

# Properties of Molecular Sieve Membranes

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## Abstract

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Zeolites are crystalline aluminosilicates with molecular sieving properties and are widely used in industry for catalysis, sorption and ion-exchange applications. Zeolite membranes are commercially interesting since this technology may be employed for continuous separation of molecules under severe conditions. MFI zeolite has suitable pore diameter for many applications and relatively high thermal and chemical stability. Zeolite films in membranes must be thin, to obtain a high flux and free from defects for high selectivity. Many parameters are affecting the properties of zeolite films and in this thesis some of them are investigated. MFI zeolite membranes were prepared using seed crystals and hydrothermal synthesis and characterized with scanning electron microscopy, single gas permeation measurements, porosimetry and separation experiments. Membranes grown in one or several steps with seeding in-between the synthesis steps were compared. It was observed that membranes comprised of small crystals and consequently high concentration of grain boundaries had low separation performance. Grain boundaries could also be opened by extensive rinsing, which reduced membrane quality. The influence of the calcination rate on the performance of zeolite membranes of a particular type was also studied. It was demonstrated that the calcination rate does not affect the membrane quality.

## List of papers

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- I Silicalite-1 membranes with small crystal size**, Charlotte Andersson, Jonas Hedlund, Fredrik Jareman, Proceedings: 14<sup>th</sup> International Zeolite conference, ISBN: 0958-46636-X, 626 (2004)
- II The influence of calcination rate on Silicalite-1 membranes**, Fredrik Jareman, Charlotte Andersson, Jonas Hedlund, Microporous and Mesoporous Materials, In press
- III Open grain boundaries in Silicalite-1 membranes by exposure to liquids**, Charlotte Andersson, Fredrik Jareman, Jonas Hedlund, Manuscript in preparation
- IV Factors affecting the performance of MFI membranes**, Jonas Hedlund, Fredrik Jareman, Charlotte Andersson, Proceedings: 14<sup>th</sup> International Zeolite conference, ISBN: 0958-46636-X, 640 (2004)

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# **1 Introduction**

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## **1.1 Background**

Zeolites are porous crystalline aluminosilicates and are widely used in applications such as catalyst in the refining of petroleum or as ion exchangers in detergents. Zeolite membranes are commercially interesting due to the potential ability to separate molecules in continuous processes in industry. Advantages compared to other membrane types are the well-defined pores and the thermal and chemical stability. Zeolite films in membranes must be thin for high flux and free from defects for high selectivity. To achieve thin and defect free films, parameters controlling the properties of zeolite membranes must be understood.

## **1.2 Scope of present work**

In the present work, the influence of various parameters on quality of MFI membranes was studied. The effect of grain boundaries was investigated by comparing membranes with small crystal size and high concentration of grain boundaries with membranes with the same film thickness but with larger crystals and lower concentration of grain boundaries. Grain boundaries was also opened by long exposure to various aqueous solutions. The influence of heating rate during calcination of membranes was also studied. The effect of film thickness and preferred orientation was also evaluated to some extent.

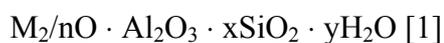
## 2 Literature survey

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### 2.1 Molecular sieves and zeolites

#### 2.1.1 General description of molecular sieves and zeolites

A molecular sieve is a material that can separate molecules based on size and shape. A subgroup of molecular sieves is zeolites. These minerals are natural and synthetic microporous aluminosilicates. The Swede Cronstedt discovered this new class of minerals in the 18 century and named it “zeolites” from the Greek word “zeo” and “litos” which means a boiling stone [1]. The zeolite framework is a three-dimensional network of oxygen ions with either  $\text{Si}^{4+}$  or  $\text{Al}^{3+}$  situated in the tetrahedral sites. This framework may be described with the following formula:



M: exchangeable cations for example  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$

n: cation valance

y: degree of hydration

All known zeolite frameworks have been assigned with a three-letter code. Today there are 133 known framework structures [2]. For a given framework, the chemical composition can be varied significantly by varying Si/Al ratio and cations. Zeolites can also be classified after the dimension of their pore openings, ranging from 3 to 13 Å with the exact pore size depending on the framework structure [2]. Two commonly used zeolites and some of their commercial applications are listed in Table 1.

Zeolite	Zeolite A	Zeolite X
Framework code	LTA	FAU
Applications	Industrial gas drying Separation of branched- and straight hydrocarbons Stabilization of beer.	Industrial gas drying CO <sub>2</sub> -CH <sub>4</sub> separation from landfill gas Elimination of fatty acids in comestible oils

*Table 1. Two common zeolites and some of their applications[2].*

Zeolites are commonly prepared by hydrothermal treatment in a synthesis mixture. The synthesis mixture mostly contains; water, a silica source, an alumina source and a templating agent. The synthesis mixture is heated and the composition of the synthesis solution, synthesis time and synthesis temperature determines which zeolite that will crystallize. Zeolite crystals, films and membranes are often rinsed in some media to remove residues from the synthesis mixture. Common rinsing medias are water [3] and aqueous solutions of ammonia [4]. Finally the zeolite is calcined, a procedure where the zeolite is heated in air to decompose and burn the templating agent that is blocking the pores.

### **2.1.2 Acid and alkaline treatment of zeolites.**

Zeolites may be modified with various post treatments, which often comprise acid or base treatment. In acid dealumination, alumina is removed from the zeolite framework with an acid, such as hydrochloric acid, to influence the catalytic properties [5]. The removal of silicon from MFI zeolites in alkaline solutions was first performed to study the changes in the crystal when in contact with an alkaline media [6]. Ogura et al [7] and Okuhara et al [8] suggested that micropores were created in the amorphous phase at the grain boundaries upon alkaline treatment. Groen et al [9] reported an increased intracrystalline mesoporosity when treating the MFI structure with alkaline medias.

## 2.2 Zeolite membranes

Zeolite films have large potential in many application areas such as sensors, catalyst and membranes [10]. Zeolite membranes are very interesting due to high thermal stability and resistance towards solvents [11]. A zeolite membrane is a self-supported or a supported zeolite film. For mechanical stability self supported films must be relatively thick, which results in low flux. In most reported works supported films were grown on porous  $\alpha$  and  $\gamma$  alumina [3,4,12] but films on other supports such as porous stainless steel [10] have also been reported.

There are basically three different methods to prepare supported zeolite films; in-situ crystallisation, vapour transport method and the seeding technique or secondary growth. In in-situ crystallisation zeolite crystals nucleate and grow directly on the support [13]. In the vapor transport method the support is coated with a aluminosilicate gel and subsequently hydrothermally treated in a vapor containing a template molecule in order to transform the gel into a film [14]. In the seeding techniques, seeds are attached to a support and subsequently grown under hydrothermal treatment. Several methods to attach seeds to a support have been reported [4,15,16].

Separation in zeolite membranes can occur by three different mechanisms, see Figure 1. One mechanism is sieving, larger molecules are excluded from the pores due to their size, while smaller molecules can diffuse through the pores. Another mechanism is adsorption resulting in high concentration on the surface of strongly adsorbing molecules, leading to effective transport of these molecules through the membrane. The third mechanism rely on differences in diffusion rates, molecules with high diffusivity may be separated from slower diffusing molecules.

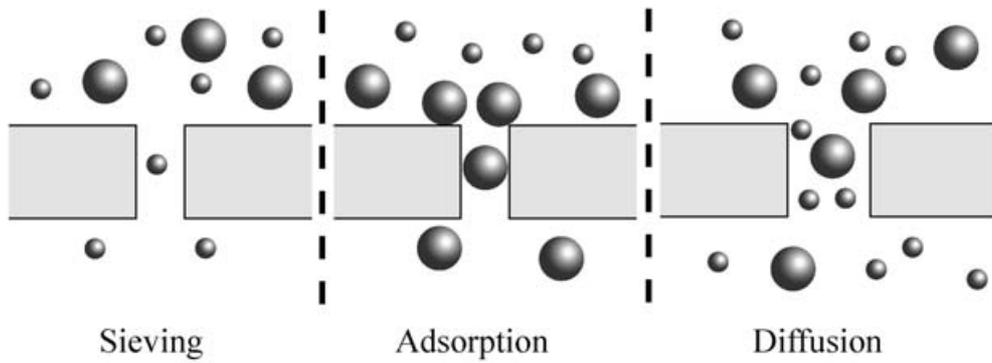


Figure 1. Three mechanisms for separation in a zeolite film.

### 2.3 MFI- membranes

Figure 2 shows the MFI structure, which is suitable in membrane applications due to suitable pore diameter and a relatively high thermal and chemical stability [11].

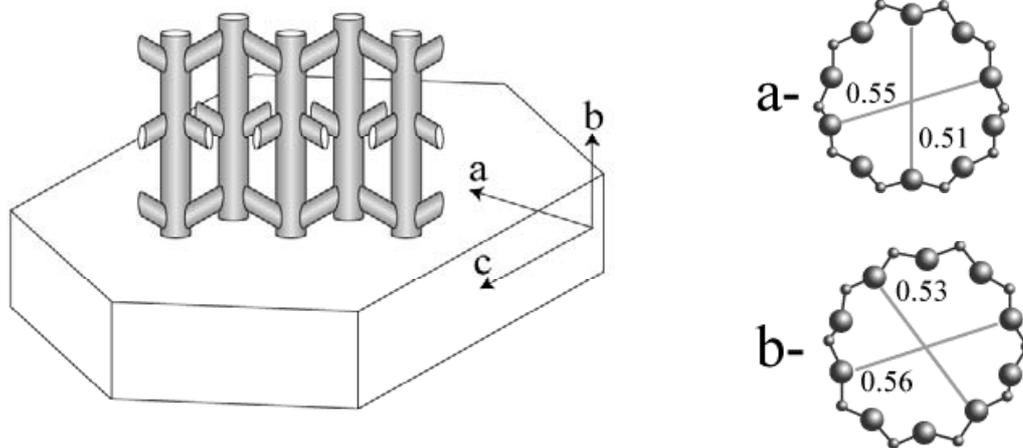


Figure 2. The MFI structure.

The pores running in the b-direction are straight and zigzag pores are running in the a-direction. The pore size is different in the two directions. The molecular sieves ZSM-5 and silicalite-1, have MFI structure. Silicalite-1 is all silica and ZSM-5 has Si/Al ratio down to 10 [1]. This work is confined to silicalite-1

membranes. Since silicalite-1 does not contain any alumina it is strictly speaking not a zeolite, but it will be referred to as a zeolite in this work.

## **2.4 Properties of MFI membranes**

### **2.4.1 Preferred orientation**

Since the pore geometry is different in the a- and b- direction the mass transport will also be different [11] and the orientation of the crystals in the film will affect the separation performance. It has been reported [17,18] that the preferred orientation in MFI - films grown by the seed film method depends on film thickness, seed size, seeding density and hydrothermal treatment conditions. Thicker films grown in a clear solution were a-oriented, while thick films grown in a template free synthesis mixture were oriented with the c- axis tilted  $13^\circ$  from the normal to the surface. Thin films were almost randomly oriented. Lai et al [19] enhanced the growth rate in the b-direction by changing the templating agent and prepared a b-oriented membrane.

### **2.4.2 Defects**

A virtually defect free film is essential to obtain high selectivity for zeolite membranes, since the diffusivity is much higher in the defects compared to the zeolite pores [20]. Defects in zeolite films are:

- Cracks
- Open grain boundaries
- Non closed films.

Pores with varying widths are defined by IUPAC as follows [21]:

- Micropores  $d_p < 2$  nm
- Mesopores  $2\text{nm} < d_p < 50$  nm
- Macropores  $d_p > 50$  nm

In zeolite membranes, defects may thus be in the form of micro meso or macropores.

### **2.4.3 Open grain boundaries**

It is believed that Knudsen diffusion prevails [20] in mesopores. Knudsen diffusivity is much larger and often not as selective as diffusivity in zeolite pores. Defective zeolite membranes should thus have high permeance and low selectivity. Lin et al [22] proposed a microstructural model, with microporous non-selective intercrystalline pores, which was assumed to be open grain boundaries, to explain the low observed xylene mixture separation factor. Lai et al [19] speculated that the observed high selectivity in their b- oriented membranes was due to a decreased amount of open grain boundaries.

### **2.4.4 Thermal expansion**

In 1995 Geus et al [23] showed that the zeolite lattice shrinks during template removal and expands upon cooling and that the calcined unit cell is smaller at room temperature compared to the unit cell in the as-synthesized zeolite. In 1997 den Exter et al [24] reported that MFI zeolite contracts in the a- and the c- direction but expands in the b-direction, when the template molecule is removed. Dong et al [3] studied the microstructural development in a MFI membrane during calcination. It was reported that intercrystalline openings in MFI membranes may increase upon removal of the templating agent due to the shrinkage of the zeolite. Dong also speculated that with a too strong chemical bond between support and zeolite, severe stress, which can cause cracks, may be induced in the film due to difference in thermal expansion between zeolite film and support.

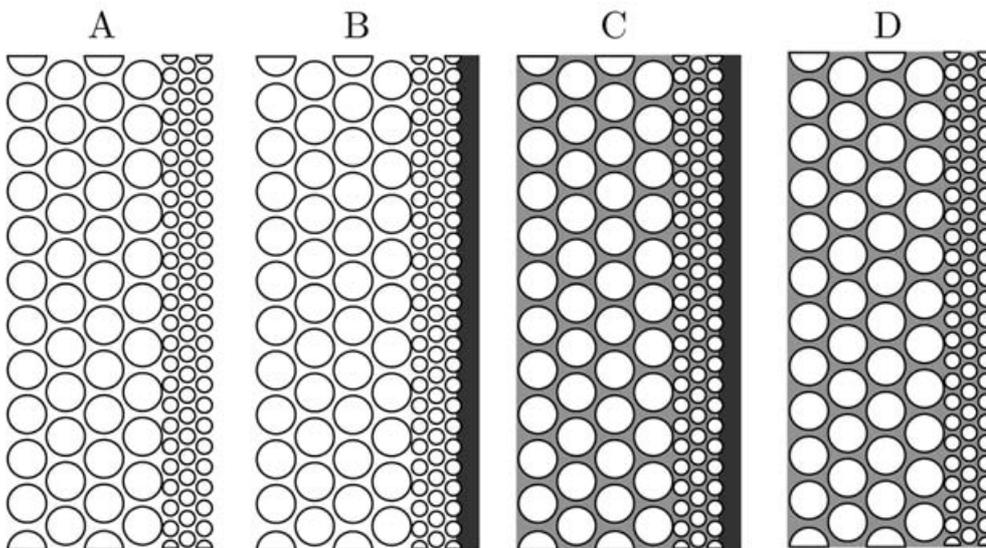
## 3 Experimental

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### 3.1 Membrane preparation

In this work thin supported silicalite-1 films were prepared on porous  $\alpha$ -alumina discs with a diameter of 25 mm. The discs are comprised of two layers, a top layer with a thickness of 30  $\mu\text{m}$  with 100nm pores and 3 mm thick layer with 3  $\mu\text{m}$  pores.

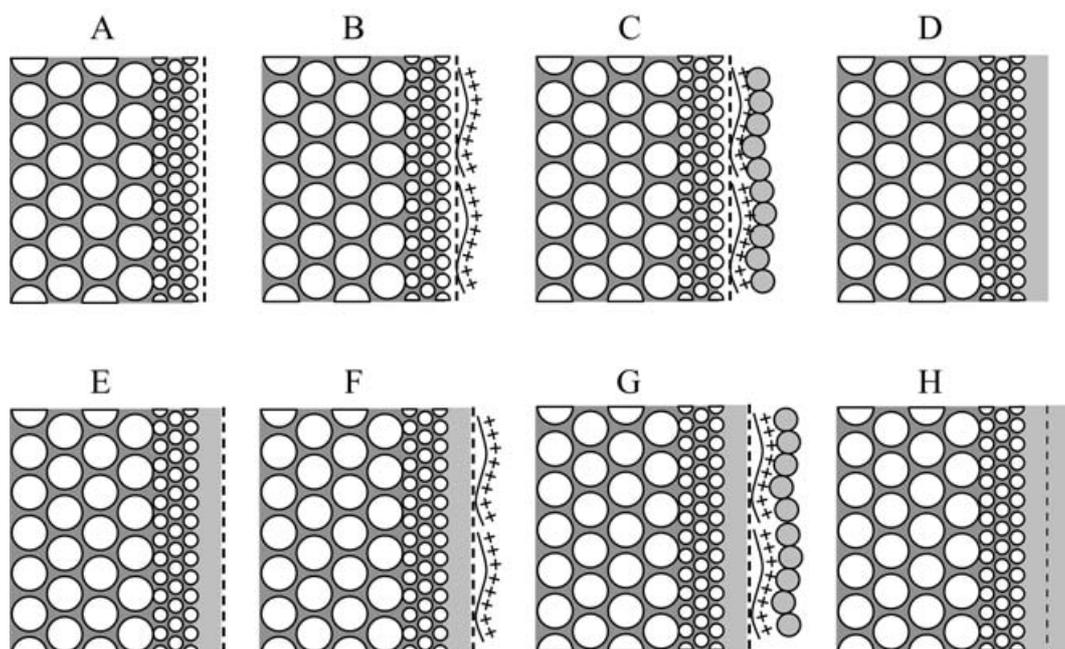
In order to prevent zeolite from growing in the support pores during synthesis, a masking procedure was employed [4,25], see Figure 3. The top surface of the support (A) is first coated with a thin PMMA layer (B). The support is subsequently impregnated with molten polyethylene wax (C). The protective PMMA layer is dissolved in acetone, leaving a free surface for film preparation (D).



*Figure 3. Masking procedure.*

Films were prepared with the seed film method [4], see Figure 4. The support was first treated with a cationic polymer solution (B), to obtain a positive surface charge. Silicalite-1 seeds with a diameter of 60 nm were then electrostatically

adsorbed on the surface of the support (C). Films were subsequently grown under hydrothermal treatment in a synthesis solution with the molar composition 3TPAOH:25SiO<sub>2</sub>:1500H<sub>2</sub>O:100EtOH (D). The synthesis vessel was heated by an oil bath at 100°C and connected to a reflux condenser. In this work, 36 and 30 hours of hydrothermal treatment were used to obtain a film thickness of about 500 nm. For films with a thickness of about 1 μm, 96 hours was used. After synthesis, the membranes were rinsed in a 0,1 M ammonia solution for 24 hours to remove synthesis mixture. The effect of various rinsing medias and rinsing time was investigated in paper III.



*Figure 4. Seed film method and multi seeding.*

To prepare membranes with small crystal size and high concentration of grain boundaries, the seed film method was developed further (Paper I), by employing multi-seeding, see Figure 4 (E-H). After a short hydrothermal treatment of 12 hours, a second layer of cationic polymer and seeds were applied (F-G). The membrane was subsequently hydrothermally treated for 12 hours and seeded, until the desired film thickness was achieved. After each hydrothermal treatment, the

membranes were rinsed for approximately 12 hours in a 0.1 M ammonia solution. After the final rinsing, all membranes were calcined to decompose the templating agent and to remove wax in the pores of the support. Most membranes were calcined for 6 hours at 500 °C with a heating rate of 0.2 °C/min and 0.3 °C/min cooling rate. The effect of varying heating and cooling rates was investigated and reported in paper II.

## **3.2 Characterization**

### **3.2.1 General characterization**

All membranes were investigated with scanning electron microscopy, using a Philips XL 30 with a LaB<sub>6</sub> filament. For the elemental analysis (EDS) an Oxford Instruments energy dispersive X-ray detector with a Ge crystal was used. Samples were mounted on alumina stubs with conductive carbon cement, to obtain side view images the membranes were cut in halves. To render the samples conductive they were sputtered in gold before the investigation.

### **3.2.2 Permeation measurement**

Single gas permeance measurements using He, H<sub>2</sub>, N<sub>2</sub> and SF<sub>6</sub> were carried out on all membranes directly after calcination. The membrane was mounted in a stainless steel cell and a gas at given pressure was fed to the cell. The permeance was calculated from the measured flow.

Porosimetry [4,26] was used to investigate the quality of the membranes. In this technique, the permeance of helium is measured as function of the partial pressure of a hydrocarbon, such as n-hexane and p-xylene. The measurement starts with a dry membrane, helium will permeate through zeolite pores and defects. The partial pressure of the hydrocarbon is subsequently increased and

larger and larger pores will be blocked in the zeolite film, which will reduce the helium permeance.

The membrane was mounted in a stainless steel cell and then heated to 300°C overnight in a flow of pure helium in order to remove adsorbed species. After drying, the cell was cooled to room temperature. The pressure, the temperature of the cell, the flow and the time was recorded for each activity of hydrocarbon. The Horvath-Kawazoe equation can be used to relate the width  $d_i$  for micropores to the partial pressure of the hydrocarbon  $P/P_0$  [27]. The Kelvin equation can be used for mesopores.

The Horvath- Kawazoe equation is written as:

$$RT \ln\left(\frac{P}{P_0}\right) = \frac{\Delta H_{Ads}}{(d - d_0)} \left[ \frac{\sigma^{10}}{9d_0^9} - \frac{\sigma^4}{3d_0^3} - \frac{\sigma^{10}}{9(2d - d_0)^9} + \frac{\sigma^4}{3(2d - d_0)^3} \right] \quad (1)$$

$$d_i = 2d - d_s \quad d_0 = \frac{d_s + d_a}{2}$$

$d_s$  = diameter of a surface atom in the zeolite pores,  $d_a$  = diameter of the hydrocarbon molecule  
 $d$  = slit pore half width,  $\sigma$  = zero interaction energy

The Kelvin equation is written as

$$d_i = \frac{-2\gamma V_m}{RT \ln(P/P_0)} \quad (2)$$

$\gamma$  = surface tension,  $V_m$  = molar volume

Each partial pressure can thus be related to a pore/defect size as shown for n-hexane in Table 2.

$P/P_0$	0.01	0.025	0.25	0.85	0.99
$d_i$ (nm)	1.08	1.27	2.65	9.18	100

Table 2. Relative partial pressure of n- hexane used in the porosimetry experiment and the corresponding pore diameter [27].

So at a relative pressure of n-hexane of 0.01, i.e. at the first point with n-hexane in the feed, all pores smaller than 1.1 nm are blocked according to equation (1) [27]. At a relative pressure of 0.025, pores smaller than 2.65 nm are blocked according to equation (2) [27].

For separation experiments the membrane was mounted in a cell in a furnace. The driving force for diffusion was a partial pressure gradient across the membrane that was maintained by a sweep gas at the permeate side. A gas chromatograph (GC) equipped with a FID (Flame Ionisation Detector) was used to analyse the composition on both sides of the membrane. From the composition and total flow it is possible to calculate the permeance and the separation factor  $\alpha$ :

$$\alpha = \frac{(x_i/x_j)_{Permeate}}{(x_i/x_j)_{Feed}}$$

$x_i, x_j$ ; molar fractions of the two components  $i$  and  $j$  in the mixture .

Separation of three hydrocarbon isomer mixtures were studied; n-/iso-butane, n-hexane/DMB and p-/o-xylene, at varying temperatures, under similar conditions as described elsewhere [4].



## 4 Results and discussion

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### 4.1 Physical properties

In this thesis, a number of types of silicalite-1 membranes were prepared by varying fabrication procedures. Table 3 shows sample codes and preparation procedures.

Membrane	Preparation method
M36h	Grown in one step with 36h hydrothermal treatment
M96h	Grown in one step with 96h hydrothermal treatment
M1	One seeding followed by 12 hydrothermal treatment
M2	As M1, but 2 seedings and hydrothermal treatments
M3	As M1, but 3 seedings and hydrothermal treatments
M4	As M1, but 4 seedings and hydrothermal treatments
M5	As M1, but 5 seedings and hydrothermal treatments
	Grown in one step with 36h hydrothermal treatment rinsed either for 24 hours, $X=1$ or 30 days, $X=30$ in
EX	Ethanol
WX	Distilled water
HX	0.1M aqueous solution of HCl
AX	0.1M aqueous solution of NH <sub>3</sub>
TX	0.1M aqueous solution of TPAOH
SX	0.1M aqueous solution of NaOH
	Grown in one step with 36h hydrothermal treatment -, calcined with a heating rate of -
X=0.2	0.2 °C/min
X=1.0	1.0 °C /min
X=2.0	2.0 °C /min
X=5.0	5.0 °C /min
R.M	Reference membrane 500nm thick [4]

*Table 3. Sample codes and preparation procedures.*

#### 4.1.1 SEM investigation

Figure 5 a) shows sample M36h and M96h is shown in b). The films are approximately 500 and 1100 nm thick and a columnar structure of the crystals can be seen in the thicker film. Figure 5 c) and d) shows membranes, M2 and M5, respectively, prepared with the multi-seeding method (paper I).

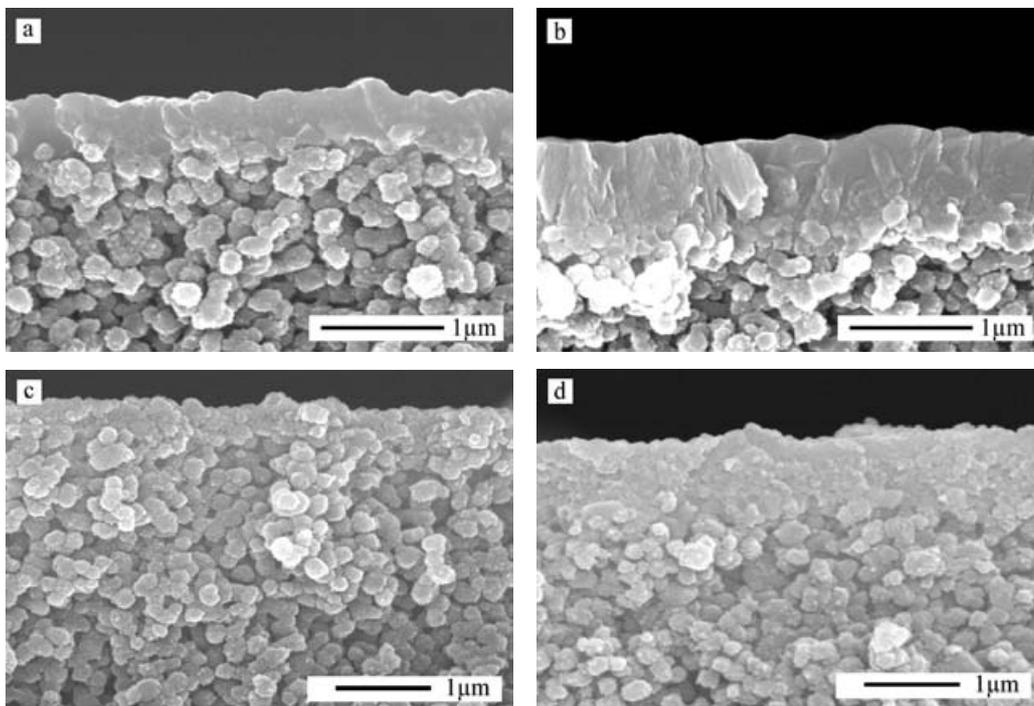


Figure 5. Side view of a) M36h b) M96h, c) M2 and d) M5.

The film in M2 is about 300 nm thick and about 800 nm in M5. The films in the latter two membranes are comprised of small crystals, with high concentration of grain boundaries, independent of film thickness, and the columnar structure observed for films grown in one step is absent.

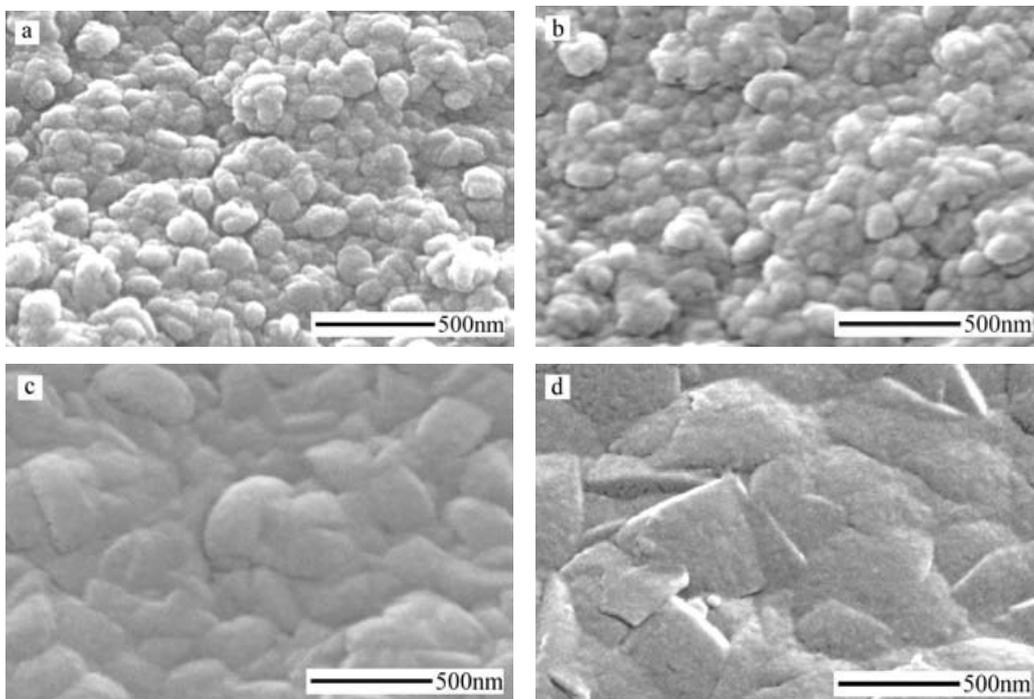
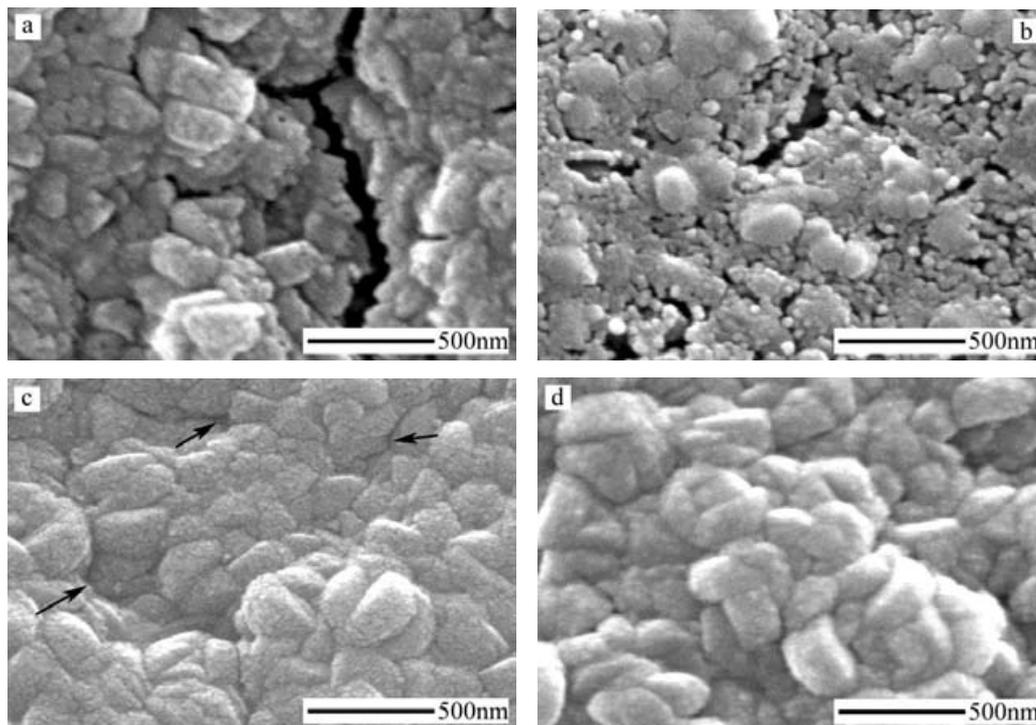


Figure 6. Surface view of a) M2, b) M5, c) M36h d) M96h.

Figure 6 a) and b) show membranes prepared with multi-seeding. Even though there is a difference in film thickness of 500 nm between these two membranes, the top surfaces of the membranes appear identical. Membranes M1, M3 and M4 had similar appearance. In contrast, a clear difference is observed in top view images of M36h and M96h, see c) and d). The crystals in the thicker film are almost twice as large as the ones in the thinner film. For films in membranes grown in one step, crystal size is increasing with film thickness.

Figure 7 shows membranes rinsed in different medias (paper III). The silicalite-1 films were originally approximately 500nm thick. The as-synthesis membranes were rinsed in ethanol, distilled water, or 0.1 M aqueous solutions of hydrochloric acid, ammonia, TPAOH, or sodium hydroxide, see Table 3. Figure 7 shows membranes S1 a), S30 b), A30, c) and E30 d). The membranes rinsed in sodium hydroxide dissolve rapidly. Features that may be relatively large open

grain boundaries in sample A30 are indicated with arrows in Figure 7c. Figure 7 d) shows E30.



*Figure 7. Surface view of membranes a) S1, b) S30, c) A30 and d) E30.*

Figure 8 shows side view images of A30 and E30. A30 has a film thickness of about 350 nm while E30 in 8 b) is about 400 nm and a similar film thickness was observed for membranes rinsed in other medias not shown here. It seems as the film in A30 is thinner than the as synthesised sample and also thinner than E30. A XRD investigation will be carried out in order to determine the average film thickness on each sample accurately.

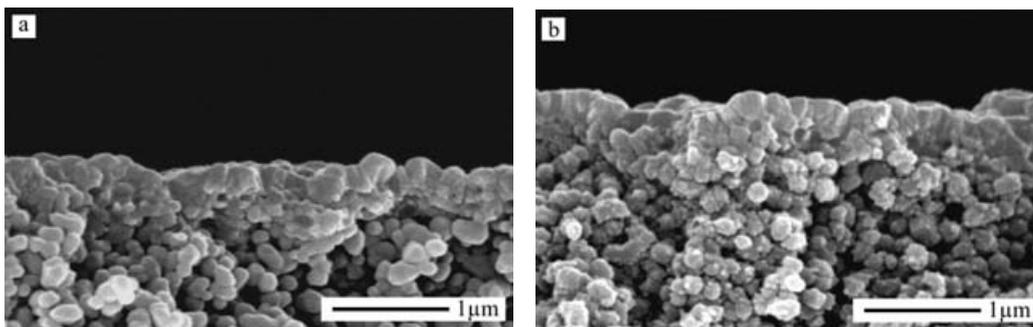


Figure 8. Side view images of a) A30 and b) E30.

#### 4.1.2 EDS investigation

Figure 9 shows EDS data for S1 and S30. It shows that S30 contains oxygen, sodium and aluminum and very little silicon, which indicates that the zeolite film was completely dissolved. A strong silicon signal was detected for S1, which indicates that this sample still has a silicalite-1 film. The planned XRD investigation will provide additional information.

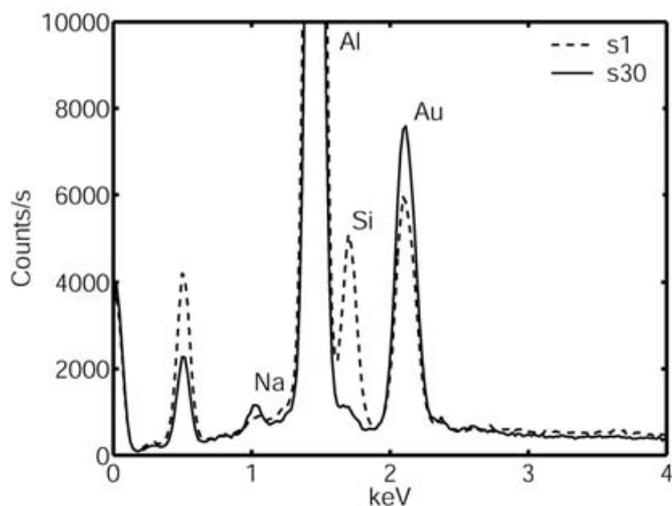


Figure 9. EDS analysis of S1 and S30.

## 4.2 Permeation properties

### 4.2.1 Effect of grain boundaries

As pointed out by Caro et al. [11,20], grain boundaries will influence the permeation properties of zeolite membranes. In order to investigate this, a multi-seeding method was developed in the present work and used to grow silicalite-1 membranes with small crystals (paper I). Membranes with one up to five repeated seedings and hydrothermal treatments were prepared. Membranes M36h and M96h grown in one step were compared with M1-M5 grown in several steps. Figure 10 a) shows porosimetry data for M1 to M5 and b) for M3, M4 and M36h.

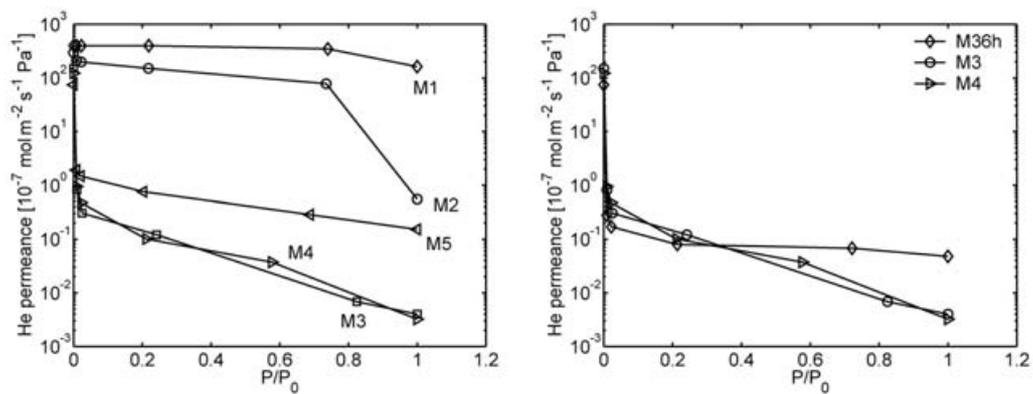


Figure 10. Porosimetry data for M1-M5 (grown in several steps) and M36h.

Figure 10 a) shows that M1 and M2 were of low quality; probably due to that the films were not closed yet. M5 had somewhat higher quality and M3 and M4 were virtually defect-free. Figure 10 b) shows that M3 and M4 are of similar quality as M36 h. The SEM investigation showed that the thickness of the films in these three membranes was similar, see paper I for more details.

Membrane		M3	One step
	T (°C)	$\alpha$	$\alpha$
n-/iso-butane	25	0.7	9
n-hexane/DMB	390	11	227
p-/o-xylene	390	1.4	16

*Table 4. Separation data for M3 and a membrane grown in one step [4].*

M3 was also characterised by separation tests. It was found that M3 had much lower separation factors than a membrane with similar film thickness grown in one step, see Table 4. The conclusion from these results is that the crystal size and hence the amount of grain boundaries is affecting the performance of MFI membranes.

The effect of prolonged exposure of MFI membranes to liquids was evaluated and reported in paper III. After completed hydrothermal synthesis, TPA-silicalite-1 membranes were rinsed in six different medias for 24 hours or 30 days. The medias were ethanol, distilled water, and 0.1 M aqueous solutions of hydrochloric acid, ammonia, TPAOH, and sodium hydroxide. Figure 11 a) shows average porosimetry data for two membranes rinsed for 24 h in various medias and average data for ten reference membranes rinsed for 24 h in a 0.1 M ammonia solution. After 24 hours, only sodium hydroxide reduced membrane quality, membranes rinsed in other medias maintained high quality. Figure 11 b) shows average data for two membranes rinsed for 30 days in various medias. The two membranes rinsed in ethanol still had the same high quality and the quality of the membranes decreased in the order E30, H30, T30, W30, A30, S30.

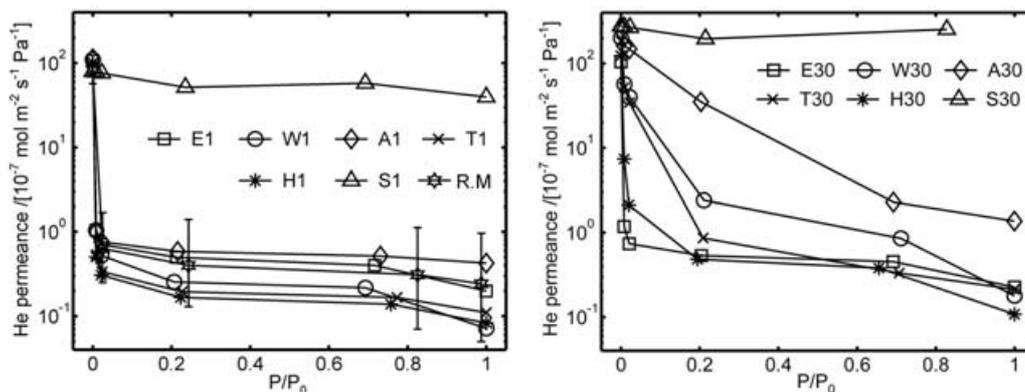


Figure 11. Porosimetry data for membranes rinsed in different medias for a) 24 hours and b) for 30 days.

Single gas experiments confirmed porosimetry results, see paper III. By applying the Horvath-Kawazoe and Kelvin equations to porosimetry data, it could be shown that long exposure to aqueous solutions leads to the formation of micropores and mesopores in the TPA-silicalite-1 film. This has implications for pervaporation applications with aqueous feeds and also for silicalite-1 membrane synthesis. Anhydrous ethanol was identified as a safe rinsing media.

#### 4.2.2 Effect of heating rate during calcination

In a previous study [23] it has been recommended to use a heating rate during calcination of 1 °C/min due to the speculation that a high heating rate may introduce defects in the membrane. A slow process is time consuming and a study to investigate the effect of varying calcination rates was performed and reported in paper II. Calcination was carried out at 500 °C for 6 hours with heating rates X varying from 0.2 °C/min to 5 °C/min. Porosimetry data and p/o- xylene selectivity for the membranes calcined with varying heating rates are shown in Figure 12. Figure a) shows average data for two membranes with varying X and average data for 10 reference membranes (R.M.) with X=0.2. Figure b) shows data for one membrane of each type (no average).

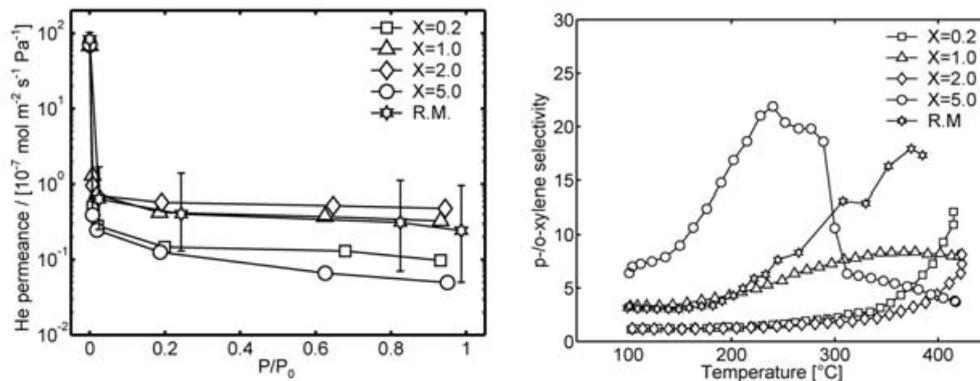


Figure 12. a) Porosimetry data and b) p/o xylene selectivity as a function of temperature for membranes with varying heating rates,  $X$   $^{\circ}\text{C}/\text{min}$  during calcination. For the reference membranes (R.M.),  $X$  was 0.2.

Porosimetry data shows that membranes with  $X=1.0$  and  $X=2.0$  had lower quality than membranes with  $X=0.2$  and  $X=5.0$ . No difference is observed by comparing with the reference membranes from earlier work with calcination rate of  $0.2^{\circ}\text{C} / \text{min}$ , since the data is overlapping. Figure 12 b) shows the separation factor of p/o-xylene for the four membranes and for a reference membrane. No correlation between calcination rate and separation performance is observed. For instance, at  $200^{\circ}\text{C}$ , the selectivity varies randomly with calcination rate. It can thus be concluded that calcination rate does not affect the properties of MFI membranes of this particular type.

#### 4.2.3 Effect of film thickness

Figure 13 a) shows the porosimetry pattern for membranes M36h with a thickness of 500 nm, and M96h, with a film thickness of 1100 nm, this data is taken from paper I.

In agreement with a previous report [25], this Figure shows that the membrane with a thicker film has significantly lower quality. Figure 13 b) shows that M5 and M96h are of equal and low quality, with a high concentration of defects. M5 was about 900 nm thick and M96 was about 1100nm. In contrast, Figure 13 b)

showed that M3, M4 and M36h, all with a film thickness of about 500 nm were of high quality. The quality thus seems independent of crystal size, but strongly dependent on film thickness. The effect of film thickness on membrane performance was discussed in paper IV.

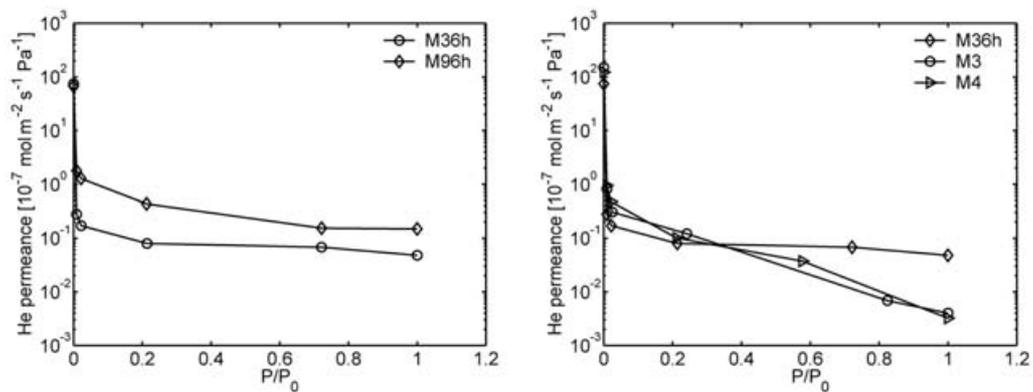


Figure 13. Porosimetry data for a) M36h and M96h and b) for M36h, M3 and M4.

## 5 Conclusion

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In this work several parameters affecting the properties of MFI membranes have been studied. A method denoted multi-seeding, which facilitates the preparation of films with small crystals and high concentration of grain boundaries, was developed and used for membrane preparation. These multi-seeding membranes were studied in order to investigate the effect of grain boundaries on membrane performance. Porosimetry showed that multi-seeding membranes were of equal quality as membranes grown in one step with similar film thickness. However, multi-seeding membranes did not separate hydrocarbon isomers as well as membrane grown in one step. It can thus be concluded that the amount of grain boundaries is affecting the separation performance of MFI membranes. Grain boundaries could also be opened by extensive rinsing. It was observed that extensive rinsing in several common rinsing medias, such as water and ammonia may reduce membrane quality by increasing the amount of open grain boundaries or micropores

It was found that thicker films ( $\sim 1\mu\text{m}$ ) are more defective than thin films ( $\sim 500\text{ nm}$ ), independent of crystal size. The heating rate during calcination is a parameter believed to affect the performance of MFI membranes. However, no correlation between heating rate and membrane quality was observed. It was concluded that heating rate during calcination is unimportant for the investigated membrane type.



## 6 Future work

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Future work will still focus on studies on how various parameters affect properties of MFI membranes. Further investigations on the influence of grain boundaries are planned. The preferred orientation and crystallite size in films produced by multi-seeding will be evaluated from XRD data. The masking procedure will be optimised to enhance membrane quality. Different techniques for repairing defects in the films will be investigated. Studies of the influence of silica/alumina ratio on membrane performance will be performed.



## 7 Reference list

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- [1] R. Szostak, *Molecular Sieves*, Blackie Academic & Professional, London, 2<sup>nd</sup> edition, (1998)
- [2] S. Auerbach, K. Carrado, P. Dutta, *Handbook of Zeolite Science and Technology*, Marcel Dekker, Inc., New York, (2003)
- [3] J. Dong, Y.S. Lin, M.Z.-C. Hu, R.A. Peascoe, E. A. Payzant, *Microporous and Mesoporous Mater.* 34 (2000) 241
- [4] J. Hedlund, J. Sterte, M. Anthonis, A.-J. Bons, B. Carstensen, N. Corcoran, D. Cox, H. Deckman, W. de Gijnst, P.-P. de Moor, F. Lai, J. McHenry, W. Mortier, J. Reinoso, J. Peters, *Microporous Mesoporous Mater.* 52, (2002) 179
- [5] P.J Kooyman, P. van der Waal and H. van Bekkum, *Zeolites* 18 (1997) 50
- [6] A. Cizmek, B. Subotic, R. Aiello, F. Crea, A. Nastro, C. Tuoto, *Microporous Materials* 4 (1995) 159
- [7] M Ogura, S-H Shinomiya, J. Tateno, Y. Nara, E. Kikuchi, M. Matsukata, *Chem. Lett.* (2000) 882
- [8] T. Suzuki, T. Okuhara, *Microporous and Mesoporous Mater.* 43 (2001) 83
- [9] J.C. Groen, L.A.A. Peffer, J. A. Moulijn, J. Pérez-Ramírez, *Microporous and Mesoporous mater.* 69 (2004) 29
- [10] A. Tavaloro, E. Drioli, *Zeolite Membranes*, *Adv. Mater.* 11 (12) (1999) 975
- [11] J. Caro, M. Noack, P. Kölsch, R. Schäfer, *Microporous Mesoporous Mater.* 38 (2000) 3
- [12] L.T.Y Au, K L Yeung, *Journal of Membrane Science*, 194 (2001) 33
- [13] M Jia, B. Chen, R.D Noble, J. L Falconer, *J. Membr. Sci.*, 90 (1994) 1
- [14] W. Xu, J. Dong, J. Li, F. Wu, *J. Chem. Soc., Chem. Commun.*, (1990) 755

- [15] G. Xomeritakis, A.Gouzinis, S. Nair, T. Okubo, M. He,R.M. Overney, M. Tsapatsis, *Chem. Eng.Sci.* 54 (1999), 3521
- [16] K. Kusakabe, T. Kuroda, A. Murata, S. Morooka, *Ind. Eng.Sci.*, 121 (1999) 139
- [17] J. Hedlund, *J. Porous Mater.* 7 (2000) 455
- [18] J. Hedlund, S. Mintova, J. Sterte, *Microporous and Mesoporous Mater.* 28 (1999) 185
- [19] Z. Lai, G. Bonilla, I. Diaz, J. G. Nery, K. Sujaoti, M. A. Amat, E. Kokkoli, O. Terasaki, R. W. Thompson, M. Tsapatsis, D. G. Vlachos, *Science*, 300 (2003) 456
- [20] M. Noack, P. Kölsch, R. Schäfer, P. Toussaint, J.Caro, *Chem. Eng. Technol.* 25 (3) (2002) 221
- [21] Y.S Lin, I. Kumakiri, B.N. Nari, H. Alsyouri, *Separation and purification methods*, 31 (2002) 229
- [22] K.Wegner, J. Dong, Y.S.Lin, *Journal of Membrane Science*, 158 (1999)17
- [23] ER. Geus, H. van Bekkum, *Zeolites* 15 (1995) 333
- [24] M.J. den Exter, H. van Bekkum, C.J.M. Rijn, F.J. Kapteijn, A. Moulijn, H. Schellevis, C.I.N. Beenakker, *Zeolites* 19 (1997) 13
- [25] J. Hedlund, F. Jareman, A-J. Bons, M.Anthonis, *Journal of Membrane Science*, 222 (1-2) (2003) 163
- [26] H.W. Deckman, D.M. Cox, A.J. Bons, B. Carstensen, R.R. Chance, E.W. Corcoran, W. De Gijnst, J.A. McHenry, J.J. Reinoso, R.B. Suanders, and P.J. Tindall, *IWZMM2001 Book of Abstracts* (2001), 9
- [27] F. Jareman, J. Hedlund, D. Creaser, J. Sterte, *Journal of Membrane Science*, 236 (2004) 81