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Preparation and evaluation of thin ZSM-5 membranes synthesized in the absence of organic template molecules

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Abstract

Porous α-alumina supports with a pore size of 100 nm were seeded with colloidal TPA-silicalite-1 crystals with a size of 120 nm. The seeded supports were calcined and treated in a synthesis solution free from organic template molecules to form ZSM-5 films on the supports. According to SEM images, the films were about 2 μm thick and no defects could be found on the as-synthesized membranes. Single gas permeation data was collected and good quality membranes (defined as having a non-detectable permeance of SF_6 after drying at 100°C) were further evaluated using binary/ternary gas mixtures. The selectivity for *n*-butane/*i*-butane had a maximum value of 17.8 at 220°C. Water was selectively separated from a helium-diluted vaporized water/ethanol azeotrope with a maximum selectivity of 12.4.

Keywords: α-Alumina; ZSM-5 film; TPA-silicate-1 crystal; Azeotrope

1. Introduction

Thin, supported zeolite membranes with well-defined pores of molecular dimensions have the potential to exhibit both high selectivity and high permeability and operate under harsh conditions, such as elevated temperatures and high pressure. The catalytic properties of zeolites are well known. Thus, zeolite membranes also have an excellent potential for applications in catalytic membrane reactors. In such a configuration, catalysis and separation of products can be performed in a single unit operation. Even though some work in this exciting field of research has been done [1,2], most papers published deal with separation only. The separation mechanisms are in many cases complex. However, Keizer et al. [3,4] classified the permeation results obtained for various two component gas mixtures on a silicalite-1 membrane by considering the occupancy on the external surface and the zeolite pores as well as the mobility in the pores.

Various zeolite species with different pore size and aluminum content, i.e. polarities, such as Faujasite type structures [5,6], A-type structures [2,7–10] and Ferrierite type structures [11] have been investigated in membrane applications. The majority of the work has however been on MFI-type structures, i.e. silicalite-1 and ZSM-5. Many industrially important species have a kinetic diameter similar to the pore opening of MFI-type structures. As a consequence, an MFI-type membrane has the potential to be a useful separation device.

Usually zeolite membranes are synthesized by direct hydrothermal treatment in a synthesis solution containing a templating agent which becomes incorporated in the pore structure. By a calcination procedure, the templating agent is removed in order to make the molecular sieve microporous. It is well known that this treatment may cause cracks, which makes the membrane less effective. In the present

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work, a method comprised of seeding the porous support with colloidal seed crystals followed by growth of the seeds into a dense film was used to prepare thin ZSM-5 membranes without the use of organic template molecules in order to avoid the potentially detrimental calcination procedure. ZSM-5 membranes prepared in a similar way have previously been investigated by our group [12]. Low fluxes and poor selectivities were found for an *n*-butane/*i*-butane mixture in the temperature range investigated, probably due to blockage of zeolite channels by adsorbed molecules such as water and/or ammonia. In the present work, selectivities and fluxes for *n*-butane/*i*-butane were investigated at higher temperatures. Catalytic conversion of ethanol into diethylether and ethylene will also be discussed.

2. Experimental

2.1. Preparation of membranes

TPA-silicalite-1 seeds with an average size of 120 nm were prepared from a synthesis solution with the composition 9 TPAOH:25 SiO_2:360 H_2O:100 EtOH. The synthesis solution was hydrothermally treated for 2 days in an oil bath at a temperature of 100°C. The alkali source was tetrapropylammoniumhydroxide (Sigma, 1.0 M aqueous solution) and the silica source was tetraethoxysilane (Merck, >98%). The seed crystals were purified by repeated centrifugation followed by redispersion in a dilute ammonia solution to obtain a seed sol. The dry content was adjusted to 1.0 wt.% and the pH to 10.0. The zeolite membranes were grown on asymmetric α-alumina supports with an average pore size of 100 nm in the top layer (Inocermic GmbH). The supports were rinsed for 20 min in acetone and methanol and rinsed in filtered (0.1 μm filter) 0.1 M ammonia solution. Following cleaning, the supports were treated for 20 min in a solution containing cationic polymer molecules (0.4 wt.% Redifloc 4150, Eka Chemicals), adjusted to pH 8.0 by addition of a dilute ammonia solution. The solution was filtered with a 0.8 μm filter prior to use. The substrates were rinsed in a filtered (0.1 μm) 0.1 M ammonia solution to remove excess polymer. In the following step, the modified supports were immersed in the seed sol for 20 min. The sol was filtered with a 0.8 μm filter prior to use. No effort was made to limit seed adsorption to the top layer of the α-alumina disk. After adsorption of seed crystals, the supports were rinsed in a filtered (0.1 μm) 0.1 M ammonia solution to remove excess crystals. A calcination procedure (500°C for 4 h) was carried out to remove template molecules from the adsorbed seed crystals. Following calcination, the supports were immediately placed in a synthesis gel for 12 h at 180°C to form ZSM-5 films. The synthesis gel was prepared by dissolving sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$ > 98%, Sigma) and aluminum sulfate ($Al_2(SO_4)_3 \cdot 18$ H_2O, Riedel-deHaën) in water in separate beakers. The contents of the beakers were carefully mixed and a dilute silica sol (Bindzil 30/220, Eka Nobel AB) was added. The molar composition of the resulting synthesis gel was 30 Na_2O:Al_2O_3:100 SiO_2:4000 H_2O. Following hydrothermal treatment, the samples were rinsed thoroughly in 1 M NH_3 and treated in a ultrasonic bath in order to remove excess synthesis mixture and sediments from the porous support.

A synthesis gel was seeded (0.05 wt.% silicalite-1 seed crystals) and hydrothermally treated for 12 h at 180°C. The obtained product was purified and freeze dried and used for XRD and EDX analysis.

2.2. General characterization

A Philips XL 30 Scanning Electron Microscope (SEM) equipped with a LaB_6 emission source was used to study the thickness and morphology of the membranes. Elemental analysis of the product formed after seeding the membrane synthesis solution was performed using an energy dispersive X-ray spectrometer (EDX, Link Isis) attached to the SEM. All samples were gold coated prior to measurements. A Siemens D5000 powder X-ray diffractometer (XRD) running in the Bragg–Brentano mode was used to collect XRD data.

2.3. Permeation measurements

Gas permeation measurements were performed in a test facility based on the Wicke–Kallenbach technique. The membranes were mounted in a stainless steel cell equipped with graphite gaskets. The permeate and retentate pressures were controlled by a regulating

valve connected to a pressure transmitter through a PID controller. The gases were fed to the system by three mass flow controllers. The equipment allowed two gases to be chosen without restrictions via a gas manifold system containing magnetic valves. Helium was used as sweep gas in all measurements. Liquids were fed to the system with a syringe pump and vaporized in an evaporator located in a heated zone kept at 170°C. A thermocouple (type K) was connected to the membrane cell in order to record the temperature of the separation process. All control and measurement signals to and from the system were connected to a data acquisition interface, controlled and monitored by a commercial software package. An online Varian 3800 gas chromatograph (GC), with a column switching system allowing for separation of a wide range of samples, was used for quantitative analyses of the gas mixtures. The GC was equipped with a capillary column (J&W DB-1, 60 m, i.d. 0.32 mm, d.f. 5 μm) and two packed columns (molecular sieve 13×, $\frac{45}{60}$ mesh, 4 ft × $\frac{1}{8}$ in. and Chromosorb 107, $\frac{80}{100}$ mesh, 6 ft × $\frac{1}{8}$ in.). A thermal conductivity detector (TCD) and a flame ionization detector (FID) connected in series detected the separated components. In the case of single gas permeation measurements, a flowmeter (ADM 1000, J&W Scientific) was used to measure flow rates higher than 15 ml/min (STP). At lower fluxes, soap bubble flowmeters (1 and 25 ml) were used.

Single gas permeation measurements (H_2, N_2, He and SF_6) were performed at room temperature with a feed gas applied at 5 bar absolute pressure. The permeate pressure was maintained at 1 bar absolute pressure. No sweep gas was used and permeances were calculated from the measured flow. The membranes were dried in air at 100°C for 12 h prior to measurements. In one experiment, the permeance of SF_6 for an as-synthesized membrane was monitored as a function of temperature during drying in the stainless steel cell.

Butane isomers were mixed in a 50/50 kPa mixture which was fed to the membrane cell at a total volumetric flow rate of 200 ml/min (STP). No absolute pressure difference was applied over the membrane. Helium was used as sweep gas at a volumetric flow rate of 200 ml/min (STP). The permeate and retentate were analyzed with a GC. Three experimental series were performed with butane isomers. In the first series, referred to as Run 1, the membrane was slowly heated up to 80°C (1°C/min) after which permeation tests were performed at up to 220°C in 20°C intervals. After keeping the membrane at 220°C for 12 h, the temperature was reduced to 100°C. Subsequently, new permeation measurements at 20°C intervals at up to 400°C were performed. This series will be referred to as Run 2. During Run 2, pure isobutane was also fed to the membrane at 260, 300 and 400°C in order to investigate whether catalytic isomerization of *i*-butane occurred. In order to study the reproducibility of the results obtained in Run 2 (after the membrane had been exposed to elevated temperatures), new measurements were performed upon cooling back to 320 and 200°C. Run 3 will represent this final test series.

The volumetric flow rate of the ethanol/water azeotrope (96%/4%) from the syringe pump was 0.2 or 0.1 ml/min. The vaporized azeotrope was mixed with helium at a volumetric flow rate of 200 or 1000 ml/min (STP). The UNIFAC method was used to determine the partial pressures of the components in the feed stream yielding 4.3/25/71.7 and 0.58/3.4/97 kPa water/ethanol/helium mixtures, respectively. These two feeds were fed to the membrane that was held at a temperature varying from 100 to 200°C with 20°C intervals. Due to catalytic activity of the membrane at higher temperatures two different selectivities were calculated. One was calculated directly from the results of the gas chromatography analysis without any consideration of the reduction of ethanol permeances due to the reactions below [13]:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O,$$

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$$

The other selectivity accounted for the conversion of ethanol to diethylether and ethylene to give an alternative measure of the selectivity of the membrane. In this case, the quantities of ethanol and water were corrected for the reactions based on the measured amounts of diethylether and ethylene.

3. Results and discussion

3.1. Membrane morphology

Fig. 1(a) and (b) shows top and side view images of a membrane. No pinholes or cracks could be found on the as-synthesized films. Crystal aggregates were

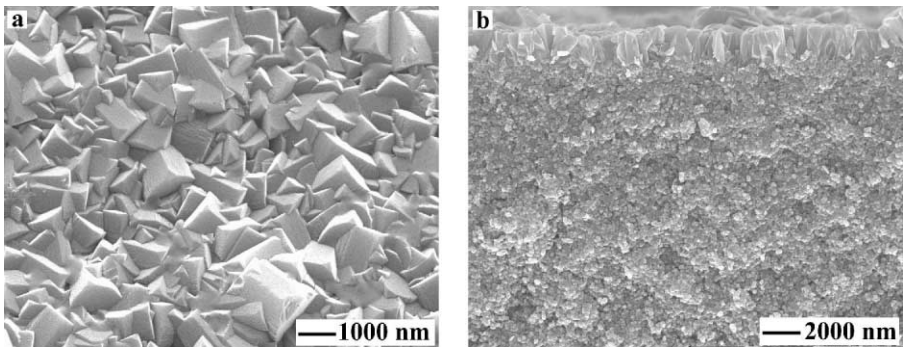

Fig. 1. Top (a) and side (b) view SEM images of an ZSM-5 membrane.

present on the film surfaces. Holes could be seen from top view SEM images (not shown here), probably resulting from detached crystal aggregates. It was however difficult to judge if these holes penetrated the film. No continuous film was formed on the back side of the support.

Even though the same synthesis procedure had been utilized for all membranes prepared in this work, the thickness of the zeolite layer varied between 1400 and 1800 nm. An exact determination was however difficult due to the rough support surface.

XRD patterns were collected from membranes prepared in this work. No other peaks than those expected from ZSM-5 and α-alumina were obtained. Fig. 2(a) shows XRD data from an ZSM-5 membrane along with data recorded from the product formed after hydrothermal treatment of a seeded synthesis solution. The relative intensities of the (1 3 3) peak and the (0 5 1) peak are larger for the membrane sample compared to the powder (which is considered to have a random orientation). This suggests a preferred orientation of the crystals constituting the membrane in accordance with findings previously reported [14]. For some membranes the effect was not as clear, probably due to randomly oriented crystal aggregates attached to the surface of the film.

The Si/Al ratio in the zeolite powder formed after hydrothermal treatment of a seeded synthesis solution was found to be 10 based on EDX analysis. The zeolite film may have an even lower ratio due to dissolution of the alumina support during membrane synthesis and incorporation of the leached aluminum

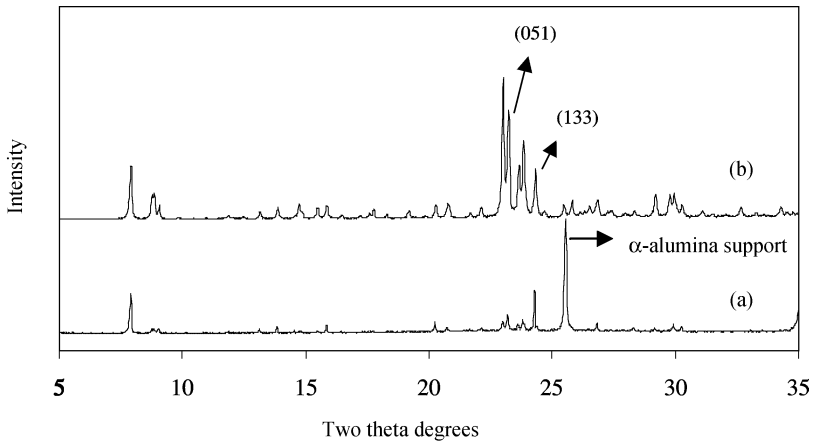

Fig. 2. XRD diffractograms for a zeolitic membrane (a); together with a powder reference sample (b).

into the zeolite layer [15,16]. Thus, a high content of adsorbed molecules such as water and ammonia in the as-synthesized membranes can be expected due to the polar nature of the formed zeolite. Since the membranes investigated in this work were not thermally pretreated, some of the adsorbed molecules can be expected to remain in the zeolite structure after drying at moderate temperatures. This might affect the permeation behavior of the membrane as demonstrated by Funke et al. [17].

3.2. Permeation measurements

3.2.1. Single gas permeation measurements

In order to crudely evaluate the membrane quality, each membrane was first tested in a single gas permeation experiment. Membranes with no measurable permeance of SF_6 after drying at 100°C for 12 h, were selected for further permeation experiments. Note that all membranes had been prepared by the same procedure. Thus, differences in permeation results are due to synthesis reproducibility difficulties. Table 1 gives a summary of the results obtained for selected membranes. Even an extremely low permeance of SF_6 dramatically affects the N_2/SF_6 ratio since the permeance of N_2 also remains very low in these cases (see M1, M2, M4 and M6 in Table 1). This is probably due to the blocking effects of adsorbed species present in the pore structure of the membrane. A much higher permeance ratio would have been expected from a completely dry membrane since the N_2 permeance probably would be much higher and the SF_6 would remain low, since SF_6 is expected to permeate mainly through defects.

Table 1
Single gas permeation measurements for selected membranes[a]

Sample	Permeance (10^7 mol/m^2 s Pa)				N_2/SF_6
	H_2	N_2	He	SF_6	
M1	8.4	3.9	4.1	0.9	4.4
M2	3.1	1.7	1.8	0.4	4.4
M3	3.9	2.0	1.9	<0.001[b]	>2000
M4	2.5	1.2	1.6	0.1	12
M5	1.2	0.62	0.7	<0.001[b]	>620
M6	3.2	1.2	1.6	0.1	12
M7	1.6	0.58	0.92	<0.001[b]	>580

[a] A transmembrane pressure difference of 4 bar was utilized.
[b] Undetectable.

Thus, the N_2/SF_6 ratio does not necessarily represent the quality of a membrane that is not fully dried even though Funke et al. [18] introduced the N_2/SF_6 ratio as criterion for a good MFI membrane. They postulate that a permselectivity higher than 80 indicates a good MFI membrane. Coronas et al. [16,19] also used N_2/SF_6 permselectivity measured at room temperature as an indication of ZSM-5 membrane quality. A permeation ratio as high as 259 was measured for zeolite membranes grown on tubular α-alumina support. The results presented here give permeation ratios greater than 580 (based on the detection limit of the SF_6 permeance) for good membranes, see Table 1. However, a direct comparison may be inappropriate since the membranes in this work were not thermally pretreated.

Table 2 shows previously reported N_2 and SF_6 permeances for MFI membranes. Even though the film thickness in the present work was as low as 2 μm the permeance was not very high compared to previously reported results for significantly thicker films [15,19–22]. Xomeritakis et al. [21] reported (for an MFI membrane with a thickness of 38 μm) a nitrogen permeance similar to the present work. Gump et al. [23] reported a nitrogen permeance four times larger than in the present work. These two reported results support our assumption that adsorbed species may be present inside the zeolite pores. However earlier reported ZSM-5 membranes synthesized in the absence of template molecules [12,24,25] show significantly lower permeances than in the present work, probably also due to adsorbed species in the zeolite channels.

The effect of temperature on membrane stability was investigated by studying the permeance of SF_6 at different temperatures. Fig. 3 shows the SF_6 permeance as a function of temperature for M7. As can be seen, the permeance was very low up to about 250°C after which it dramatically increased. After cooling the membrane back to ambient temperature the permeance remained very high, as indicated by the arrow in Fig. 3. A likely explanation for this result is the formation of defects in the film. In contrast to as-synthesized membranes, cracks with a width of 50–200 nm were found in the zeolite film after this test, see Fig. 4. Dong et al. [26] described template-removal associated crack formation in MFI membranes. The present work shows that cracks can form in MFI membranes even if no template was present in the as-synthesized membrane.

Table 2
Comparison of N_2, SF_6 and butane isomers permeational properties (the temperature in K is given within brackets, if nothing is noted the permeance was given at room temperature)

	Film thickness (1/μm)	Permeance (10^{10}/(mol/m^2 s Pa))					
		N_2	SF_6	N_2/SF_6	*n*-Butane	*i*-Butane	$\alpha_{n/i\text{-butane}}$
Present work	2	2000	<1	>2000	830 (493)	45	17.8
[25][a]	6	0.14	0.006	23	0.1[b] (423)	0.15[b]	–
[24][a]	3	3.7 (378)	0.099	37	0.099[b] (378)	0.074[b]	2
[12][a]	1.5	9.9 (418)	0.87	11.38	0.5[b] (418)	0.4[b]	0.7
[19]	–	400		6.00	700 (410)	60	11
[15]	100	270 (418)			120 (423)	90	1.3
[21]	38	1600	160	10.00	320[b]	8.6[b]	37[c]
[22]	50	–	–	–	756		48
[20]	–	8800		240.00	700 (350)	20	20

[a] Template free synthesized ZSM-5 membranes.
[b] Single gas measurements.
[c] Permselectivity.

3.2.2. Permeation of a 50/50 n-butane/i-butane mixture

Fig. 5 illustrates the *n*-butane/*i*-butane selectivity as a function of temperature for M3 and Fig. 6 shows the permeances obtained in Run 1. During the first heating cycle up to 220°C (Run 1) the selectivity was close to unity up to 160°C and the permeance of both gases was very low, approximately 5×10^{-10} mol/m^2 s Pa. Between 160 and 200°C the selectivity increased dramatically to 17.8. The permeance increased for both *n*-butane and *i*-butane, see Fig. 6, although the *n*-butane permeance increased much more resulting in the higher selectivities. In Run 2 the selectivity and the *n*-butane permeance were 6.7 and 13.7 times higher, respectively, than in Run 1 at 105°C (compare Runs 1 and 2 in Figs. 5 and 6). This clearly indicates that the zeolite pores were at least partly blocked by adsorbed species at low temperatures during Run 1, which reduced the permeance and selectivity. The isomers probably permeated mainly through defects or grain boundaries present in low quantities. The selectivity reached a maximum of 16.7 at 220°C. Higher temperatures resulted in a lower selectivity. In the temperature range 280–300 and 380–400°C some events took place, see Run 2 in Figs. 5 and 7, which led to particularly sharp drops in selectivity. Between these intervals, the permeance increased more for *i*-butane than for *n*-butane, which might

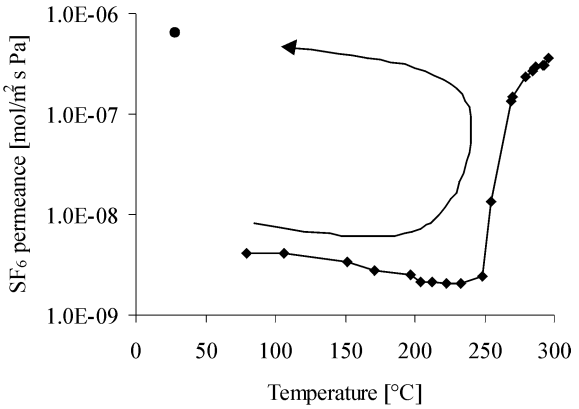

Fig. 3. Permeance of SF_6 for membrane M7 as a function of increasing temperature and after cooling the membrane to room temperature. A transmembrane pressure difference of 4 bar was utilized.

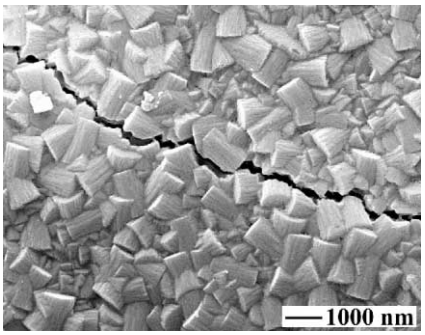

Fig. 4. Top view SEM image of membrane M7 taken after SF_6 permeation measurements conducted during drying up to 300°C.

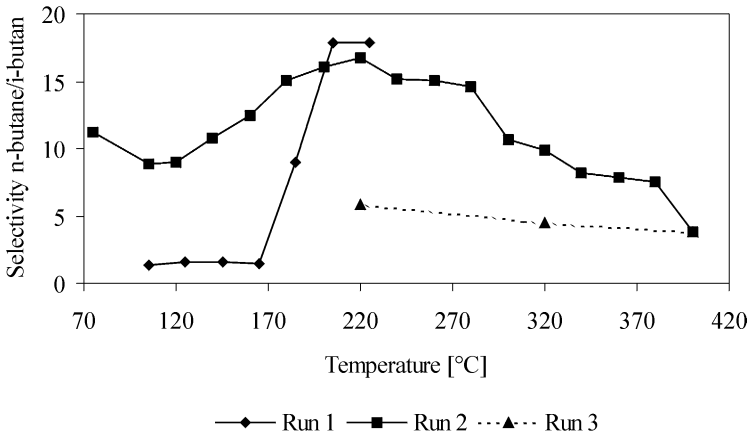

Fig. 5. Selectivities for a 50/50 kPa *n*-butane/*i*-butane mixture for membrane M3 using helium as sweep gas.

be due to the formation of cracks in the zeolite film or simply the effect of temperature on the transport mechanisms. Others have observed an optimal temperature for *n*-butane/*i*-butane selectivity with MFI based membranes [19,20]. At 400°C the selectivity had dropped to 3.8. When decreasing the temperature in Run 3 the high selectivities obtained in Run 2 were not regained, see Fig. 5. At 220°C the selectivity was only 5.8 which is considerably lower than the maximum of 16.7 found in Run 2. The permeation of both isomers was also much higher in Run 3 compared to Run 2, see Fig. 7. The lower selectivities of Run 3 indicate that the molecules increasingly permeated through paths larger than the zeolite pores at higher temperatures. However, these paths cannot be large and/or numerous since the membrane was still able to separate the two butane isomers. Even in Run 3 the selectivity decreased with temperature which suggests that part of the decrease in selectivity with temperatures greater than 220°C observed in Run 2 was caused by the effects of temperature on the transport mechanisms. However, the particularly large changes in selectivity between 280 and 300°C and between 380 and 400°C are mainly caused by crack/defect formation due to the thermal instability of the membrane.

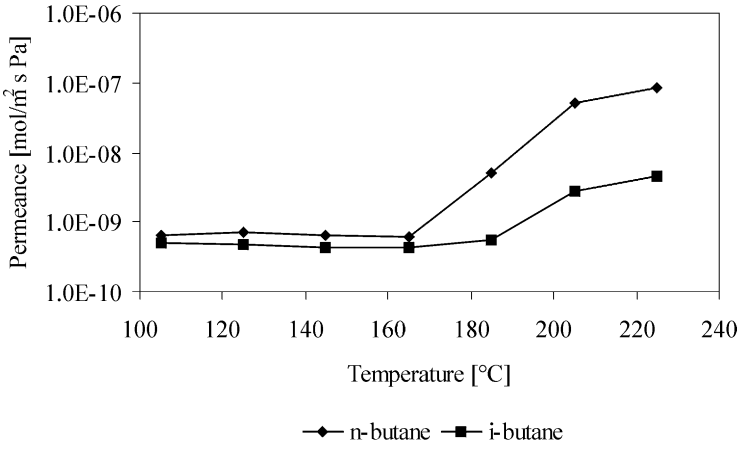

Fig. 6. The permeance of the butane isomers in Run 1 as a function of temperature. A 50/50 kPa mixture of butane isomers were fed to the membrane and helium was used as a sweep gas.

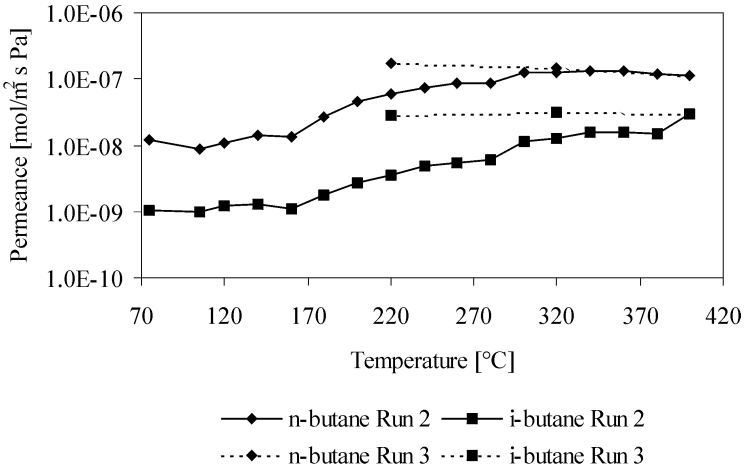

Fig. 7. Permeances of the butane isomers in Runs 2 and 3. A 50/50 kPa butane isomer mixture was used as feed and helium was utilized as a sweep gas.

A catalytic isomerization of *i*-butane to *n*-butane would have increased the apparent selectivities obtained. Pure *i*-butane was fed to the membrane at 260, 300 and 400°C during Run 2. At these conditions no *n*-butane was detected in the permeate. Thus, the selectivities presented in this work only represent the separation ability of the membrane.

Noack et al. [24] prepared template free ZSM-5 membranes on α-alumina disks using the same synthesis conditions as used in the present work as well as in earlier work [12,14]. Permeances of mixtures of *n*-butane and *i*-butane of two different compositions (90:10, 10:90 mol.%) were studied. Low (<2) selectivities were obtained. However, the temperature range under investigation was 25–130°C, and the membrane was dried at mild conditions (150°C at 10^{-3} mbar for 16 h) prior to measurement. Lai and Gavalas [25] also synthesized template free ZSM-5 membranes with similar synthesis conditions as in the present work with the exception that multiple hydrothermal treatments were used. The membranes were, in this case as well, dried under mild conditions (vacuum 160°C overnight). The permeation properties were similar to earlier reported results [12,24], see Table 2. These results suggest a pore blocking effect at low temperatures similar to what has been observed in the present study.

The results obtained in the present work can be compared with related studies as in Table 2. If nothing is mentioned about the membrane test facility, similar experimental conditions as in this study were utilized. This is worth mentioning since the experimental set up can have an influence on the results obtained [20]. Gump et al. [20] synthesized an MFI-type membrane on a tubular α-alumina support. The Si/Al ratio of the synthesis solution was 100 and it contained TPAOH molecules as templates. A maximum selectivity of about 20 and an *n*-butane permeance of around 7×10^{-8} mol/m^2 s Pa was measured at a temperature of 80°C. At ambient temperature the selectivity was about 10 with an *n*-butane permeance of approximately 2×10^{-9} mol/m^2 s Pa. These results are similar to ours with the exception that the maximum selectivity was found at 220°C in the present study. An MFI-type membrane (silicalite-1) was prepared on a porous α-alumina disk by Keizer et al. [3]. A selectivity of 52 at 25°C was achieved with an *n*-butane permeance of around 3.2×10^{-8} mol/m^2 s Pa. After heating the membrane to 200°C, the selectivity had dropped to 11, whereas the permeance increased to about 4.2×10^{-8} mol/m^2 s Pa. The thickness of the membrane was around 3 μm. These results are similar to the ones found in the present work. Butane isomer separation measurements were performed on ZSM-5 membranes prepared on porous α-alumina supports [19]. In contrast to the experimental methods used by other groups mentioned above, a pressure drop of 138 kPa was applied over the membrane and no

sweep gas was utilized. The maximum selectivity for these membranes was 11 and 6.2 at 135°C. The Si/Al ratio in the synthesis solution was 600 and 100 and the synthesis was carried out in the presence of template molecules. The selectivity dropped to 5.7 and 2 at about 240°C. The permeances at maximum selectivity were 6.5×10^{-8} and 1.1×10^{-7} mol/m^2 s Pa. One should keep in mind that the mass transport through defects in the membrane probably increases as a result of transmembrane pressure difference, thus giving lower selectivities and higher fluxes. Gora et al. [22] reported a separation selectivity of 48 and an *n*-butane permeance of 756×10^{-10} mol/m^2 s Pa for a 50/50 *n*/*i*-butane mixture at room temperature for a non-supported 50 μm silicalite-1 membrane. Although the zeolite film thickness was approximately 25 times greater, the *n*-butane permeance was higher than in the present work. This inconsistency may be due to the presence of species, such as sodium in the zeolite pore structure that partly block the micropores in the present work. Xomeritakis et al. [21] used seeds and prepared a ~38 μm thick silicalite-1 membrane. The permeation flux ratio of a 50/50 *n*/*i*-butane mixture was 37 with an *n*-butane permeance of 318×10^{-10} mol/m^2 s Pa, i.e. similar to the results in the present work. On the other hand, Xomeritakis et al. [21] reports a very different N_2/SF_6 flux ratio of 10. This discrepancy may be due to the high aluminum content in the film in the present work or simply due to the fact that the membrane was not completely dry when the N_2 and SF_6 permeances were measured.

3.2.3. Permeation of a ternary ethanol/water/He mixture

Due to its polar nature, a ZSM-5 membrane with high aluminum content is water selective in a water/ethanol system in contrast to its aluminum free analog silicalite-1 that is ethanol selective [27]. Thus, the main separation mechanism in the system is differences in polarities rather than molecular sieving. Fig. 8 shows the selectivity for the separation of the water/ethanol azeotrope diluted with helium as a function of temperature. True separation was observed below 150°C, whereas at higher temperatures it was found that the membrane catalyzed the dehydration of ethanol to form diethylether and ethylene, see Fig. 9. At 200°C the flux of diethylether and ethylene even exceeds the flux of ethanol. To rule out the support as responsible for the catalysis the same experimental conditions were used, but a support without zeolite film was mounted in the cell. No diethylether or ethylene could be found in the permeate in this case. In the case of a poor quality zeolite membrane, low product concentrations were found in the permeate, probably due to dilution with unreacted feed. No products could be detected in the retentate from a good quality membrane, which indicates that the reaction mainly takes place in the zeolite pores.

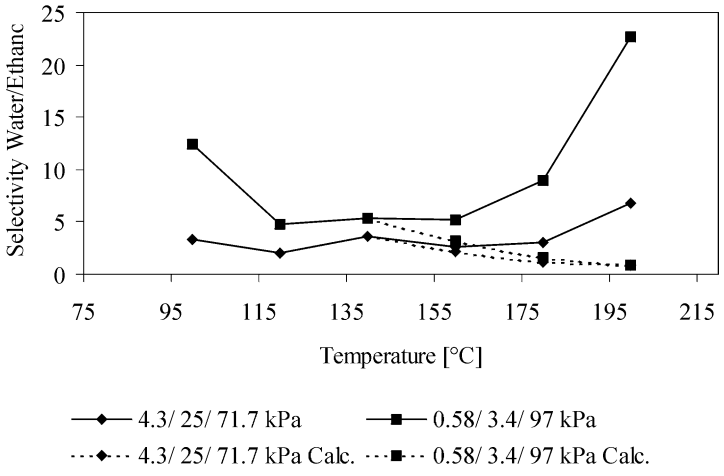

Fig. 8. Separation selectivities for two different compositions of water/ethanol/helium mixtures. The dashed lines show the selectivities after compensating for products (ethylene, diethylether and water) formed by dehydration of ethanol catalyzed by the membrane.

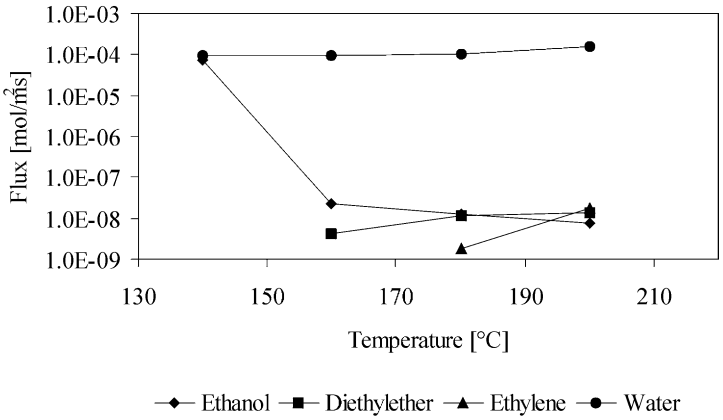

Fig. 9. Fluxes of ethanol, ether, ethylene and water as a function of temperature. The composition of the feed mixture was 0.58/3.4/97 kPa water/ethanol/helium. Helium was used as a sweep gas.

The catalyzed reactions misleadingly increased the selectivity based on ethanol and water. The dashed lines show the calculated selectivity after compensating for the formation of diethylether, ethylene and water. From about 95 to 150°C the selectivity dropped with increased temperature. The selectivities calculated from the reaction products indicate that the large increase in selectivity obtained beyond 150°C was simply due to the consumption of ethanol by the reactions. The selectivities calculated from the reaction products cannot be considered to represent the true water/ethanol selectivity. Lower selectivities were obtained for the less diluted azeotrope mixture, see Fig. 8. This trend may be caused by pore blockage by ethanol at lower dilution and/or effects of saturation of water already at high dilution. Permeances of water and ethanol are presented in Fig. 10. It can be seen that the water permeance is higher at lower partial pressures compared with the run with higher partial pressures. The permeance of ethanol seems to be independent of the partial pressure.

As far as we know, this is the first time gas phase separation of the ethanol/water azeotrope has been investigated using MFI-type membranes.

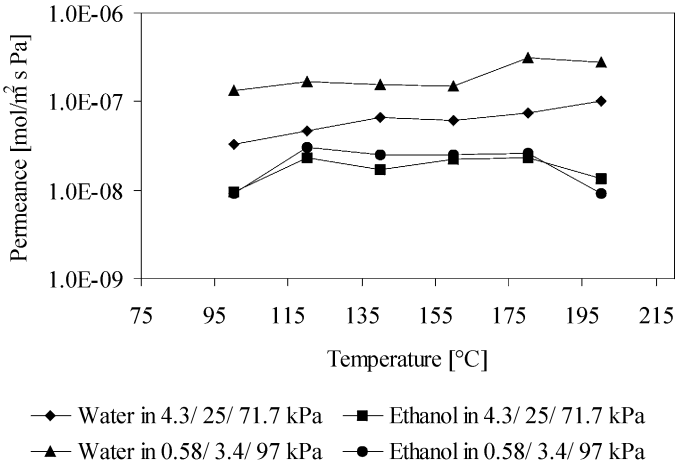

Fig. 10. Permeances of water and ethanol for two different water/ethanol/helium mixtures. A sweep gas (helium) was used.

4. Conclusions

A seeding technique was used to synthesize ZSM-5 membranes on porous α-alumina supports. The synthesis was carried out in a gel free from organic templates, making a calcination step unnecessary. The as-synthesized membranes were dried at 100°C for 12 h prior to single gas permeation measurements at room temperature. Membranes with no measurable flux of SF_6 were considered to be of high quality. In a series of seven membranes, three were found to meet this standard. From the permeation measurements of an *n*-butane/*i*-butane mixture it was concluded that a high drying temperature (>200°C) is necessary to make the zeolite pores available for gas permeation. A maximum selectivity of 16.7 was measured at 220°C. Beyond about 270°C crack formation severely deteriorated the performance of the membranes. The formation of defects is at least partly responsible for lower selectivities at elevated temperatures. All membranes that were exposed to higher temperatures showed the same tendency to form cracks. Experiments with vaporized ethanol/water azeotrope diluted with different amounts of helium were conducted. At temperatures higher than 150°C, the zeolite film catalyzed the formation of diethylether and ethylene. Higher selectivities were found for the more diluted azeotrope, the selectivity was 12.4 at 100°C.

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