Parallel Pathways for Transport in ZSM-5 Zeolite Membranes

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Changes in ZSM-5 zeolite membranes during preparation were studied by characterizing the gas permeation properties as the zeolite synthesis template was removed by calcination for 4 h at progressively higher temperatures or for longer times at 573 K. Both zeolite and intercrystalline pores appear to be present; the nonzeolitic pores are larger and have lower ideal selectivities, but these pores are small enough and/or in low enough concentrations that high ideal and mixture selectivities are obtained for the final membranes. The tetrapropylammonium hydroxide template is removed from the larger intercrystalline pores first, and thus ideal selectivities changed significantly with calcination temperature or time. The N_2/SF_6 ideal selectivities also depend on the measurement method; they were higher for a pressure drop across the membrane than when a sweep gas was used, apparently because of the change in driving force for SF_6, which adsorbs more strongly than N_2. Permeances continue to increase as membranes are calcined up to 873 K, but the N_2/SF_6 ideal selectivities are the same for calcination from 673 to 873 K.

Introduction

One objective of this study is to obtain a better understanding of the changes that take place in ZSM-5 zeolite membranes during calcination as the synthesis template decomposes and its products are removed from the zeolite pores. Another objective is to determine if pores other than zeolite pores are part of the zeolite membrane and to characterize them. Our previous studies showed that ZSM-5[1,2] and silicate membranes[3–6] are effective for separations of mixtures of organics, and high ideal selectivities for N_2 to SF_6 were obtained. Molecular sieving did not control these organic separations, however, and the membranes appeared to have nonzeolitic pores since molecules that are similar in size to or bigger than the ZSM-5 pores permeated at significant rates. Since these nonzeolitic pores, which may be the intercrystalline regions between the zeolite crystals, are expected to lose their template at a lower temperature than the zeolite pores, studying gas permeances as a function of calcination temperature might provide insight into the structure of the membrane.

The zeolite membranes were synthesized using an in situ technique in which a porous support was placed in contact with a precursor synthesis gel at elevated temperature. A dense, continuous zeolite layer forms on the substrate during hydrothermal synthesis. The precursor gel contains an organic template, tetrapropylammonium hydroxide (TPAOH), that serves as a structure-directing agent. After hydrothermal synthesis and drying (at low temperature), a zeolite membrane without defects should be impermeable to gases because the organic template is occluded into the zeolite framework when it crystallizes. A membrane with larger pores can also be impermeable if the template is strongly held in those pores. Zeolite membranes are calcined in air at elevated temperatures to decompose and remove the organic templates. Some membranes were also made with additional cleaning of the support and of the final membrane in an effort to improve separation properties.

In previous studies, silicalite and ZSM-5 membranes were calcined at 673 to 823 K[1,3,7–10] for various times, and various heating rates (0.17–1 K/min) were used to reach these final calcination temperatures. The effects of calcination temperature and time have not been extensively studied. Bakker et al.[10] reported that krypton started permeating through a silicalite-1 zeolite membrane at 543 K during temperature-programmed

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oxidation (TPO) in air (heating rate about 1 K/min). At 623 K, krypton permeation increased sharply, but permeation did not change above 673 K because the template was completely removed. On the basis of the TPA degradation behavior, the authors thought that the small krypton molecule might permeate through nonzeolite pores below 623 K. Similar results were reported for silicalite-1 membranes by van de Graaf et al.,[11] who saw permeation in their membrane start at 500 K, with a major breakthrough at 610 K, while calcining at a heating rate of 1 K/min. The Kr permeation was constant while calcining at 673 K. The amount of Kr that permeated at 600 K before complete calcination was 4.8% of the total flux at 600 K after calcination. By comparison to TGA of silicalite crystals, they concluded that Kr permeation up to 600 K during calcination was from flow through pores that develop from calcination of amorphous gel or TPA in intercrystalline regions. From measurements of 1,3,5-triisopropylbenzene permeation, they concluded the nonzeolite pores were less than 1 nm in diameter. They also pointed out that permeation through nonzeolite could be significant for weakly adsorbing species, which have low concentrations in the zeolites.

Bakker et al.[10] measured permeation of isooctane/methane and isooctane/methane/*n*-butane mixtures through silicalite-1 membranes to determine the presence of nonzeolite pores. Because isooctane has a large kinetic diameter (0.62 nm), permeation through silicalite pores (0.51×0.57 nm) was expected to be slow, but isooctane permeated through the membrane. Methane was blocked by *n*-butane but not by isooctane. Bakker et al. concluded that the membrane was composed of silicalite pores and larger pores and that methane and *n*-butane permeated through both types of pores but that isooctane only permeated through the intercrystalline pores.

Yan et al.[12] reported that triisopropylbenzene vapor (kinetic diameter of 0.85 nm) did not permeate through their ZSM-5 membranes at 458 K and thus concluded that they had membranes without defects. Sano et al.[13] also used organic molecules of different sizes to determine the extent of nonzeolite pores in a silicalite membrane. The largest molecules that were able to permeate easily through the membranes were *m*- and *p*-diisopropylbenzene (0.71 nm for the para isomer), whereas 1,3,5-triisopropylbenzene and perfluoro-*n*-butylamine (1.02 nm) hardly permeated. The authors concluded that small pores of about 1-nm diameter originated from silicalite grains.

In the current study, we used pure gas permeances to characterize membranes after various calcination treatments. Nitrogen and SF_6 were used for most of the studies because they differ significantly in diameter and thus in diffusivity, with SF_6 being similar in size to the zeolite pores. However, N_2 and SF_6 also differ significantly in adsorption properties. To maximize the differences in their permeances, the measurements were made using pure gases and a pressure drop across the membrane. For comparison to other studies, permeances were also measured using a sweep gas on the permeate side of the membrane. Nitrogen and SF_6 permeances were measured at several temperatures, and permeances for other gases were measured at 300 K. In addition, *n*-butane/isobutane separation selectivities were measured for some membranes as a function of temperature to verify that selective membranes had been prepared.

Membranes prepared previously in our laboratory had high N_2/SF_6 ideal selectivities but still permeated isooctane (0.62 nm) and 2,2-dimethylbutane (0.62 nm), indicating that some permeance was probably through nonzeolite pores.[2,5] Thus, a N_2/SF_6 ideal selectivity of 200 is not indicative of a membrane composed solely of zeolite pores. Despite this, membranes with high N_2/SF_6 ideal selectivities have high separation selectivities for *n*-butane/isobutane,[1] *n*-hexane/2,2-dimethylbutane,[2] and *n*-hexane/benzene[6] mixtures, though these separations are not due to molecular sieving.

Experimental Methods

Zeolite Membrane Preparation. Zeolite ZSM-5 membranes were prepared by in situ synthesis from gels onto 0.7-cm i.d., *γ*-alumina tubes with 5-nm diameter pores (US Filter). The gel, with a Si/Al atomic ratio of 100, was a modification of the silicalite gel of Grose and Flanigen.[14] The modified gel's molar composition was TPAOH:SiO_2:H_2O:NaOH:$Na_2Al_2O_4$·$3H_2O$ = 1:21:987:3:0.105. To avoid bypass during permeance measurements, approximately 1 cm on each end of 4.7-cm-long tubular supports was coated with a glazing compound (GL 611A, Duncan), which was calcined at temperature of 1173 K for 30 min. This high-temperature treatment increased the porosity and probably sintered the *γ*-alumina layer.

Two sets of membranes were used. After the glazing procedure, the supports were washed in distilled water at room temperature before membranes M1−M5 were prepared. In an effort to improve the quality of the membranes, the supports *and* the resulting membranes were cleaned more extensively for membranes X1−X3. These supports were placed in a beaker of boiling water for 1 h and then dried at 443 K before membrane preparation. After preparation these membranes were also placed in boiling water for 1 h and then dried. In addition, the gel was aged for 1 day after 3 days of stirring before preparing membranes X1−X3.

The ZSM-5 membranes were synthesized using the same procedure reported by Coronas et al.[1] Membranes prepared by these procedures were shown by XRD and SEM to consist of a thin layer of intergrown zeolite crystals.[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 filled the inside of the tubular support. 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. All synthesis was conducted at 443 K, and the synthesis times were 15 h for the first layer and 8 h for the second layer.

Calcination Procedures. The synthesized ZSM-5 membranes were calcined in air to remove the TPAOH template from the zeolite framework. The calcination procedure was carried out in a computer-controlled muffle furnace using a slow temperature ramp. The heating rate was 0.6 K/min and the cooling rate was 1.2 K/min. To determine the temperature at which the pores opened, the membranes were held at a

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given temperature for 4 h, cooled, removed from the oven, and placed in a module for permeation measurements. The membranes were then calcined for another 4 h at a higher temperature using the same procedure. The highest temperature used was 873 K, but the final calcination temperature for some membranes was 753 K. One membrane was only calcined at 573 K in a series of 4-h treatments, with permeances being measured after each treatment.

Permeation Measurements. Single-gas permeation rates were measured at room temperature for H_2, N_2, CO_2, n-C_4H_{10}, i-C_4H_{10}, and SF_6. Membranes M1–M5 were sealed in a stainless steel module by silicone O-rings,[15] and permeation rates were measured with a pressure drop across the membrane (138 kPa) and without a sweep gas in a dead-end system. The permeate pressure was 92 kPa. The change in flux with time was measured by a mass flow meter and recorded automatically by a computer. After strongly adsorbing components were used, the membranes were held at 473 K in N_2 flow for 1 or 2 h to recover the original N_2 permeance. For some membranes, N_2 and SF_6 permeances were also measured at 473 K after various calcination treatments.

The permeation rates of N_2 and SF_6 through membranes X1–X3 were also measured in a stainless steel module with silicone O-rings but in a different system that used a flowing feed and a helium sweep gas. The feed pressure of the pure component was 100 kPa and the flow rate was 40–50 cm³/min. The permeate side was held at 100 kPa, and a helium sweep gas at 100 cm³/min flowed across the shell side of the membrane. The permeate and retentate flow rates were measured with a bubble flow meter, and the concentrations of N_2 or SF_6 in the permeate and retentate were measured with a HP model 5890 GC with TC detector. Permeation rates were measured at 300 K for membranes X1 and X3, and at 300, 373, and 473 K for membrane X2.

A similar module was used to separate 50/50 mixtures of n-butane/isobutane as a function of temperature. Gas flow rates were set by Tylan mass flow controllers, and the pressure drop across the membrane was 138 kPa. No sweep gas was used, and the permeate side was at 92 kPa. The permeate and the retentate were analyzed online by the same GC. The separation selectivities for the mixtures are the ratios of permeances, and the log-mean, partial-pressure drops were used in the calculations.

Zeolite Powder and Characterization. ZSM-5 powder was synthesized using the same preparation method used for the membranes. About 40 mL of gel with a Si/Al atomic ratio of 100 was poured into a Teflon tube and reacted in an autoclave at 443 K for 15 h. After synthesis, the ZSM-5 crystals were collected by filtration, washed several times with distilled water, and dried at 443 K.

Thermal decomposition of the TPAOH template in ZSM-5 powder was studied by TGA on a Cahn microbalance, model TG-131, in flowing air. Two temperature programs were used. One increased the sample temperature from 300 to 763 K at a heating rate of 2 K/min. The other increased the sample temperature from 300 to 523 K at a heating rate of 10 K/min, held this temperature for 4 h, and then increased the zeolite successively to 573, 623, and 673 K, with a 4-h hold at each temperature.

Results and Discussion

Zeolite Powder Characterization. The change in weight of the ZSM-5 crystals during calcination was measured by TGA. Figure 1 shows the percentage change in weight and the derivative of the weight with temperature, as the crystals were heated from 300 to 763 K at a heating rate of 2 K/min. The crystals
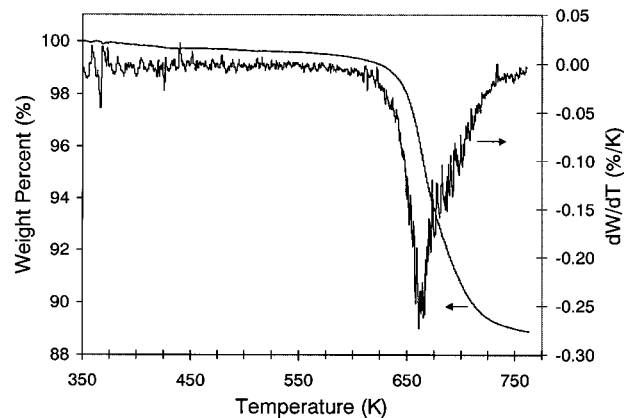
Figure 1. Percentage weight change of ZSM-5 zeolite powder versus temperature as the temperature was increased at a rate of 2 K/min.

dehydrated up to 473 K with less than 1% weight loss,[16] but these crystals had been dried previously at 443 K. Most of the weight loss was between 625 and 763 K. The TPAOH template decomposed with a maximum rate near 670 K.

Thermal decomposition of the organic template in zeolite powder has been previously studied by TGA, DTA, DSC, and IR spectroscopy,[11,16-20] and two regions were observed for near-100% crystalline zeolite precursors.[17] One region was attributed to dehydration between 373 and 523 K and the other at 673–723 K to decomposition of the template occluded in the zeolite framework. Others reported that the template decomposed between 633 and 823 K.[18] Infrared spectroscopy of zeolite single crystals indicated that the template started to decompose at 613 K for a heating rate of 10 K/min.[19] Bibby et al.[20] also observed a maximum rate of TPAOH decomposition around 680 K. The temperature for the maximum rate of weight loss increases as the heating rate increases;[16] it was 645 K for a heating rate of 0.2 K/min and 741 K for a heating rate of 50 K/min. van de Graaf et al.[11] reported, for a heating rate of 1 K/min, that silicalite-1 crystals had a maximum rate of weight loss at 631 K. They also saw weight loss at 494 K that was attributed to decomposition of TPA in amorphous residual get and on the crystal surface. Thus, our ZSM-5 crystals exhibit behavior similar to that reported by others.

Holding the crystals at constant temperature for 4 h before raising to a higher temperature essentially corresponds to a low heating rate, and thus template decomposition is expected to take place at lower temperature than observed when the crystals were continuously heated. Indeed, that is what is observed in Figure 2 when the zeolite crystals were held for 4 h at a given

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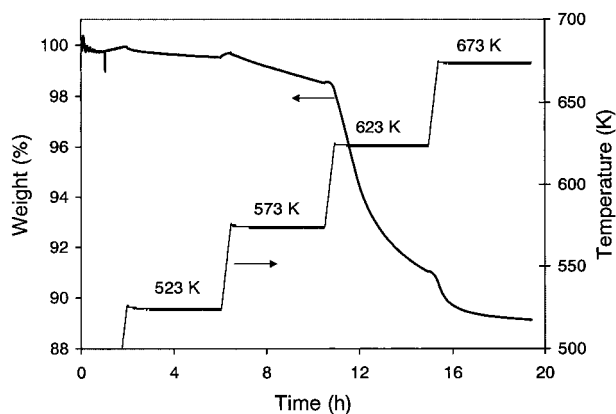
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Figure 2. Percentage weight change of ZSM-5 zeolite powder and temperature versus time. The temperature was ramped at 10 K/min and then held for 4 h at a given temperature before ramping 50 K higher.
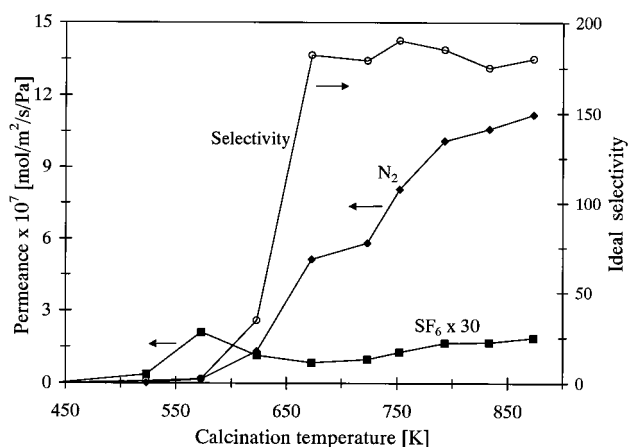
Figure 3. Single gas permeances of N_2 and SF_6 and N_2/SF_6 ideal selectivity at room temperature for membrane M1 as a function of calcination temperature. The membrane was calcined for 4 h at each temperature, and the permeances were measured with a pressure drop across the membrane.

temperature before increasing the temperature 50 K. Some template decomposed at 573 K, but the rate was low and the zeolite only lost 1.4% of its weight in 4 h. At 623 K, the template decomposed faster, and the zeolite crystals lost 7% of their original weight in 4 h. By 673 K, most of the template had apparently decomposed.

Changes in Permeances with Calcination Temperature. *Permeances measured with Pressure Drop.* The single gas permeances of N_2 and SF_6 were measured at room temperature by the pressure drop method after membrane M1 was calcined for 4 h at a given temperature. After calcination for 4 h at 443 K, membrane M1 was impermeable to N_2 at room temperature. As shown in Figure 3, after calcination for 4 h at 523 K, both N_2 and SF_6 permeated, and their permeances were essentially the same, 1.2×10^{-9} mol/ m^2 s Pa. Note that the SF_6 permeance in Figure 3 has been multiplied by 30 for clarity. The N_2 permeance increased 3 orders of magnitude as the calcination temperature increased from 523 to 793 K. For higher calcination temperatures, the N_2 permeance increased more slowly. The SF_6 permeance also increased as the calcination temperature increased above 523 K, but in contrast to the behavior observed for N_2, the SF_6 permeance reached a maximum for a calcination tem-
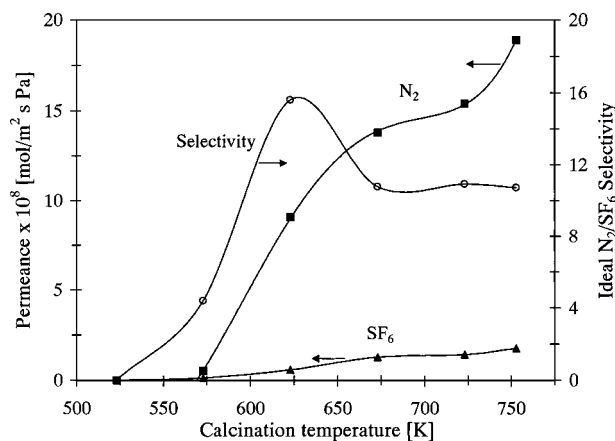
Figure 4. Single gas permeances of N_2 and SF_6 and N_2/SF_6 ideal selectivity at room temperature for membrane X1 as a function of calcination temperature. The membrane was calcined for 4 h at each temperature, and the permeances were measured with 1 atm pressure on each side and a helium sweep gas on the permeate side.

perature of 573 K and then decreased until 673 K. Above 673 K, the SF_6 permeance increased with calcination temperature the same way the N_2 permeance increased.

The N_2/SF_6 ideal selectivity at room temperature for membrane M1 is also shown in Figure 3 as a function of calcination temperature. After calcination at 573 K, the ideal selectivity was only 2.3, but it increased sharply following calcination at 623 and 673 K. Note that the permeances continued to increase for calcination temperatures above 673 K, but the ideal selectivity was almost constant at 180. The permeances for membrane M2, which was prepared by the same procedure, were also measured by the pressure drop method. Their dependencies on calcination temperature were almost identical to those for membrane M1, including the maximum in SF_6 permeance. This indicates that the reproducibility of the preparation method and of the permeance measurements is excellent.

Permeance Measured with Sweep Gas. In contrast to membranes M1 and M2, membranes X1−X3 were essentially impermeable to N_2 at room temperature, for a pressure drop of 138 kPa, after calcination at 523 K. That is, the change in cleaning procedure (cleaning the support in boiling water and cleaning the membrane in boiling water before calcination) apparently improved membrane quality so that the pores did not open until higher calcination temperatures. Nitrogen and SF_6 permeated after membranes X1−X3 were calcined at 573 K.
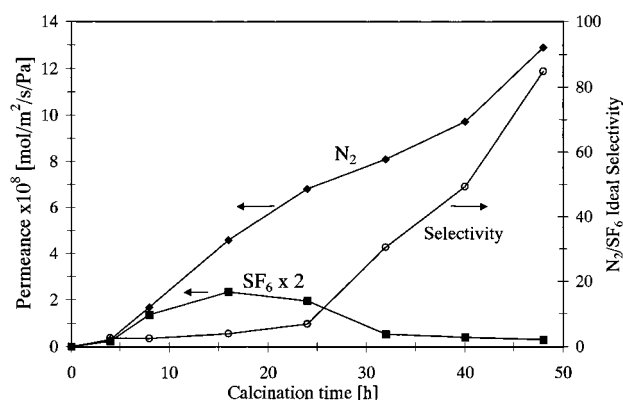
Figure 4 shows the N_2 and SF_6 permeances at room temperature and the N_2/SF_6 ideal selectivity, as a function of calcination temperature, for membrane X2. These permeances were measured using a helium sweep gas on the permeate side instead of a pressure drop to provide the driving force. Note that when a sweep gas was used the SF_6 permeances were much higher than when pressure drop was used. The N_2 permeance increased significantly after calcining the membrane at 623 K, and a N_2/SF_6 ideal selectivity of 16 was measured. This was the maximum selectivity, however, and the selectivity decreased after calcining at 673 K. Note that both N_2 and SF_6 permeances increased as the

calcination temperature increased up to 753 K, and the permeances do not appear to have reached a maximum after 4 h calcination at 753 K. This is similar to the behavior observed for membrane M1.

The ideal selectivity after calcination at 673–753 K was constant around 11 for permeances measured by the sweep gas method. This selectivity is much lower than the value of 150 measured for the same membrane with the pressure drop method. The N_2 permeance for membrane X2, after calcination at 753 K, was 4.3×10^{-7} mol/m^2/s/Pa when measured by the pressure drop method. This permeance is twice as high as that measured by the sweep gas method. Note that it is about half of the permeance of membrane M1. Similar behavior to that in Figure 4 was observed for membrane X3, and a maximum N_2/SF$_6$ ideal selectivity of 16 (sweep gas method) was obtained following calcination at 623 K. The ideal selectivity decreased to 12 for higher calcination temperature. Thus, the membrane preparation and the resulting permeance behavior are reproducible. The N_2/SF$_6$ ideal selectivities of 11–12 are similar to those reported by Bakker et al.,[21] who used a sweep gas. They measured an ideal selectivity of 7.5 at room temperature for silicalite-1 membranes on stainless supports.

The N_2 permeances were lower with the sweep gas method apparently because of back diffusion of the He sweep gas from the permeate side to the feed side. For example, after calcination at the higher temperature, approximately 20% of the retentate was helium, whereas the permeate was mostly helium. In contrast to N_2, *the SF$_6$ permeance was more than an order of magnitude higher when a sweep gas was used instead of a pressure drop for a driving force*. This behavior for SF$_6$ was predicted by van den Broeke,[22] who attributed the higher flux with the sweep gas to a larger driving force created by the lower partial pressure of SF$_6$ on the sweep side. Since SF$_6$ adsorbs relatively strongly on ZSM-5 (the heat of adsorption of SF$_6$ on silicalite is about 35 kJ/mol[21,23] and it is probably similar on ZSM-5), a large fraction of the zeolite pores is occupied when the permeate pressure is 92 kPa. Thus when the pressure drop method is used, the SF$_6$ occupancy on the permeate side is high, and for a feed pressure of 235 kPa, the occupancy is not much higher on the feed side. Since the driving force for permeation is the difference in occupancy and not the difference in pressure, the driving force is low when a pressure drop is used even though the pressure difference is 135 kPa. In contrast, when a sweep gas at 100 kPa is used, the partial pressure of SF$_6$ on the permeate side is low and the fraction of the zeolite pores occupied on the permeate side is also low. This provides a much larger driving force and thus a higher permeance, as we observe.

Permeance as Function of Calcination Time. Calcining a membrane for many hours at 573 K yielded a membrane that was similar to that obtained by

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Figure 5. Single gas permeances of N_2 and SF$_6$ and N_2/SF$_6$ ideal selectivity at room temperature for membrane M3 as a function of calcination time at 573 K. The permeances were measured with a pressure drop across the membrane.

Table 1. Single Gas Permeances, Measured by the Pressure Drop Method at Room Temperature, for Membrane M4 after Calcination at Each Temperature for 4 h

calcination temp (K)	permeances $\times 10^7$ (mol/m^2 s Pa)				
	H$_2$	N$_2$	CO$_2$	n-C$_4$H$_{10}$	i-C$_4$H$_{10}$
473	0				
523	0.078	0.026			
573	0.33	0.082	0.069	0.0099	
673	14.8	5.0	5.7	0.029	0.0031
753	32.3	10.7	11.1	0.029	0.0035

calcining at higher temperatures. The single gas permeances of N_2 and SF$_6$ at room temperature are shown in Figure 5 for membrane M3 as a function of calcination time at 573 K. This membrane was prepared by the same method used for membrane M1, and the permeances were measured by the pressure drop method. After 8 h of calcination at 573 K, the N_2/SF$_6$ ideal selectivity was 2.4. The N_2 permeance increased with calcination time, and was 1.29×10^{-7} mol/m^2 s Pa after 48 h of calcination. The SF$_6$ permeance initially increased with calcination time, but reached a maximum and then decreased at longer times. The N_2/SF$_6$ ideal selectivity continued to increase with calcination time, and after 48 h of calcination, the N_2/SF$_6$ ideal selectivity was 84. Neither the N_2 permeance nor the N_2/SF$_6$ selectivity appeared to have reached a maximum after 48 h. Since a membrane prepared by the same procedure (membrane M1) had a N_2 permeance that was about 6 times higher after calcination at higher temperatures, much longer than 48 h is probably required to obtain the maximum permeance and selectivity for membrane M3.

Permeance of Other Gases as Function of Calcination Temperature. Single gas permeances of H$_2$, N$_2$, CO$_2$, n-C$_4$H$_{10}$, and i-C$_4$H$_{10}$ at room temperature are presented in Table 1 for membrane M4 after 4-h calcinations at successively higher temperatures. This membrane was prepared by the same procedure used for membrane M1, and the permeances were measured with the pressure drop method. After calcination at 473 K, membrane M4 was impermeable to H$_2$, but H$_2$ and N$_2$ permeated after calcination at 523 K. As was observed for N$_2$ and SF$_6$ permeances in the other membranes, the permeances of all gases increased the most when the calcination temperature increased from 573 to 673 K. The H$_2$, N$_2$, and CO$_2$ permeances

increased factors of 40–80 when membrane M4 was calcined at 673 K, but the *n*-butane permeance only increased a factor of 3, so that the ideal selectivities for light gases relative to *n*-butane increased significantly. This is the same temperature range where the N_2/SF_6 ideal selectivities increased for the other membranes and corresponds to the temperature region where the template is removed from the zeolite pores. Note, however, that the ideal selectivities of light gases to more strongly adsorbing gases increased but the H_2/N_2 and the H_2/CO_2 ideal selectivity did not increase following calcination in this temperature range.

When the membrane was further calcined at 753 K, the H_2, N_2, and CO_2 permeances approximately doubled, but the n-butane and isobutane permeances increased much less. The *n*-butane/isobutane ideal selectivity decreased slightly, from 9.4 to 8.4, after this final calcination, but the H_2/n-butane and the $H_2/$isobutane ideal selectivities increased about a factor of 2. In contrast, the N_2/SF_6 ideal selectivities did not increase for calcination temperatures above 650 K for any of the membranes studied. Note that after calcination at 753 K, *the $H_2/$isobutane ideal selectivity was greater than 9000*. The N_2/SF_6 ideal selectivity was 210 after calcination at 753 K. Thus, this membrane would appear to be a highly selective membrane. These permeances were measured with the pressure drop method, and the $H_2/$isobutane ideal selectivity is expected to be significantly lower if the sweep gas method were used for the same reasons that the N_2/SF_6 ideal selectivity was lower for the sweep gas method. The He sweep gas would decrease the H_2 permeance, whereas the strongly adsorbed isobutane would have a higher permeance because the occupancy driving force would be larger when a sweep gas was used.

Separation of *n*-Butane/iso-Butane Mixtures. Membrane X2 was used, after calcination at 753 K, to separate a 50/50 mixture of *n*-butane and isobutane. The selectivity went through a maximum as a function of temperature, and the *n*-butane/isobutane maximum separation selectivity was 144 at 375 K for a pressure drop of 138 kPa. Thus, after calcination at 753 K, this membrane was highly selective for butane separations even though nonzeolitic pores were present. Similarly, the separation selectivity for an *n*-butane/isobutane mixture (50/50), measured for membrane M4 after calcination at 753 K, was 106 at 413 K for a pressure drop of 69 kPa.

Permeances at Elevated Temperature. The N_2 and SF_6 permeances were measured at 300 and 473 K for membrane M5 after calcination at successively higher temperatures. Membrane M5 was prepared by the same method as membrane M1, and the permeances were measured by the pressure drop method. As shown in Table 2, after calcination at 523 K, the permeances were low, and N_2 and SF_6 permeated at essentially the same rate at 300 K. The N_2 permeance increased a factor of 5 as the permeation temperature increased from 300 to 473 K, whereas the SF_6 permeance increased only a factor of 2.5 so that the N_2/SF_6 ideal selectivity was about 2 at 473 K. In contrast, following calcination at 573 K, the N_2 permeance increased less than a factor of 2 between 300 and 473 K, and the SF_6 permeance only increases a factor of 2. After calcination

Table 2. Single Gas Permeances for Membrane M5, Measured by the Pressure Drop Method, after Calcination at Each Temperature for 4 h

calcination temp (K)	permeances $\times 10^7$ (mol/m² s Pa)			
	N_2		SF_6	
	300 K	473 K	300 K	473 K
523	0.047	0.24	0.044	0.11
573	0.74	1.3	0.29	0.62
623	6.9	9.5	0.030	3.5
753	11.6	19.9	0.055	6.4

Table 3. Single Gas Permeance for Membrane X2, As Measured by the Sweep Gas Method, as a Function of Calcination Temperature and Permeation Temperature

calcination temp (K)	permeance $\times 10^8$ (mol/s/m²/kPa)					
	N_2			SF_6		
	300 K	373 K	473 K	300 K	373 K	473 K
573	0.53	0.57	1.7	0.12	0.16	0.65
673	14	14.4	17.9	1.3	3.7	7.1
753	19	16.7	20	1.8	4.9	8.2

at 573 K, the N_2 permeance at 300 K increased a factor of 15 over the permeance following calcination at 523 K, and the SF_6 permeance at 300 K increased less, so the ideal selectivity was 2.5.

The SF_6 permeance had a larger temperature dependence following calcination at 623 and 753 K. As observed for membranes M1 and M2, the SF_6 permeance at 300 K was an order of magnitude *lower* after calcination at 623 K, even though the N_2 permeance was an order of magnitude higher. However, the SF_6 permeance *increased more than 2 orders of magnitude* when the permeation temperature increased from 300 to 473 K. This strong temperature dependence reflects the fact that SF_6 occupancy decreases with increased temperature, and thus the driving force for permeation is larger at higher temperature. At 300 K, the driving force for SF_6 permeation was low because the occupancy was high on both sides of the membrane when the pressure drop method was used to measure permeances, as discussed previously. Thus after calcination at 623–753 K, the N_2/SF_6 ideal selectivity was 210–230 at 300 K. At 473 K, the SF_6 occupancy was much lower so that the driving force for permeance was higher, and thus the flux was much higher. Since N_2 does not have a high occupancy in ZSM-5 at 300 K, its permeance did not increase much with temperature. Thus, at 473 K, the N_2/SF_6 ideal selectivity was only around 3 after calcination at 753 K. The differences in temperature dependence of permeance following calcination at low and high temperatures indicate that the pores formed at low temperature have significantly different transport properties from those formed at high temperatures.

The permeances of N_2 and SF_6 were measured by the sweep gas method for three membranes that were prepared with the additional cleaning steps. The permeances for membrane X2 as a function of calcination temperature and permeation temperature are shown in Table 3; similar behavior was observed for membranes X1 and X3. As reported above, the N_2/SF_6 ideal selectivities measured by the sweep gas method are lower at 300 K than those measured by the pressure drop method. The N_2 permeances in Table 3 show similar behavior with permeation temperature, as seen in Table 2. After calcination at 573 K, N_2 permeance

has a stronger temperature dependence than following calcination at higher temperature. In contrast, SF_6 permeance changes much less with temperature. Instead of increasing 2 orders of magnitude, the SF_6 permeance only increased about a factor of 5 as the permeance temperature increased from 300 to 473 K. Because the SF_6 occupancy on the permeate side of the membrane was lower at 300 K with the sweep gas method than for the pressure drop method, the SF_6 permeances at 300 K is higher in Table 3 than in Table 2. Thus, as the permeation temperature increased, the SF_6 occupancy did not change as much, and the SF_6 permeance appears less activated when the pressure drop method was used.

The temperature dependence of SF_6 permeance in Table 3 is different following calcination at 573 K from that following calcination at higher temperature. Note that after calcination at 573 K, the SF_6 permeance did not increase much when the permeation temperature was increased from 300 to 373 K, but it increased a factor of 4 when the permeation temperature was raised to 473 K. In contrast, the SF_6 permeance increased almost a factor of 3 as the permeation temperature was increased from 300 to 373 K for the membrane calcined at 673 or 753 K. These changes indicate that pores different from zeolite pores formed at lower calcination temperature.

Parallel Pathways for Transport. The changes in permeances with calcination temperature for the ZSM-5 membranes indicate that both zeolite and nonzeolite pores form during calcination. The TGA measurements for the ZSM-5 crystals (Figure 2) indicate that a significant fraction of the template decomposes in the zeolite crystals during 4 h at 573 K, and 4 h at 623 K removes the majority of the template. For the membrane, the pores appear to open at higher temperatures. In Figure 3, the selectivity increases the most after calcination at 673 K, and the N_2 and SF_6 permeances continue to increase even for calcination at 873 K. Note, however, that weight loss was measured for the crystals whereas permeances were measured through the membrane. The crystals in the membrane could lose most of their template without forming a complete pathway for transport through the membrane. Gases only permeate when the last blocked portion of the pathway is open.

Gases permeated through membrane M1 after calcination at 523 K (Figure 3), but the permeances were low, and the TGA experiments in Figure 2 show that the crystals also lost weight at 523 K. Thus, the pores that formed at 523 K could be zeolite pores. Our experimental evidence indicates that most pores that open at the lower calcination temperatures are nonzeolite pores; they have lower selectivities and different activation energies for permeances than the pores that form by high-temperature calcination. For example, after calcination of membrane M5 at low temperature, the N_2/SF_6 ideal selectivity was 1 (Table 2), whereas it was more than 200 after calcination at higher temperature. Also, the change in SF_6 permeance with temperature for membrane M5 was small after low-temperature calcination, but large after calcination at high temperature. These nonzeolite pores are not large because the permeances are activated and because high

n-butane/isobutane separation selectivities are obtained for these membranes. Also, the fraction of gas that permeates through the nonzeolite pores is not large, though we cannot determine the fraction since nonzeolite pores probably also open during calcination above 523 K. In addition, the fraction of gas that permeates through nonzeolite pores depends on the molecule, the temperature, and the pressure.

For a silicalite membrane on a stainless steel support, Bakker et al.[10] reported that Kr permeation started around 543 K and increased strongly above 623 K during temperature-programmed oxidation at 1 K/s. Permeation should start at lower temperatures when a lower heating rate is used; holding the membrane for 4 h at a constant temperature is the same as using a low heating rate. Nitrogen permeation starts after calcination at 523 K for membranes M1−M5 and after calcination at 573 K for membranes X1−X3. Thus, our ZSM-5 membranes exhibit behavior similar to their silicalite membranes. Indeed, the N_2/SF_6 ideal selectivities at 300 K are similar when measured by the sweep gas method, and we also observe that *n*-butane is effective at blocking CH_4 permeation.[24] For both types of membranes, the CH_4 flux drops at least 2 orders of magnitude when *n*-butane is added.

The TGA results in Figure 2 indicate that the TPAOH template in zeolite crystals slowly decomposes at 573 K. Thus, when membrane M3 was calcined for 48 h at 573 K, the N_2 permeance was 1.3×10^{-7} mol/m^2 s Pa, and it had not yet reached a maximum. Apparently, many more hours would be required to decompose all the template. Note that the N_2/SF_6 selectivity was still increasing as the calcination time increased, indicating that less selective pores (nonzeolite) had formed at the shorter time and more selective ones (zeolite) formed at the longer calcination times. However, the maximum in SF_6 permeance with time in Figure 5, which is similar to the maximum in SF_6 permeance with temperature in Figure 3, probably indicates that the adsorption properties of the surface change. Since SF_6 adsorbs more strongly than N_2, it should be affected more by a change in surface properties. This maximum may reflect the presence of template decomposition products on the surface of the nonzeolite pores. The membrane surface was light brown only after calcination at 573 K. As shown by the changes in SF_6 permeance with measurement method, the SF_6 permeance is sensitive to the occupancy, which changes with heat of adsorption. If the heat of adsorption of SF_6 is weaker on the surface with template decomposition products, then the driving force could be stronger and the permeance higher. Indeed, for zeolite membranes that were calcined at 753 K, the SF_6 permeance could be increased by adsorption of organic molecules.[25] Moreover, when the pressure drop method was used, the SF_6 permeance at 300 K decreased when the calcination temperature was raised above 573 K (Table 2), but it did not decrease when the sweep gas method was used (Table 3). This is a further

(24) Gardner, T. Q.; Noble, R. D.; Falconer, J. L. Unpublished results, 1998.

(25) Funke, H. H.; Frender, K. R.; Green, K. M.; Wilwerding, G. J.; Sweiter, B. A.; Falconer, J. L.; Noble, R. D. Influence of adsorbed molecules on the permeation properties of silicalite membranes. *J. Membr. Sci.* **1997**, *129*, 77.

indication that the increase was probably due to different adsorption properties.

Calcination at Higher Temperatures. When the calcination temperature increased from 673 to 753 K, the H_2, N_2, CO_2, and SF_6 permeances all increased about a factor of 2, as shown in Table 1 and Figure 3. This indicates that not all the template was removed by 673 K. The N_2/SF_6 ideal selectivity did not change for calcination above 673 K, and thus the increased permeances are not an indication that larger pores preferentially form or that the membrane cracked at the higher temperatures. Note, however, that the *n*-butane and isobutane permeances were essential unchanged, so the H_2/n-butane ideal selectivity increased from 510 to 1110. The *n*-butane/isobutane ideal selectivity at room temperature decreased slightly from 9.3 to 8.3. These changes may reflect that much of the butanes permeation is through the nonzeolite pores and that the amount of these pores does not increase much at higher calcination temperature while the number of zeolite pores does. It is also possible that some pores smaller than the zeolite pores form in the intercrystalline regions at higher temperatures. The changes in some ideal selectivities relative to others indicate the difficulty in characterizing these membranes by ideal selectivities. If some template decomposition products are removed at the high temperatures, the adsorption properties and thus the permeation properties can also change.

Conclusions

At least two types of pores form when ZSM-5 zeolite membranes are calcined; the tetrapropylammonium hydroxide template is removed from the larger nonzeolitic pores first, and these pores have lower ideal selectivities. These pores probably have a distribution of sizes and some also open at the same temperature that zeolite pores open, and thus ideal selectivities changed significantly with calcination temperature or time. The zeolite pores do not appear to be completely open, even at 873 K, but the membranes are selective after heating to this temperature. High separation selectivities for *n*-butane/isobutane mixtures are obtained for membranes with these nonzeolitic pores, indicating that they are small or in low concentration. Membranes with high ideal selectivities can be obtained by calcination at temperatures as low as 573 K at sufficiently long times. The N_2/SF_6 ideal selectivities depend on the measurement method; they were higher for a pressure drop across the membrane than when a sweep gas was used, apparently because of the change in driving force for SF_6. Washing the alumina supports and the finished membranes in boiling water appears to improve separation properties.