

LICENTIATE THESIS

Synthesis, Characterization and Properties of Zeolite Films and Membranes

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Licentiate thesis

Institutionen för Kemi och metallurgi
Avdelningen för Kemisk teknologi

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membranes**

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May 2001

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ABSTRACT

The work presented in this thesis was aimed to synthesize zeolite films in the absence of organic additives to avoid the potentially detrimental calcination procedure. Furthermore, the support surface was seeded with colloidal seed crystals prior to film growth. This technique has previously been used to prepare thin zeolite films. The films were characterized by Scanning electron microscopy (SEM), X-ray diffraction (XRD) and gas permeation experiments. Films of three different types of zeolites were synthesized in this work; FAU-type zeolite, ZSM-5 and zeolite NaA. The thickness of the FAU-type zeolite films could be controlled by varying the synthesis temperature and duration. However, a maximum film thickness was found. Prolonged hydrothermal treatment caused the film thickness to decrease due to the transformation of FAU into zeolite P. The adsorbed seeds were oriented with the $\langle 111 \rangle$ pyramid parallel to the surface of the support. During growth, the crystals constituting the films became randomly oriented.

The ZSM-5 films were tested as membranes for the separation of butane isomers. The selectivity for n-butane/i-butane had a maximum value of 17.8 at 220 °C. Furthermore, the ZSM-5 membranes were found to be catalytically active, converting ethanol into diethylether and ethylene.

The growth of silicious species into the porous support during zeolite NaA membrane synthesis was examined. Higher temperatures of synthesis resulted in relatively more growth into the porous support compared to the film growth on top of the support. By using a multi-step synthesis procedure at low temperature, thicker films with less growth into the support could be prepared.

LIST OF PAPERS

I Faujasite-type films synthesized by seeding

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Published in Micropor. Mesopor. Mater. 38 (2000) 25-34.

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

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Accepted for publication in Catalysis Today.

III Effects of synthesis parameters on intra-pore zeolite formation in zeolite A membranes

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Accepted for presentation at the 13th IZC, Montpellier, 2001 and for publication in the conference proceedings.

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1. INTRODUCTION

1.1 Properties of zeolites

Zeolites are aluminosilicates with an open structure composed of a three dimensional network of SiO_4 and AlO_4 tetrahedra sharing all the corners with each other. A general formula for the chemical composition may be expressed as:



where M = extraframework cation.

The exchange of silicon for aluminum in the framework results in a net negative charge which must be compensated by extraframework cations. In general, these may be any alkali, alkaline-earth or rare earth cation as well as organic cations such as the tetramethylammonium ion. Water molecules are located in the channels and cavities, as are the neutralizing cations. Zeolites may be classified in various ways on the basis of structural differences, one of them being based on the size of the pore openings. Depending on the structure, the size of the pores is in the range 3 to 8 Å. The

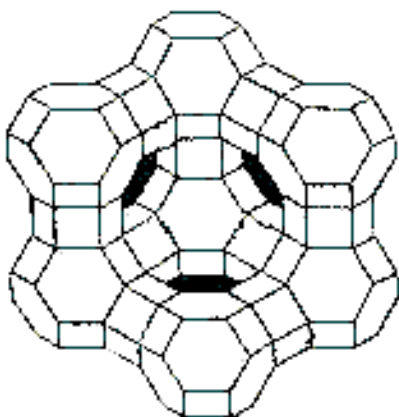


Figure 1. The framework structure of Faujasite

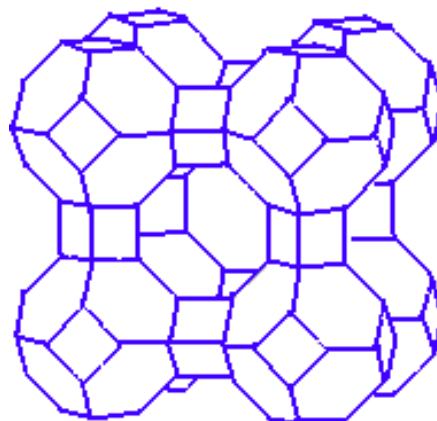


Figure 2. The framework structure of zeolite A.

apertures are bounded by oxygen atoms of connected tetrahedra. In general, these rings involve 6, 8, 10 or 12 oxygen atoms. However, other factors are involved in determining the final pore size. For example, the location, size and coordination of the extraframework cations. The latter is a well known parameter in the case of zeolite A, in which the channel aperture size can be tailored by using different sized extra framework cations.

The interconnected regular three dimensional network of micropores at a molecular scale and the extraframework cation content are the key factors determining the physical and chemical properties of zeolites. The size of the pores gives the zeolites molecular sieving properties, i.e if the molecule is larger than the pore size, it will not enter the structure. The shape of the pore may also influence the adsorption capability. The extraframework cations are in many cases exchangeable, which allows for the introduction of acid sites bonded to the non-saturated oxygen atoms.

Three different zeolite structures were investigated in this work: the faujasite [FAU] group zeolites (see Figure 1), zeolite A [LTA] (see Figure 2) and ZSM-5 [MFI]. All of them have found important applications and are therefore synthesized in an industrial scale. Zeolite X and Y are the synthetic analogues to the natural faujasite. The difference between these two zeolites is the Si/Al ratio which is 1-1.5 and 1.5-3 in zeolite X and Y, respectively [1]. The channel system has equidimensional channels intersecting in a perpendicular fashion. The free aperture diameter for the channels is 8 Å in NaY [2]. Zeolite A has a Si/Al ratio of ca. 1 [3]. The three dimensional channel system has, like in FAU-type zeolites, equidimensional channels intersecting perpendicular to each other. The free aperture diameter for the channels is 4 Å in zeolite NaA [3]. ZSM-5 has a three dimensional pore system consisting of sinusoidal channels (5.1×5.5 Å) and intersecting straight channels (5.3×5.6 Å) [4]. ZSM-5 can be synthesized with a wide variety of Si/Al ratios, mainly in the range 5-100 [5].

1.2 Potential applications of zeolites

The unique properties of zeolites make them attractive in a variety of industrial applications. The potential acid sites, the high specific surface and the well defined pore dimension are features suitable for a selective catalyst material. For example, zeolite Y is an active component in catalytic cracking catalysts. Due to the molecular sieving ability, zeolites are used in various separation processes such as water removal from gases. However, the batch processes utilized requires regeneration of the sorption material. Since the beginning of the 80's, the development of zeolite membranes has attracted the attention of many research groups. A zeolite membrane has the advantage that it can potentially sieve out molecules in a continuous process. For example, hydrophilic zeolite membranes derived from NaA were commercialized for alcohol dehydration and solvent dewatering [6]. Various zeolites with different pore size and aluminum content such as Faujasite type structures [7, 8], A-type structures [9-13] and Ferrierite type structures [14] were investigated in membrane applications. However, most literature concerning this field deals with MFI-type structures [15-19]. Molecular sieve membranes also have a great potential as a component in membrane reactors. A membrane reactor can be used to combine reaction and separation in a continuous process. The selectivity of a reaction can be improved by selectively removing one of the products from the reaction mixture or by the controlled addition of a reactant through the membrane. Removing one of the products in an equilibrium limited reaction can increase the conversion. For example, Van de Graaf et al increased the catalyzed conversion of propene into ethene, cis-2-butene and trans-2-butene by selectively removing trans-2-butene using a silicalite-1 membrane [20, 21]. A catalytically active membrane allows the combination of catalyzed reactions and separation of products.

1.3 Synthesis of zeolites and zeolite films

Generally, zeolites are crystallized by hydrothermal treatment of a clear synthesis solution or synthesis gel containing a silica source, an aluminum source and an alkali source (alkali hydroxide or/and organic bases). The composition of the synthesis mixture, the temperature during synthesis and synthesis duration are the main parameters determining which zeolite phase will be formed. In some cases, organic additives are required in order to crystallize the desired product. For example, the molecular sieve Silicalite-1 is not possible to crystallize in the absence of organic additives. Moreover, the addition of organic additives to the synthesis gel of aluminum-rich zeolites results in the crystallization of more silica-rich structures [22]. Frequently used additives are the tetramethylammonium (TMA)⁺ ion and the tetrapropylammonium (TPA)⁺ ion. The organic molecules become trapped in the pores of the zeolite and must be removed in order to render the structure microporous. This is usually done by calcination which entails oxidation of the organic molecules at high temperature. In large-pore zeolites, such as the faujasites, the organic molecules can be removed by ion-exchange.

Zeolite membranes are most commonly synthesized on porous supports of alumina or steel. There are three main routes to synthesize continuous, supported zeolite films and membranes. The most common method is to treat the support directly with a molecular sieve precursor solution, called *in-situ* crystallization or direct synthesis in the literature. Different approaches of this method are discussed in a recent report by Jansen et al. [23]. Direct synthesis relies on both nucleation and growth of molecular sieve crystals on the surface of the support. The second method, called the vapor phase transport method, was first described by Xu et al. [24]. MFI zeolite was crystallized from an amorphous dry aluminosilicate gel under the vapors of triethylamine (Et₃N), ethylenediamine (EDA) and water. Since then, the method has been used to synthesize membranes of various zeolites such as ANA, MOR, FER and MFI [25, 26]. The third method involves the growth of seed crystals attached to the

support. When surface seeding is used, nucleation is no longer necessary. Several methods for the attachment of seeds to the surface have been proposed. Zeolite Y films were synthesized on tubular α -alumina supports using a seeding technique in which the support was rubbed with NaX zeolite crystals that acted as growth centers [27]. The same seeding approach was utilized to synthesize Zeolite A and faujasite membranes [28]. In the synthesis of highly oriented films of zeolite A, glass supports were immersed in a colloidal zeolite A suspension in order to obtain seed crystal layers [29]. The support surface can be modified in order to facilitate seed adsorption from a seed crystal sol [16, 30-43]. In the literature, this seeding technique is denoted the seed film method. Negatively charged colloidal molecular sieve crystals are electrostatically adsorbed on substrates pretreated in order to render the surface positively charged. The pretreatment depends on the type of surface. Negatively charged surfaces are directly charge modified by adsorption of cationic polymer molecules. Neutral materials such as gold are chemically treated prior to polymer adsorption in order to obtain a negatively charged surface. The seed film method was utilized to prepare films of a number of molecular sieves such as silicalite-1, ZSM-5, zeolite NA and faujasite on various supports such as vegetal fibers, carbon, gold, silicon, quartz and alumina. The effect on crystal orientation of various synthesis parameters such as seed crystal size and film thickness has also been studied [39]. In recent work, the film formation process of silicalite-1 on gold was investigated by reflection absorption infrared spectroscopy (RAIR) [43]. Furthermore, films prepared utilizing the seed film method have been tested as membranes [16] and sensors [44]. Recently, a combination of surface seeding and the vapor phase method was proposed by Tsay et al [45]. A layer of colloidal MFI zeolite was deposited on a porous support, pre-coated with a silica layer. The composite was heated under saturated water vapor to obtain a thin zeolite membrane.

1.4 Defect formation in molecular sieve films

Most papers written on the subject of zeolite membrane preparation deal with MFI type molecular sieves synthesized in the presence of organic template molecules. The removal of the template molecules by calcination often cause cracks in the membrane which is detrimental for the molecular sieve effect. Crack formation in MFI type molecular sieves during removal of the template molecules has been under study. Geus et al [46] investigated the development of cracks during calcination in large TPA-silicalite crystals. On the basis of this study, a safe calcination procedure (a low heating rate to 400 °C) for supported, polycrystalline MFI membranes were proposed by the authors. den Exter et al concluded that the orientation of the crystals in MFI type films also influences the crack formation during calcination [47]. Dong et al. studied the microstructure evolution in supported MFI zeolite films during calcination [48]. The authors claim that crack formation is induced by a compression stress that develops in the zeolite film during cooling after calcination when the zeolite crystals are chemically bonded to the support after template removal. However, the quality was improved with a suitable temperature program for calcination. Another approach to overcome problems with defect formation during calcination, is to repair them after they have formed. Yan et al. substantially increased the *n*-butane:isobutane ideal selectivity of a ZSM-5 membrane by a selective coking procedure which plugged micro defects but left the intracrystalline pore space of the membrane unaffected [49]. However, the increased selectivity was accompanied by a substantial flux decrease.

1.5 Zeolite formation within the porous support during membrane synthesis

An important feature of any membrane to be used on an industrial scale is a high permeability, which increases the efficiency while the selectivity is high. Zeolite

membrane synthesis on a porous support is often accompanied by the formation of siliceous species within the pores of the support. Contradictory findings regarding the effect of this internal siliceous layer on the performance of the membrane have been reported. Piera et al. achieved higher MeOH/O₂ and EtOH/O₂ selectivity for MFI membranes with a larger amount of silicalite-1 inside the porous support [50]. However, the permeation of N₂ was much lower for membranes with intra-support layers than for membranes where most of the silicalite existed as a thin layer on the top of the support. Both flux and selectivity in the separation of n-butane/isobutane were highly enhanced in ZSM-5 membranes where the internal siliceous layer was assumed to be both thinner and more crystalline [51]. The same group used a diffusion barrier during ZSM-5 membrane synthesis and managed to decrease the thickness and increase the crystallinity of the internal siliceous layer [52, 49]. Both flux and selectivity in n-butane/isobutane separation experiments were highly enhanced by this treatment. The findings mentioned above indicate that the penetration of siliceous species into the porous support during membrane synthesis has a negative effect on the efficiency of the membrane.

2. SCOPE OF THIS WORK

The seed film method has been developed for the preparation on ultra thin continuous molecular sieve films on various substrates [53]. The main goal of this work was to develop preparative procedures for new types of zeolite films using the seed film method. A further objective was to utilize template free precursor gels in order to avoid a calcination procedure which might cause strain and consequently cracks in zeolite films synthesized on porous substrates. The characterization of the films was performed by SEM and XRD, with special emphasis on the penetration depth in the cases where porous substrates were used. This work was also aimed at testing the films as membranes in a membrane test facility.

3. EXPERIMENTAL

3.1 Zeolite film synthesis

Colloidal crystals of zeolite Y, A and Silicalite-1 were synthesized utilizing a method developed by our group [54]. Clear homogeneous solutions were hydrothermally treated in the presence of organic additives. After completion of the crystallization, the crystals were purified by repeated centrifugation followed by re-dispersion in a dilute ammonia solution to obtain a seed sol. Special care was taken in this procedure when preparing zeolite Y seeds (paper I), in order to ion exchange the template molecules with ammonia. The dry content was adjusted to 1.0 wt% and the pH to 10.0.

Polished α -alumina substrates (Paper I) and porous α -alumina asymmetric supports (Paper II-III) were cleaned and treated in a solution containing cationic polymer molecules (0.4 wt% Redifloc 4150, Eka Chemicals) in order to render the surface positively charged. Negatively charged seed crystals were adsorbed on the charge modified substrates. For the polished α -alumina substrates, the substrate modification followed by seed adsorption was repeated in order to improve the surface coverage. To avoid adsorption of dust particles on the substrates, the solution of cationic polymer molecules and the seed sol were filtered in the later work (papers II-III). The seeded porous substrates (Paper II-III) were calcined in order to remove the templates incorporated in the pores of the seed crystals. Zeolite films were grown on the substrates by hydrothermal treatment in a synthesis gel. In earlier work (Paper I), film growth was effected both at the bottom of the reactor and in the clear phase formed in the upper part. In paper III, a so called repeated synthesis was also performed where fresh synthesis solution was added during hydrothermal treatment.

3.2 Characterization methods

Dynamic light scattering (DLS) was used to follow the growth of the seed crystals using a Brookhaven Instrument BI200SM light scattering system.

The thickness and morphology of the films as well as the penetration of siliceous species in the porous support were investigated using a Philips XL 30 Scanning Electron Microscope (SEM) equipped with a LaB₆ emission source. Elemental analyses of seed crystals and crystals formed in the bulk of the synthesis gel were performed using an Energy Dispersive X-ray system (EDX, Link Isis) attached to the SEM.

A Siemens D5000 powder X-ray diffractometer (XRD) in the Bragg-Brentano mode was used to collect XRD data in the range 5-35 °2θ.

A few Fourier transform infrared (FTIR) spectroscopy measurements (Paper I) were performed with a Perking Elmer 2000 FTIR spectrometer. The mid-infrared region was recorded.

Single gas permeation measurements (Paper II-III) 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. Permeance was calculated from the measured flow on the permeate side of the membrane. The membranes were mounted in a stainless steel cell and a rubber o-ring was used to obtain a gas tight connection. The membranes were dried at 100 °C (Paper II) or at room temperature (Paper III) prior to permeation measurements. A flow-meter (ADM 1000, J&W Scientific) was used to measure flows higher than 15 ml/min (STP). At lower flows, soap bubble flow-meters (1 and 25 ml) were used.

Permeation measurements for gas mixtures were performed using a test facility based on the Wicke-Kallenbach technique (Paper II), where a concentration gradient was created by the use of a helium sweep gas on the permeate side of the membrane. The membranes were mounted in a stainless steel cell equipped with graphite gaskets. The pressure was maintained at 1 bar on both sides of the membrane. The

temperature in the membrane cell was monitored during measurements. An online Varian 3800 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) was used for quantitative analyses of the gas mixtures.

4. RESULTS AND DISCUSSION

4.1 Faujasite type films (Paper I)

In membrane applications, a high flux of the permeating species increases the efficiency. A thin membrane offers less resistance and is therefore desirable. In the present work, continuous and template free faujasite type films with a minimum thickness of 150 nm were prepared utilizing the seed film method. Surface seeding has previously been utilized in the synthesis of faujasite type films on inorganic membranes, however the continuous films were several microns thick [27-28, 55]. The method presented in this work allows for the preparation of truly thin films of faujasite. Thus, the developed film preparation procedure is of interest for the synthesis of highly efficient membranes. Furthermore, no calcination of the as-synthesized films was required since the synthesis was carried out in the absence of organic templates.

Seeded alumina wafers were hydrothermally treated in a zeolite precursor solution in order to obtain dense zeolite films. The template molecules present in the as-synthesized seed crystals were ion-exchanged with ammonium ions in order to obtain template free films. SEM images were used to study the morphology and thickness of the films. An aluminosilicate gel is rapidly precipitated during hydrothermal treatment of the film synthesis solution, leaving an almost clear solution in the upper part of the synthesis mixture. The film growth in the clear solution as well as in the lower part of the synthesis vessel was investigated.

4.1.1 Film growth in the upper part of the synthesis solution

The film surface morphology follows a similar trend during growth in 60, 80 and 100 °C in the upper part of the synthesis vessel. In the early stage of film growth, the size distribution of the crystals is narrow. Upon a prolonged hydrothermal treatment however, some crystals appears to grow faster and encapsulate the surrounding

crystals. Thus, the amount of crystals per unit area is decreasing with increasing thickness. The events described above are however taking place at different synthesis times due to the different growth rates at each temperature investigated.

4.1.2 Film growth in the lower part of the synthesis solution

During film growth at 100 °C , the amount of crystals per unit area is decreasing with increasing thickness which indicates competitive growth of the crystals constituting the films, see Figure 3. Films synthesized in the lower part of the synthesis mixture were thicker than films synthesized in the upper part using the same synthesis

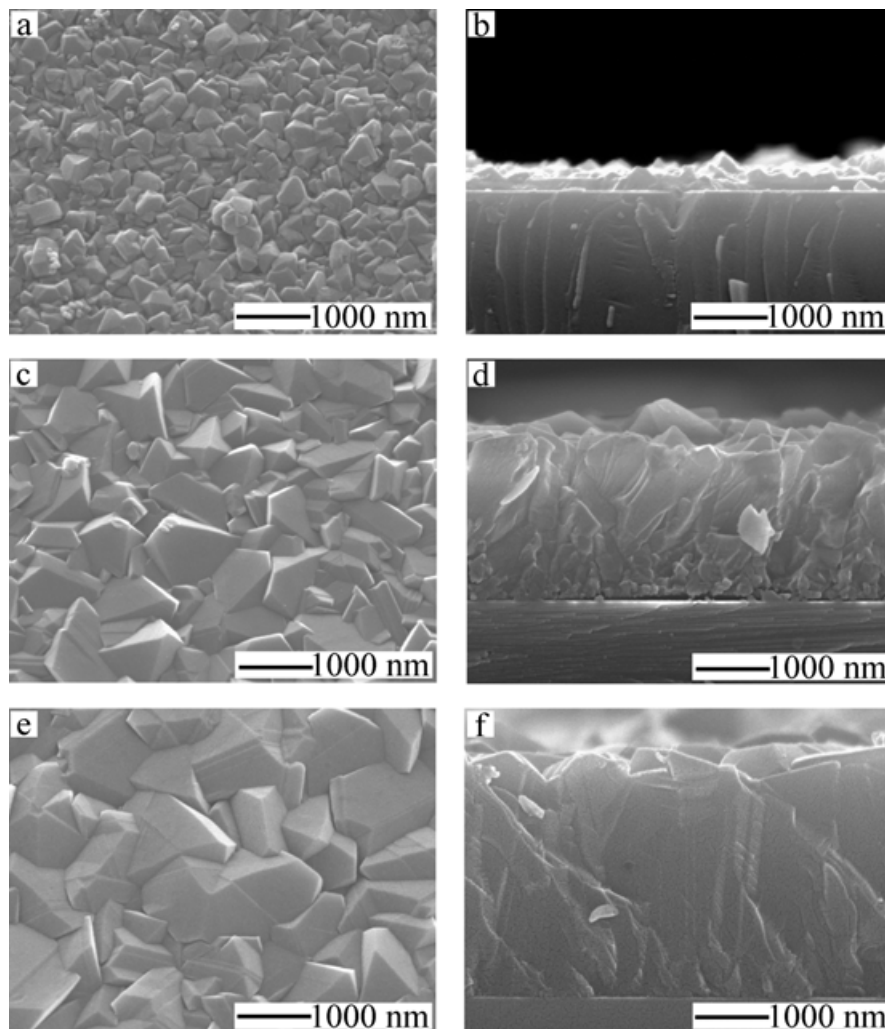


Figure 3. SEM images of films synthesized for 1 h (a,b), 6 h (c,d) and 12 h (e,f) in the bottom part of the synthesis solution at 100 °C.

duration and temperature. A possible explanation for these results may be the attachment of crystals formed in the bulk onto the growing film. This is more likely to happen when the film is grown in the bottom of the synthesis gel, since the concentration of crystals formed in the bulk should be higher in this area. This speculation is supported by the fact that the film thickness is approximately the same as the surface crystal size, estimated by SEM top view images, for all films synthesized in the upper part of the synthesis solution. For films hydrothermally treated in the bottom of the synthesis solution on the other hand, a deviation between these two values is obtained, which increases with the film thickness. A film synthesized for 12 h is about 2700 nm thick whereas the estimated length of the largest crystals seen on the surface of the film is about 1400 nm, see Figure 3 (e, f).

4.1.3 Film dissolution and crystal orientation

The film thickness increased up to a certain time of hydrothermal synthesis and then decreased upon a prolonged treatment. This phenomenon was investigated by analyzing purified crystals formed in the bulk of the synthesis solution after different periods of synthesis times by XRD. It was found that the fraction of faujasite in the crystalline bulk product was decreasing while the amount of zeolite P was increasing with synthesis duration, see Figure 4. Hence, it is likely that the zeolite P crystals formed after prolonged hydrothermal treatment is growing at the expense of the crystals in the bulk as well as of crystals constituting the film. Thus, the reason for the decrease in zeolite Y film thickness is likely to be due to the formation of zeolite P.

The orientation of the crystals constituting the films was investigated using XRD data. A powder sample of faujasite was used as a reference and considered to have random orientation of the crystals. Major peaks in the XRD pattern obtained from adsorbed seed crystals are the (hhh) peaks indicating a preferred orientation of the seed crystals with the (111) faces of the octahedra parallel to the substrate surface. The seed crystals seem to be adsorbed with the (111) face of the octahedra facing the

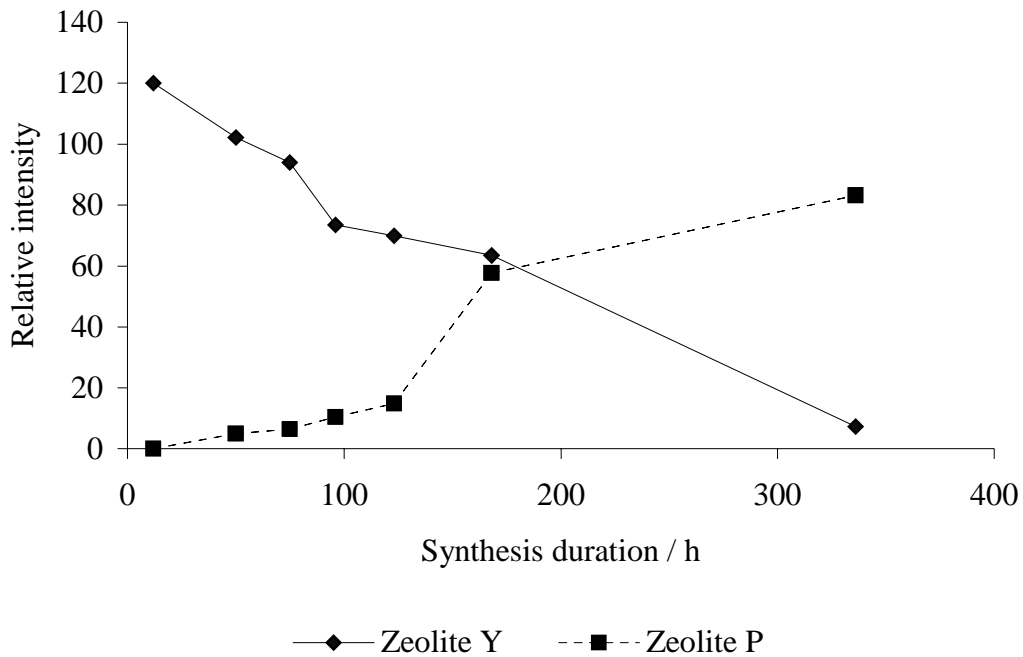


Figure 4. The fraction of Faujasite and zeolite P of the bulk product as a function of synthesis duration.

wafer. During film growth however, the orientation of the crystals becomes more random. This is the case for films grown in the lower part of the synthesis solution as well as in the upper part. A possible explanation for the change in orientation is a secondary nucleation taking place during film growth or attachment of crystals formed in the bulk of the synthesis gel onto the rough surface of the growing film.

SEM images of the surface of the films indicate competitive growth of the crystals constituting the films (see section 4.1.1 and 4.1.2), which suggests a development towards a preferred orientation. However (according to the results presented above) this is not the case, and further investigation is necessary to fully understand this contradiction.

4.2 ZSM-5 membranes (Paper II)

ZSM-5 membranes were prepared by seeding the porous support with colloidal seed crystals followed by growth of the seed crystals in a synthesis solution free of organic template molecules. Hence, a potentially detrimental calcination procedure was not necessary. The membranes were tested for the separation of butane isomers as well as for the selective removal of water from a helium-diluted vaporized water/ethanol azeotrope. ZSM-5 membranes prepared in a similar way have previously been under study by our group [16] as well as by Noack et al. [15]. Poor separation of the butane isomers was obtained. The results presented here will show that the poor selectivity in earlier work probably was due to blockage of the zeolite pores by adsorbed species at moderate temperatures. Furthermore, a deeper knowledge of the membrane properties was obtained by studying the separation behavior at higher temperature.

4.2.1 General characterization

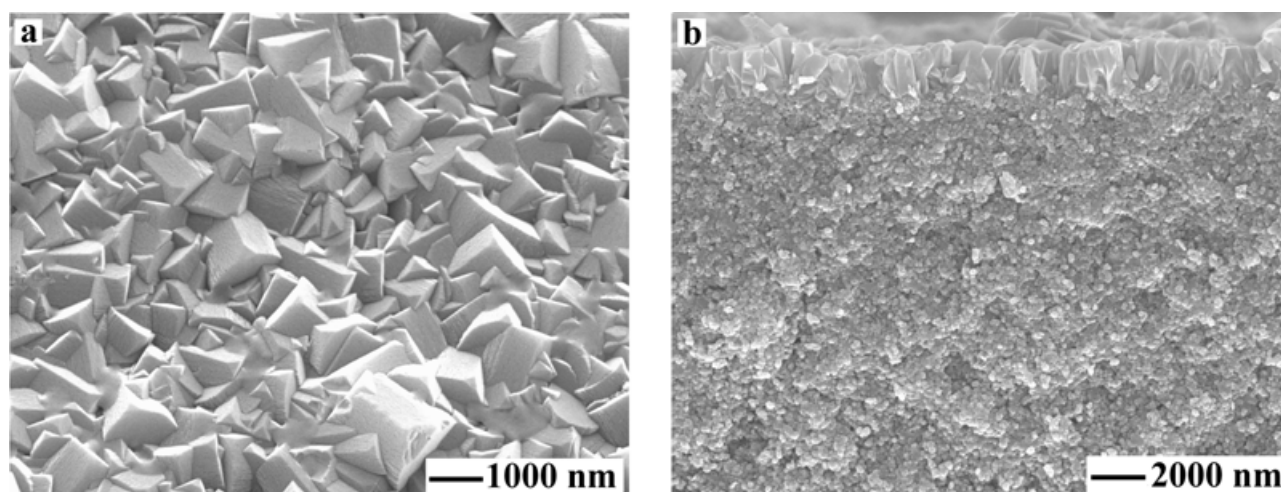


Figure 5. Top (a) and side (b) view SEM images of a ZSM-5 membrane.

Figure 5 (a, b) shows top and side view images of a ZSM-5 membrane. No pinholes or cracks could be found in the as-synthesized films. XRD patterns collected from the membranes prepared in this work, suggest a preferred orientation of the crystals constituting the membrane in accordance with findings previously reported [38]. 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 same result was obtained in previous work [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 zeolite.

4.2.2 Permeation measurements

4.2.2.1 Single gas permeation measurements

Table 1 gives a summary of the results for selected membranes prepared according to the same procedure. Thus, differences in permeation results are due to reproducibility difficulties. Even an extremely low permeance of SF₆ dramatically affects the N₂/SF₆ ratio since the permeance of N₂ also remains very low in these cases (see M1, M2, M4 and M6 in Table 1). Since the membranes investigated in this work were dried at a moderate temperature (100 °C, 12 h), most of the adsorbed molecules are expected to remain in the zeolite structure. These molecules block the pores of the zeolite, forcing most of the molecules to permeate through defects present in low quantities in the membrane. Hence, low gas permeations and ideal selectivities are obtained.

The effect of temperature on membrane stability was investigated by studying the permeance of SF₆ at different temperatures for a membrane. 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. 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 membrane after this test.

Sample	Permeance, $10^7 / (\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1})$				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*	>2000
M4	2.5	1.2	1.6	0.1	12
M5	1.2	0.62	0.7	<0.001*	>620
M6	3.2	1.2	1.6	0.1	12
M7	1.6	0.58	0.92	<0.001*	>580

* Lower than the detection limit

Table 1. Single gas permeation measurements for selected membranes. A transmembrane pressure difference of 4 bar was utilized.

4.2.2.2 Permeation of a 50/50 n-butane/i-butane mixture

Membranes with no measurable permeance of SF_6 in the single gas experiments (after drying at 100 °C), were selected for further tests. Figure 5 illustrates the n-butane/i-butane selectivity as a function of temperature for M3. In Run 1, the membrane was heated up to 80 °C after which permeation tests were performed up to 220 °C. Both the gas permeance and the selectivity were poor up to 160 °C (see Figure 6). Between 160 °C and 200 °C the selectivity increased dramatically to 17.8 (see Figure 6). The permeance increased for both n-butane and i-butane although the n-butane permeance increased much more, resulting in the higher selectivities. After keeping the membrane at 220 °C for 12 h, the temperature was reduced to 100 °C. Subsequently, new permeation measurements up to 400 °C were performed (Run 2). In Run 2 both the selectivity (compare Run 1 and Run 2 in Figure 6) and the n-butane

permeance were much higher than in Run 1 at 105 °C. 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 (see Figure 6) after which it decreased, mainly between 280 °C to 300 °C and between 380 °C and 400 °C. At

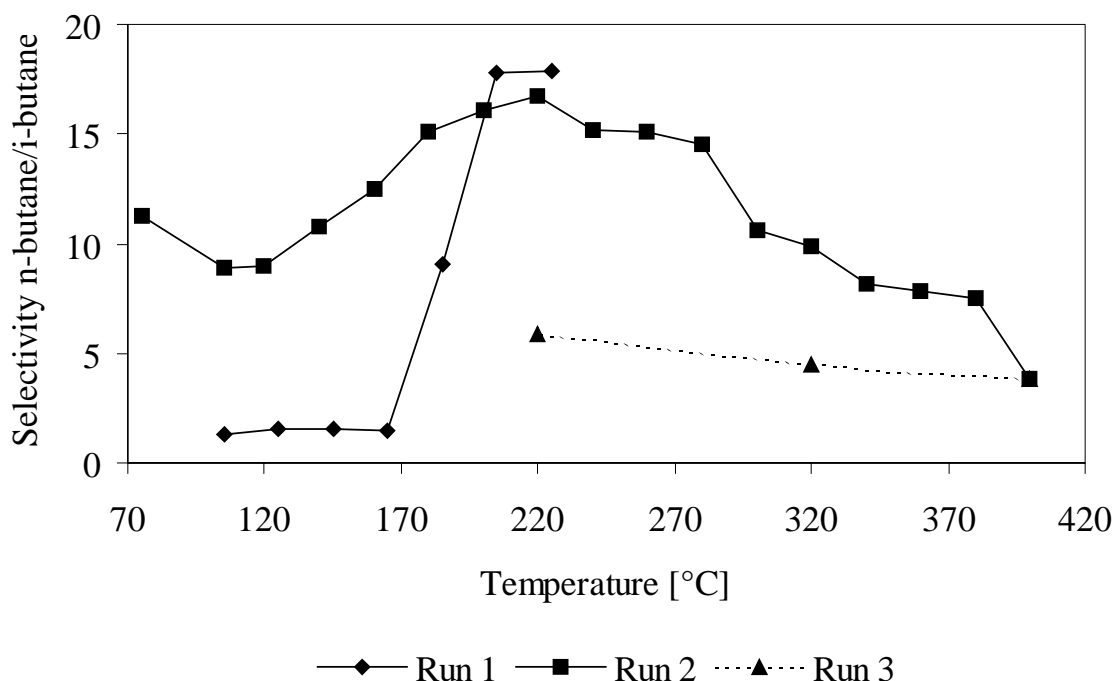


Figure 6. Selectivities for an 50/50 kPa n-butane/i-butane mixture for membrane M3 using helium as sweep gas.

these particular temperature intervals, defects were probably formed. At 400 °C the selectivity dropped to 3.8. Others have observed the existence of an optimal temperature for n-butane/i-butane selectivity for MFI membranes [56-57]. In order to confirm the crack formation during Run 2, new measurements were performed upon cooling back to 320 °C and 200 °C (Run 3 in Figure 6). When decreasing the temperature in Run 3 the high selectivities obtained in Run 2 were not regained. The permeation of both isomers was also much higher in Run 3 compared to Run 2. The

lower selectivities of Run 3 indicate that the molecules increasingly permeated through paths larger than the zeolite pores at higher temperatures and confirm that cracks formed during Run 2.

4.2.2.3 Permeation of a tertiary ethanol/water/He mixture

Figure 7 shows the selectivity for the separation of the water/ethanol azeotrope diluted with helium as a function of temperature. True separation was observed below

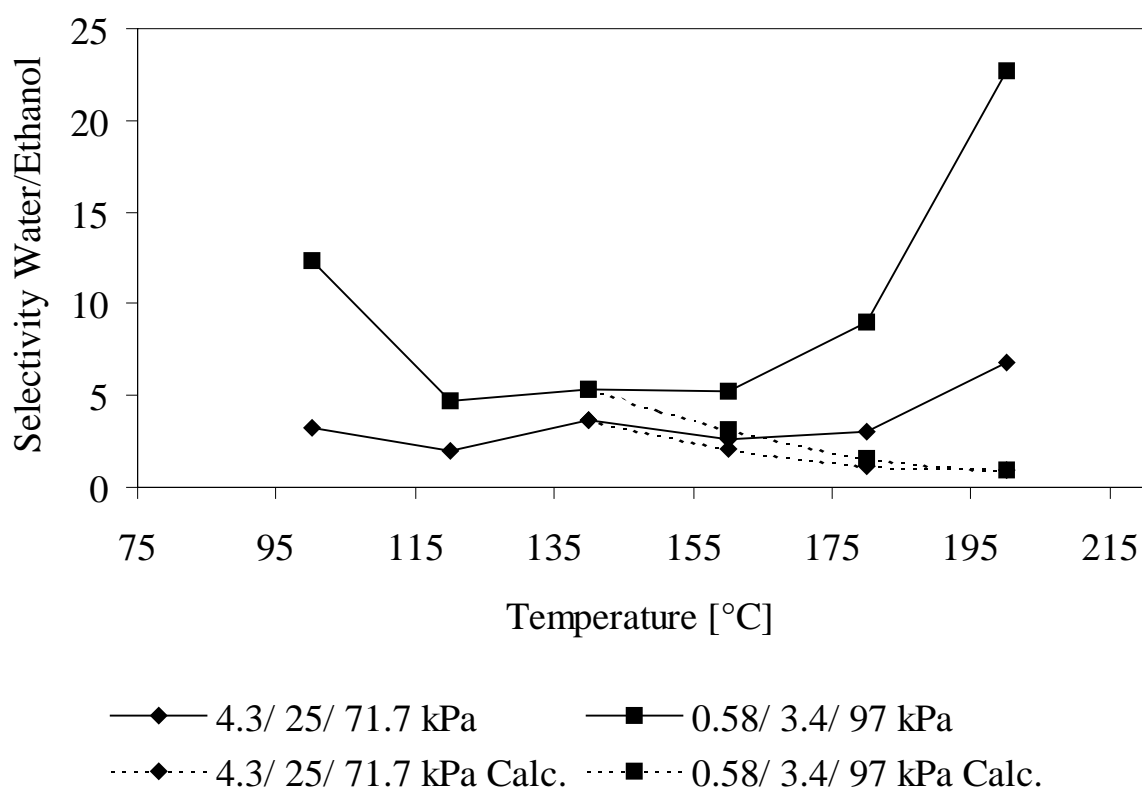


Figure 7. Separation selectivities for two different compositions of water/ethanol/helium mixtures. The dashed lines show the selectivities after compensating for products (ethylene, diethylether and water) formed by dehydration of ethanol catalysed by the membrane.

150 °C, whereas at higher temperatures it was found that the membrane catalyzed the dehydration of ethanol to form diethylether and ethylene. 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 °C 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 reaction. Lower selectivities were obtained for the less dilute (He) azeotrope mixture, see Figure 7.

4.3 Penetration of siliceous species in the porous support during membrane synthesis

During the synthesis of supported membranes, siliceous species may form within the pores of the membrane support and reduce the flux through the membrane and possibly increase the crack formation. Therefore, synthesis methods limiting the zeolite formation to a thin film on the support top surface is of interest. In paper II, ZSM-5 membranes were synthesized by the growth of seeds adsorbed on the substrate surface in a synthesis gel where no zeolite was formed in the absence of seeds. Thus, by controlling the location of the seeds, it should be possible to control the location of the film. Hence, the use of seed crystals too large to enter the porous support during seeding, would limit the film penetration depth. In order to investigate this hypothesis, the ZSM-5 membrane growth was performed by seeding the porous substrate with 60 and 120 nm silicalite-1 seeds, respectively. The average pore size of the porous support was 100 nm. Hence, the larger seed crystals should be too large to enter the pores of the substrate. Table 2 shows the results of the single gas permeation experiments (after drying at 100 °C or 12 h) as well as other relevant data for selected membranes synthesized using 60 and 120 nm seeds, respectively. utilization of 60 nm seeds is accompanied with a flux reduction, see Table 2. Moreover, according to side view SEM images, the growth of zeolite into the pores of the support is less when larger seeds were utilized.

Seed crystal size (nm)	Synthesis temperature (°C) and duration (h)	Permeance · 10 ⁷ / (mol / m ² · s · Pa)		
		H ₂	He	SF ₆
60	100, 12	0.36	0.21	<0.001*
60	100, 12	0.04	0.002	<0.001*
120	100, 12	3.9	1.9	<0.001*
120	100, 12	1.2	0.7	<0.001*

* Undetectable

Table 2. Results of single gas permeation experiments as well as relevant data for selected membranes synthesized using 60 and 120 nm seeds, respectively.

The results of the single gas permeation measurements clearly show that the

4.3.1. Penetration of siliceous species into the porous support during zeolite A membrane synthesis (III)

The effect of the synthesis conditions on the growth of zeolite into the pores of the support during membrane synthesis was investigated (III). Zeolite A seed crystals, with an average size of 140 nm as measured by DLS, were adsorbed on porous α -alumina supports in order to facilitate film growth according to the seed film method. No seed crystals could be found inside the top layer of the support since most of the seeds were larger than the pore openings.

4.3.1.1 Effect of synthesis temperature

Side view SEM images of Zeolite A membranes, with similar film thickness on top of the support, prepared using varying synthesis temperatures were compared. At a synthesis temperature of 50 °C, 75 °C and 100 °C, the support penetration is about 300, 1500 and 2700 nm respectively. Thus, the penetration at comparable film thickness on top of the support appears to be more effective if the synthesis is carried out at higher temperatures.

4.3.1.2. Effect of repeated synthesis

A repeated synthesis procedure was performed, where fresh synthesis gel was added periodically to the cooled and cleaned samples. A higher film growth rate was observed compared to the one-step synthesis approach. However, the growth rate of zeolite into the support was not increased utilizing the multi-step approach. This is demonstrated in Figure 8 (b, d) which shows side view SEM images of membranes synthesized for 6 and 9 h at 75 °C in two and three steps of 3 h. Membranes synthesized in one step with the same total synthesis duration is also shown in Figure 8 (a, c) for comparison. The films synthesized by a multi-step procedure are substantially thicker than the corresponding films synthesized in one step, while the penetration depth is essentially the same.

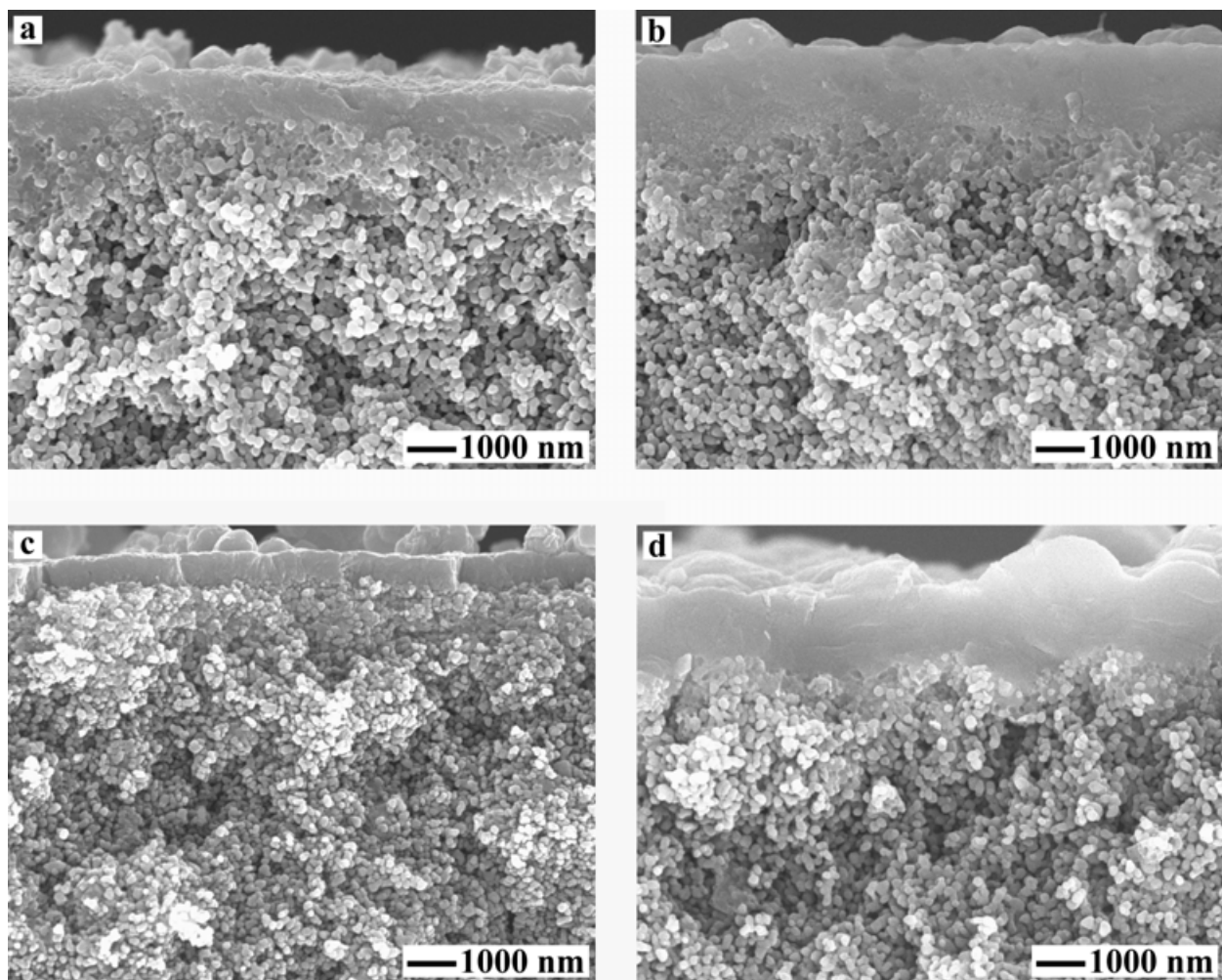


Figure 8. Side view SEM images of membranes synthesized for 6 and 9 h in one step (a, c) and in 2 and 3 steps (b, d) at 75 °C.

4.3.1.3 Single gas permeation experiments

The membranes were expected to be fully hydrated since they were dried at room temperature prior to the permeation measurements. Water molecules (and other species such as ammonium ions) are blocking the pores in the zeolite structure. Thus, the gases were expected to permeate through defects. A low or non detectable permeance is therefore an indication of a membrane with a low density of defects. Table 3 shows the results of the single gas permeation measurements, as well as relevant data, for a few membranes synthesized at 75 °C. The H₂/SF₆ ratio is low for all membranes

Synthesis time / h	Film thickness / nm	Penetration depth / nm	H ₂ permeance 10 ⁷ / (mol / m ² · s · Pa)	H ₂ /SF ₆
3	400	1440	20.8	3.0
6	500	1500	0.135	3.1
9	600	1200	126	5.3
3+3	1000	2300	0*	-
3+3+3	1700	1000	0*	-

* Undetectable

Table 3. The results of the single gas permeation measurements, as well as relevant data, for selected zeolite A membranes synthesized at 75 °C.

with a measurable gas flux. A much higher ratio would have been expected from a completely dry membrane since the H₂ permeance probably would be much higher and the SF₆ would remain low, since the large-sized SF₆ molecules are expected to permeate mainly through defects. Thus, the H₂/SF₆ ratio does not necessarily accurately represent the quality of a membrane that was not dried. A repeated synthesis procedure resulted in much lower gas permeation which indicates that these films are of higher quality than the films synthesized in one step.

In one experiment, the permeance of various gases (SF₆, N₂, He) through a

membrane (synthesized for 6 h at 100 °C in S1) was measured as a function of drying temperature up to 50 °C. A rapid increase in the permeance of all gases was observed. The obtained selectivities are similar to those expected for a Knudsen type flow through the membrane, which clearly indicates that defects were formed in the membrane during drying. Furthermore, membranes synthesized by a multi-step procedure show an equally high sensitivity to increased temperatures.

5. CONCLUSIONS

A method comprised of seeding the support with colloidal seed crystals followed by growth of the seeds into a dense film was used to prepare thin films of FAU type zeolite, ZSM-5 and zeolite A. The organic template molecules present in the seed crystal were removed prior to film growth by either ion exchange (FAU-type zeolite) or calcination (ZSM-5 and zeolite A). The film growth was conducted under hydrothermal conditions in the absence of organic template molecules, which resulted in template free zeolite films. Hence, no potentially detrimental calcination procedure was necessary to render the zeolite structure microporous. The thickness of the FAU-type zeolite could be controlled by varying the synthesis temperature and duration. However, a maximum of the film thickness was found. Prolonged hydrothermal treatment caused the film thickness to decrease due to the transformation of FAU into zeolite P. ZSM-5 films were tested as membranes in the separation of the butane isomers with successful results. Furthermore, the ZSM-5 membranes were found to be catalytically active, converting ethanol into diethylether and ethylene. The filter penetration depth of silicious species in the porous support during zeolite NaA membrane synthesis was examined. Higher temperatures of synthesis resulted in a deeper penetration. By using a multi step synthesis procedure at low temperature, thicker films with less penetration were grown. Furthermore, according to single gas permeation data, the films synthesized in several steps were of higher quality.

6. RECOMMENDATION FOR FUTURE WORK

Additional experiments will be dedicated to further optimize the synthesis conditions for the preparation of high quality membranes of the zeolite types discussed in the present thesis as well as other types of zeolites. An important part the work will be to study the affect of the synthesis conditions on the behavior of the membrane during drying/heating. Permeation measurements as well as SEM are techniques suitable for this purpose. A further objective is to study the structure and microstructure modifications of various zeolite films *in situ* at high temperature by means of real time XRPD. The heat sensitivity of the membranes prepared in this work might be due to the intergrowth of the zeolite with support pores. This hypothesis should be investigated further, possibly by means of recently developed masking techniques [58]. The nature of the formed zeolite as well as the orientation of the crystals constituting the films/membranes are expected to result in differences in permeation properties. Therefore, a deeper knowledge of these topics is of interest. For example, the reason for the change in orientation during film growth in the case of faujasite may be investigated by grazing incidence x-ray diffraction.

7. ACKNOWLEDGMENTS

First of all, I would like to thank Professor Johan Sterte for giving me the opportunity to work in his group. Also, his ideas and advise were of great help during this work. I thank my supervisor, Dr. Jonas Hedlund, for the discussions and all practical help that made this work possible. I am grateful to Mr. Fredrik Jareman for our co-laboration and also for his fellowship in the lab. I hope we will continue to work together in the future. I thank Dr. Derek Creaser for being the "always on call" english dictionary, and also for his insightful suggestions regarding the work. I am grateful to our Secretary Ingrid Granberg for all the administrative help, and also for all the nice chats. What would we do without you? I would like to thank Dr. Lubomira Tosheva and Ms. Vania Engström, for always taking the time to help me, both at work and in private. Thank you for being such good friends. I thank Mr. Zheng Wang, Mr. Olov Öhrman, Mr. Olle Niemi and Mr. Valeri Naidenov for their companionship. I appreciated the interesting discussions with Mrs. Margareta Lidström-Larsson, and hope that we will continue to have them in the future. Her opinions were always appreciated. A special thank to my "big sister" Mrs. Qinghua Li, for her encouragement and support. In her, I have a true friend for life. For all my other colleagues at the department, I hope we will have a nice future together. Financial support from the Swedish Research council for Engineering Sciences (TFR) is acknowledged.

I am deeply indebted to my parents who always encourage and support me in everything I do.

Finally, I would like to dedicate this work to my family Ania and Alessandro because you are the light of my life, bringing me happiness and unconditional love.

Magdalena Lassinantti

March 2001

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