbutane was flushed from the system and the *n*-hexane permeance of 51×10^{-9} mol/(s m² Pa) was measured at 374 K. Note that exposing the membrane to 2,2-dimethylbutane at elevated temperature had the same effect as exposing the membrane to *n*-hexane for the *n*-hexane permeance. The permeance of 51×10^{-9} mol/(s m² Pa) is almost identical to the *n*-hexane permeance of 47×10^{-9} mol/(s m² Pa) measured after *n*-hexane exposure. In contrast, after the membrane was exposed to *n*-hexane at higher temperature, the 2,2-dimethylbutane permeance was less than half the value measured after exposure to 2,2-dimethylbutane at higher temperature. Thus, exposure to *n*-hexane at higher temperature decreases permeances of both *n*-hexane and 2,2-dimethylbutane, but exposure to 2,2-dimethylbutane only decreases the *n*-hexane permeance. Apparently some *n*-hexane and 2,2-dimethylbutane are irreversibly held in the pores following exposure at 460 K or they decompose at 460 K.

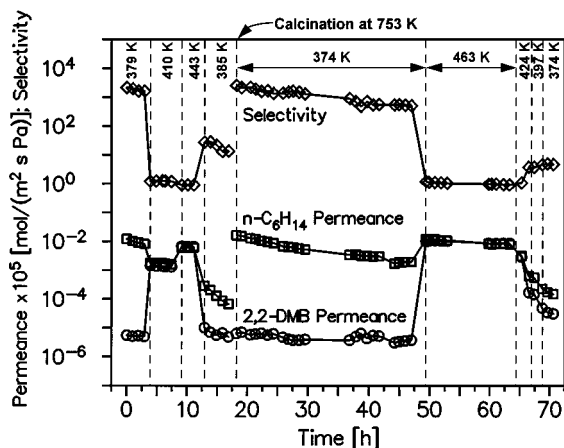
Hexane/2,2-Dimethylbutane Separations. As observed for silicalite membranes by Funke et al. (1997a) and Pereux (1994), the ZSM-5 membranes on γ - and α -alumina supports are able to separate mixtures of *n*-hexane and 2,2-dimethylbutane. As shown in Figure 10 for membrane M1, which is supported on γ -alumina and prepared by procedure 1, *n*-hexane permeated faster than 2,2-dimethylbutane at 375 K. In this and in subsequent figures, each point is the average of four measurements taken every 15 min. During the first 23 h on stream, the *n*-hexane permeance steadily decreased, whereas the 2,2-dimethylbutane permeance exhibited a smaller fractional decrease. As a result, the *n*-hexane/2,2-dimethylbutane separation selectivity decreased from 406 during the first hour to 193 after 22 h (Table 4). The times for the *n*-hexane permeance and for the selectivity to decrease to half their initial values (half life) were 9.3 and 17 h, respectively. Both these plots were fit well by straight lines on a ln(permeance) or ln(selectivity) versus time plot.

The membrane behavior changed dramatically when the temperature was increased from 375 to 463 K. The *n*-hexane permeance increased about a factor of 5, but the 2,2-dimethylbutane permeance increased almost 3

Table 4. Permeances and Separation Selectivities of a 50/50 Binary *n*-Hexane/2,2-Dimethylbutane Mixture as a Function of Temperature

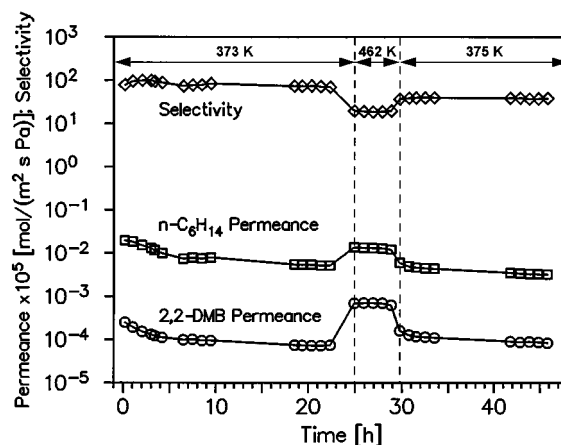
membrane	temp (K)	permeance $\times 10^9$ (mol s ⁻¹ m ⁻² Pa)		<i>n</i> -C ₆ H ₁₄ /2,2-DMB separation selectivity
		<i>n</i> -C ₆ H ₁₄	2,2-DMB	
M1/ γ -Al ₂ O ₃	375 (initial)	134	0.33	406
	375 (22 h)	27	0.14	193
	463 (5 h)	137	125	1.1
	374 (16 h) ^a	8.1	0.16	51
M2/ γ -Al ₂ O ₃	374 (initial)	165	0.064	2580
	374 (29 h)	19	0.038	500
	463 (14 h)	79	86	0.9
	374 (2 h) ^a	1.5	0.31	4.8
M3/ α -Al ₂ O ₃	373 (initial)	197	2.5	79
	373 (22 h)	52	0.74	70
	462 (4 h)	120	6.2	19
	375 (16 h) ^a	32	0.83	39
M4/ α -Al ₂ O ₃	373 (initial)	204	9.5	21
	373 (13 h)	145	8.0	18
	461 (3 h)	140	32	4.4
	376 (14 h) ^a	23	4.3	5.3

^a Measured after higher temperature (461–463 K) permeation measurements.

**Figure 11.** *n*-Hexane and 2,2-dimethylbutane permeances and *n*-hexane/2,2-dimethylbutane separation selectivity as a function of time for membrane M2 at different temperatures for a 50/50 *n*-hexane/2,2-dimethylbutane mixture. After 17 h of measurements, the membrane was calcined at 753 K for 8 h.

orders of magnitude, so that the selectivity decreased from 193 to 1.1. When the temperature was again lowered to 374 K, the *n*-hexane permeance was almost the same as its previous value at 375 K, but the 2,2-dimethylbutane permeance was 3.3 times higher after the measurements at 463 K, and thus the separation selectivity was only 70. The selectivity further decreased to 52 over the next 16 h.

The same kind of behavior was seen for membrane M2, which was also prepared by procedure 1 on γ -alumina. As shown on Figure 11, membrane M2 had a *n*-hexane/2,2-dimethylbutane separation selectivity higher than 2000 at 379 K. At higher temperatures, however, no separations were obtained. Raising the temperature by 31 K increased the permeance of 2,2-dimethylbutane by more than 2 orders of magnitude but decreased the *n*-hexane permeance by almost an order of magnitude, so that the permeances of the two isomers were essentially identical, as shown in Figure 11. Both permeances increased by the same amount when the temperature was increased to 443 K, so that the selectivity remained at 1. After the membrane was held a total of 7 h at 410 and 443 K, its temperature was lowered to 385 K, and the 2,2-dimethylbutane per-

**Figure 12.** *n*-Hexane and 2,2-dimethylbutane permeances and *n*-hexane/2,2-dimethylbutane separation selectivity as a function of time for membrane M3 at different temperatures for a 50/50 *n*-hexane/2,2-dimethylbutane mixture.

meance decreased more than the *n*-hexane permeance so that a selectivity of 28 was obtained. Note that the 2,2-dimethylbutane permeance was almost the same as that obtained originally at 379 K, but the *n*-hexane permeance was much less, and it continued to decrease until it was more than 2 orders of magnitude lower than on the fresh membrane at 379 K.

The exposure to organics at higher temperatures apparently was responsible for this dramatic decrease in permeance, but this change was reversible. After 17 h on stream, the membrane was removed from the module and calcined in air for 8 h at 753 K. As shown in Figure 11, after calcination the permeance of *n*-hexane at 374 K was slightly larger than previously measured at 379 K, and it slowly decreased with temperature over the next 29 h. This decay corresponds to a half-life of 9.4 h for the *n*-hexane permeance, which is the same value measured for membrane M1. Interestingly, the 2,2-dimethylbutane permeance was not affected by the calcination step, perhaps indicating that 2,2-dimethylbutane was permeating through a different pathway in the membrane than *n*-hexane. During the 29 h after calcination, the 2,2-dimethylbutane permeance decreased by less than half. Thus, after calcination the separation selectivity was 2580, but it decreased to 500 over the next 29 h on stream. The separation selectivity decreased with a half-life of 13 h. When the temperature was raised to 463 K, the selectivity again dropped to 1. After 18 h at 463 and 424 K, the membrane was returned to 374 K, and again the *n*-hexane permeance was lower than before the high-temperature exposure, and the 2,2-dimethylbutane permeance was higher.

Membrane M3, which is supported on α -alumina and prepared by procedure 2, also separated *n*-hexane/2,2-dimethylbutane mixtures, but the temperature dependence was dramatically different. At 373 K, the separation selectivity for membrane M3 was around 100, which is more than an order of magnitude lower than that for membrane M2. The permeances and selectivity also decreased more slowly with time on stream, as shown in Figure 12; the *n*-hexane permeance half-life was 13 h and the selectivity half-life was 58 h. When the temperature was raised to 462 K, both *n*-hexane and 2,2-dimethylbutane permeances increased, but the membrane still separated the mixture with a selectivity of 18. When the temperature was returned to 375 K after

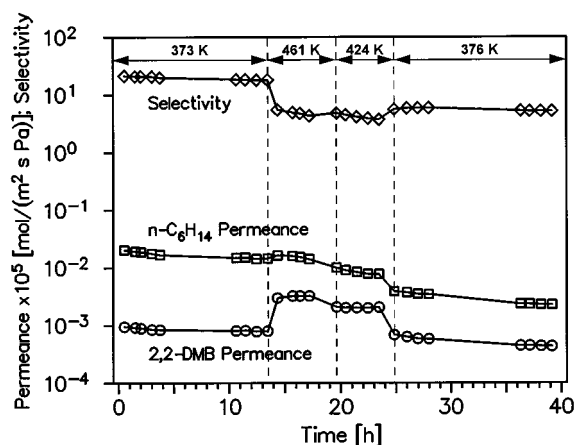


Figure 13. *n*-Hexane and 2,2-dimethylbutane permeances and *n*-hexane/2,2-dimethylbutane separation selectivity as a function of time for membrane M4 at different temperatures for a 50/50 *n*-hexane/2,2-dimethylbutane mixture.

Table 5. Half-lives for Permeances and Separation Selectivities of a 50/50 Binary *n*-Hexane/2,2-Dimethylbutane Mixture at 373–375 K

membrane	decay half-life (h)	
	<i>n</i> -hexane permeance	<i>n</i> -C ₆ H ₁₄ /2,2-DMB separation selectivity
M1/ γ -Al ₂ O ₃	9.3	17
M2/ γ -Al ₂ O ₃	9.4	12
M3/ α -Al ₂ O ₃	13	58
M4/ α -Al ₂ O ₃	28	53

4 h at 462 K, the *n*-hexane permeance was almost the same as before the temperature was raised and the 2,2-dimethylbutane permeance was 2.2 times higher so that the selectivity was lower.

Membrane M4, which is also supported on α -alumina and was prepared by procedure 3, exhibited similar behavior to membrane M3. The permeances and selectivities are shown in Figure 13. The *n*-hexane/2,2-dimethylbutane separation selectivity was lower (only 21 at 373 K), but membrane M4 still separated the hexane isomers 461 K, with a selectivity of 4.4. As shown in Table 5, the half-lives were also longer than those for membranes M1 and M2. Table 4 summarizes the differences in the 2,2-dimethylbutane permeances with temperature for the two types of membranes. The permeances of 2,2-dimethylbutane in the mixture increased by factors of 8.4 and 4.0 for membranes M3 and M4, respectively, when temperature increased from 373–374 K to 461–462 K. In contrast, for membranes M1 and M2, the corresponding factors when the temperature was increased are 893 and 2263, respectively. This is the same type behavior observed for isobutane permeance as the temperature increased; isobutane permeances exhibited a strong temperature dependence for membranes prepared by procedure 1 but not for membranes prepared by procedures 2 and 3.

Effect of Single Gas Permeation on Separations.

Figure 14 shows permeances and selectivities for mixtures after exposure to just one of the isomers at elevated temperature. Following exposure of freshly-calcined membrane M2 to 2,2-dimethylbutane for 2 h at 498 K, the selectivity was 100 at 373 K. In contrast, membrane M2 had a separation selectivity of almost 2600 when calcined but not exposed to 2,2-dimethylbutane at high temperature. After 5 h of exposure to the mixture, during which time the selectivity decreased, the membrane was exposed to pure *n*-hexane at 498 K.

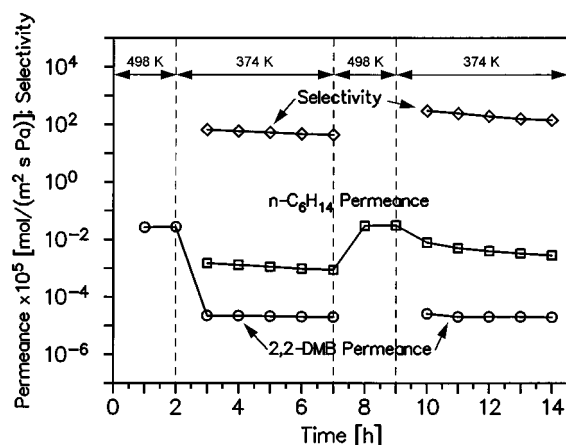


Figure 14. *n*-Hexane and 2,2-dimethylbutane permeances for both single gases and mixtures (50/50 *n*-hexane/2,2-dimethylbutane) for membrane M2 as a function of temperature. The *n*-hexane/2,2-dimethylbutane separation selectivity is also plotted for the conditions where a mixture was used.

The subsequent separation selectivity at 374 K was significantly higher, mainly due to an increased *n*-hexane permeance. It was not as high as when the membrane was calcined, however. Thus, the permeation behavior through these membranes has a complicated dependence on the membrane temperature history and exposure to organics.

Discussion

Effect of Membrane Preparation. We previously demonstrated that permeation and separation properties for ZSM-5 membranes depend on the method of preparation, which can be affected by the support (Coronas et al., 1997). In that study only alumina supports were used. Membranes prepared by procedure 1, whether on α - or γ -alumina, have high N₂ permeances after calcination and N₂/SF₆ ideal selectivities greater than 100 at room temperature. They also appear in SEM to have a continuous layer of zeolite crystals on the inside surface of the support tubes. In contrast, a continuous layer of zeolite was not seen on the inside surfaces of α -alumina tubes when procedures 2 and 3 were used, and the permeation properties were different from membranes made by procedure 1. Methods 2 and 3 used much more synthesis gel and the membrane ends were not plugged during preparation. On α -alumina supports, procedures 2 and 3 formed membranes with lower N₂ permeances (after calcination) and much lower N₂/SF₆ ideal selectivities. Also, the temperature where *n*-butane/isobutane separation selectivities had maxima were 15–30 K higher for membranes prepared by procedures 2 and 3 (M3 and M4) than for membranes prepared by procedure 1 (M1 and M2). Moreover, at higher temperatures, where membranes prepared by procedure 1 have selectivities close to 1, the membranes prepared by procedures 2 and 3 were still able to separate organic mixtures.

The behavior for separation of butane isomers is quite similar to what we reported previously for membranes prepared by the same procedures (Coronas et al., 1997), and demonstrates the reproducibility of the membrane preparation. The current studies further show that hexane isomers also exhibit significant differences for the different preparation methods. Membranes prepared by procedure 1 have significantly higher selectivi-

ties, whereas membranes prepared by procedures 2 and 3 are able to separate hexane isomers at higher temperatures and they are not deactivated as much by the high-temperature exposure. Also, membranes prepared by procedure 1 exhibit orders of magnitude changes in *n*-hexane and isobutane permeances in mixtures as the temperature increases, but the changes in permeance are much smaller for membranes prepared by procedures 2 and 3.

If ZSM-5 membranes are assumed to form in all cases, then two differences in the membrane structure, as the result of different preparation methods, can be responsible for the different permeation behavior: the fraction of non-zeolitic pores and the membrane thickness. The membranes are composed of many zeolite crystals intergrown to form a continuous layer when prepared by procedure 1. Thus these membranes can have transport both through the zeolite crystals and in parallel through the intercrystalline regions. Membranes prepared by procedures 2 and 3 can have transport both through the zeolite crystals and between the crystals and the alumina surface. Because of the different preparation methods, the fraction of molecules that transports through the zeolite pores can be significantly different for the different preparations. The dramatic differences in how permeances change with temperature for the different preparations indicate that the same processes are not limiting both types of membranes. Because the membranes prepared by procedures 2 and 3 have lower N_2 permeances, they may also be thicker and thus molecules would have a more tortuous path through the intercrystalline regions (or regions between crystals and pore).

For membranes on stainless steel supports, the preparation method had less influence than for membranes on alumina supports. Tables 1 and 2 show that N_2 permeances and N_2/SF_6 ideal selectivities for the three membranes on stainless steel supports are similar. As observed for membranes on the alumina supports, however, the maximum *n*-butane/isobutane separation selectivities are at higher temperatures (407–410 K) for membranes made by procedures 2 and 4 (M6 and M7) than for a membrane made by procedure 1 (M5 has maximum selectivity at 379 K).

Comparisons of N_2/SF_6 and Isomer Selectivities.

In general, membranes made by procedure 1 on γ -alumina have the highest N_2 permeances, N_2/SF_6 ideal selectivities, and maximum *n*-butane/isobutane separation selectivities. Higher ideal selectivities do not correlate with higher separation selectivities for hydrocarbon isomers, however. As Table 2 shows, M1 and M2 have similar N_2/SF_6 ratios, but the maximum *n*-butane/isobutane separation selectivity is 16 for M1 and 54 for M2. Membranes M3 and M4 have N_2/SF_6 selectivities that are an order of magnitude lower, but their maximum *n*-butane/isobutane selectivities are 11 and 6.2, respectively. Membranes on stainless steel have similar N_2 permeances and low N_2/SF_6 ideal selectivities, but the higher N_2/SF_6 selectivity for membrane M5 corresponds to the highest *n*-butane/isobutane separation selectivity.

We do see a correlation in the isomer separation properties on the various membranes. For membranes where both mixtures of isomers were studied (M1–M4), a higher butane isomer separation selectivity at ~375 K for a given membrane corresponds to a higher hexane isomer selectivity. The hexane isomer separation se-

lectivity is higher than that for butane isomer separation selectivity for each of the membranes. At 463 K membranes M1 and M2 do not separate either hexane isomers or butane isomers because the permeance of the branched alkane increases orders of magnitude as the temperature is raised for procedure 1 membranes. In contrast, membranes M3 and M4 have hexane isomer separation selectivities of 19 and 4.4, at 461–462 K, respectively, and they have butane isomer selectivities of 5.7 and 2.0 at 512–514 K, respectively.

Separation Mechanism. The *n*-hexane/2,2-dimethylbutane separation selectivity is larger than *n*-butane/isobutane separation selectivity, as might be expected based on molecular size. The branched chain isomer has the larger kinetic diameter (*n*-butane and *n*-hexane (0.43 nm), isobutane (0.50 nm), 2,2-dimethylbutane (0.62 nm)). As we showed previously (Coronas et al., 1997), however, separation in our membranes is not due to molecular sieving for the butane isomers; instead, *n*-butane blocks the permeance of isobutane so that the separation selectivities are much higher than the ideal selectivities. As can be seen from Table 3 and Figure 14, the ideal selectivities for the hexane isomers are only about 2 at 374 K for membrane M2, which has a separation selectivity greater than 2000. Thus, the separations of hexane isomers in our membranes are also not due to molecular sieving but instead due to the blocking of the branched alkane by the linear alkane. In the presence of *n*-hexane, the 2,2-dimethylbutane permeances decreased by as much as 3 orders of magnitude. As the length of the *n*-alkane chain increases, the heat of adsorption in ZSM-5 also increases because the alkane length is greater than the distance between channels (Richards and Rees, 1987). Apparently the *n*-hexane's heat of adsorption is significantly larger than that for 2,2-dimethylbutane so that *n*-hexane is more effective at blocking 2,2-dimethylbutane than *n*-butane is at blocking isobutane.

Because both zeolite pores and non-zeolitic pores are available for transport, and 2,2-dimethylbutane is larger than isobutane, non-zeolitic pores that are larger than the zeolite pores may be more important or even the dominant pathway for 2,2-dimethylbutane transport. We cannot rule out transport of 2,2-dimethylbutane through the zeolite pores, however, even though the X-ray diffraction diameter of ZSM-5 pores is smaller than the 0.63 nm diameter of 2,2-dimethylbutane. The X-ray diffraction diameter is not a good indication of the diameter available for transport, and 2,2-dimethylbutane has been reported to permeate in silicalite and ZSM-5 crystals (Karger and Ruthven, 1992).

The transport of hexane isomers when used as single gases and their permeance changes after exposure to one of the isomers at elevated temperature indicate how complicated transport is through these membranes. For example, as shown in Table 3, after membrane M2 was exposed to *n*-hexane at 462 K, the permeance of *n*-hexane at 374 K was only about 1/4 of the permeance of a freshly calcined membrane. In contrast, after membrane M2 was exposed to 2,2-dimethylbutane at 462 K, the permeance of 2,2-dimethylbutane was higher. Similar behavior was seen for membrane M3. Decomposition in the zeolite pores of the organic at elevated temperature could explain the decreased permeance because some of the pore became smaller due to carbon deposition. The increase in 2,2-dimethylbutane after exposure at elevated temperature cannot be due to pore

blocking, however. Instead, the surface adsorption properties or the pore entering properties apparently change as a result of the high temperature exposure. We have observed similar but more dramatic behavior for SF₆ permeance through silicalite membranes following exposure of a membrane to 1,3,5-trimethylbenzene at elevated temperature (Funke et al., 1997b). For one membrane, the SF₆ permeance at room temperature increased a factor of 24 after 1,3,5-trimethylbenzene exposure and heating to 453 K. The structure of the membrane was not changed by this exposure since calcination restored the original membrane properties.

The decrease in the *n*-hexane permeance was much greater when the membrane was exposed to a *n*-hexane/2,2-dimethylbutane mixture for a number of hours, as shown in Figure 11. After permeance measurements at 420 and 434 K, the *n*-hexane permeance for membrane M2 at 385 K was more than an order of magnitude lower than it was at 379 K prior to the high temperature exposure. In contrast, the 2,2-dimethylbutane permeance was higher after this exposure. Similarly in Figure 12, the 2,2-dimethylbutane permeance was higher at 375 K after exposure to the mixture at elevated temperature. The *n*-hexane permeance in the mixture also increased after higher temperature exposure to *n*-hexane as a single gas, as shown in Figure 14. It seems unlikely that the pore sizes have increased by these exposures; instead the changes in the permeances in the opposite direction for *n*-hexane and 2,2-dimethylbutane might be because they move through different pathways.

Membrane Stability. For all membranes, the permeance of *n*-hexane decreased with time on stream, and thus the *n*-hexane/2,2-dimethylbutane selectivity decreased also. The membrane deactivated faster at higher temperature. The organics (or perhaps a impurity that is present in low concentration) either decompose in the membrane to form a carbeneous species or get trapped in the pores. This deactivation can be reversed by calcination at 753 K, and temperatures below 753 K may also reverse the process, but they were not tested. Membrane M2, which has the higher selectivity, also deactivated faster; the selectivity at 374 K dropped 2 orders of magnitude after measurements at higher temperatures. However, for 29 h, the selectivity was above 500 for membrane M2, so it was still very effective for separations; its highest selectivity was 2580. Moreover, the membrane can be regenerated. Membrane M3 selectivity only dropped a factor of 2 after high-temperature measurements, but its selectivity was lower. Membrane M3 has a different structure, and as already mentioned, membranes prepared by procedures 2 and 3 exhibit many other differences in permeation properties from membranes prepared by procedure 1. Stability appears to be better in membranes prepared by procedures 2 and 3.

Effect of Water. Water can affect the permeation of other molecules through zeolite membranes, and we previously reported lower permeances of N₂ and SF₆ when humidified feeds were used for silicalite membranes (Funke et al., 1997b). For example, at room temperature the N₂ permeance decreased a factor of 2.5 when the feed was humidified. Water has the strongest effect for the ZSM-5 membrane when liquid water was injected close to the membrane module. In this case (treatment H), the *n*-butane/isobutane separation selectivity decreased by 20%, due to a decrease in *n*-

butane permeance and an increase of 11% in isobutane permeance. Apparently water selectively blocks pores and inhibits *n*-butane from blocking isobutane, so its permeance increases. However, the effect of water on the membrane permeances is not dramatic, and small water impurities in the stream would not be expected to be a significant problem as long as separations are carried out at elevated temperatures.

Summary

ZSM-5 membranes are stable for separations of *n*-butane/isobutane mixtures, and water only has a small effect on the permeances at 400 K and above. Selectivities as high as 57 were measured.

ZSM-5 membranes are able to separate hexane/2,2-dimethylbutane mixtures with high separation factors (>2500), but the selectivities decrease with increasing temperature. This separation is not due to molecular sieving but is due the ability of *n*-hexane to strongly inhibit the permeation of 2,2-dimethylbutane by blocking adsorption or pore entering.

Separation selectivity for organic isomers depends on the preparation method, and membranes prepared with a small amount of synthesis gel inside the alumina support have higher selectivities below 400 K, but rapidly lose their selectivities at higher temperature. Membranes prepared with a larger amount of synthesis gel have lower selectivities but are able to separation hexane isomers at 462 K. Changing the preparation method can change both the membrane thickness and the amount of non-zeolitic pores that are available for transport.

Slow degradation in the membrane permeances and selectivities were observed at 375 K when hexane isomer mixtures were separated. The permeances degraded much faster at 420 K and higher, and organic decomposition in the zeolite is probably responsible for the degradation.

The same preparation procedures that were used for α - and γ -alumina are less effective for preparing ZSM-5 membranes on porous stainless steel supports, but these membranes are able to separate *n*-butane/isobutane mixtures, although with low selectivities.

The N₂/SF₆ ideal selectivity at room temperature does not correlate with whether a membrane can separate organic isomers at elevated temperature. The *n*-butane/isobutane separation selectivity correlates, however, with the *n*-hexane/2,2-dimethylbutane separation selectivity.

Permeation properties of organics in zeolite membranes are complicated; exposure of a membrane to *n*-hexane at elevated temperature can increase the permeance of 2,2-dimethylbutane.

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