SYNTHESIS OF MFI TYPE ZEOLITE MEMBRANES IN A CONTINUOUS SYSTEM

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ABSTRACT

SYNTHESIS OF MFI TYPE ZEOLITE MEMBRANES IN A CONTINUOUS SYSTEM

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MFI type zeolites, are the most widely studied zeolites for membrane separations. Conventionally, zeolite membranes are prepared in batch systems by hydrothermal synthesis in autoclaves. This method has several disadvantages for use in industrial scale for the synthesis of membranes with large areas and complex geometries that are commonly used in membrane modules.

The objective of this study is to prepare MFI type zeolite membranes on tubular alumina supports in a continuous system where the synthesis solution is circulated through the tubular supports. Syntheses were carried out using clear solutions, at atmospheric pressure and at temperatures below 100°C. The membranes were characterized by N_2 , SF₆, n-butane and isobutane permeances, X-ray diffraction and scanning electron microscopy.

A 2- μ m membrane was synthesized using the composition 80SiO₂: 16TPAOH: 1536H₂O at 95°C in the continuous system. The membrane showed N₂ permeance of 4.4 x 10⁻⁷ mol/m².s.Pa and N₂/SF₆ selectivity of 11. The membrane synthesized in the batch system showed a N₂ permeance of 3.4 x 10⁻⁷

mol/m².s.Pa and a N_2/SF_6 selectivity of 27. Both membranes showed nbutane/isobutane mixture (50%-50%) selectivities of about 6 at temperatures of 150 and 200°C. Among many zeolite membranes reported in literature, these membranes are one of the few zeolite membranes synthesized in a flow system and the first MFI type membranes synthesized in a continuous flow system with circulation of the synthesis solution. The permeances and selectivities of the membranes synthesized in the continuous system are comparable with the MFI type membranes synthesized in batch systems in literature.

Key words: MFI, zeolite membranes, continuous system, flow system, low temperature

ÖΖ

SÜREKLİ SİSTEMLERDE MFI TİPİ ZEOLİT MEMBRAN SENTEZİ

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MFI tipi zeolitler membran uygulamaları için en sık çalışılan zeolitlerdir. Zeolit membranlar, bugüne kadar çoğunlukla kendinden basınçlı, kesikli sistemlerde hidrotermal yöntem ile sentezlenmiştir. Bu yöntemin endüstriyel boyutta zeolit membranların sentezlenmesi aşamasına geçildiğinde yaratabileceği çeşitli sorunlar vardır. Bu sorunlar özellikle büyük ölçekte kullanılan geniş yüzey alanına ve karmaşık geometrilere sahip membran şekilleri söz konusu olduğunda ortaya çıkmaktadır.

Bu çalışmanın amacı tüp şekilli alumina destekler üzerinde sürekli bir sistemde MFI tipi zeolit membranlar sentezlemektir. Sentez sistemi kapalı bir sistem olup membranın içinden akıtılan sentez çözeltisi sisteme geri döndürülerek bir döngü sağlanmıştır. Sentez, berrak çözeltiler kullanılarak, atmosfer basıncında ve 100°C'den düşük sıcaklıklarda yapılmıştır. Sentezlenen membranlar X-ışını kırınımı, taramalı elektron mikroskobu ve N₂, SF₆, n-bütan ve izobütan geçirgenlikleri ile karakterize edilmiştir.

Sürekli sistemde 80SiO₂: 16TPAOH: 1536H₂O başlangıç bileşimi ile 95°C'de, 2 µm kalınlığında bir membran sentezlenmiştir. Membran 4.4 x 10⁻⁷ mol/m².s.Pa'lık bir N₂ geçirgenliği göstermiş, N₂/SF₆ ideal seçiciliği ise 11 olarak bulunmuştur. Aynı bileşim, silika kaynağı ve sentez sıcaklığı kullanılarak kesikli sistemde sentezlenen membrana kıyasla bu membranın daha ince ve homojen olduğu görülmüştür. Kesikli sistemde sentezlenen membran 3.4 x 10⁻⁷ mol/m².s.Pa'lık bir N₂ geçirgenliği göstermiş, N₂/SF₆ ideal seçiciliği ise 27 olarak bulunmuştur. Bu membranların ikisinin de 150 ve 200°C'de n-bütan/izobütan karışım (50%-50%) seçiciliği 6 olarak bulunmuştur.

Literatürdeki MFI membranlar göz önünde bulundurulduğunda bu çalışmada sentezlenen membranlar akış içeren bir sistemde şu ana kadar sentezlenmiş birkaç membrandan biri, bunların arasında geri dönüşümlü bir sistemde sentezlenen ilk MFI tipi membranlardır. Bu membranların gaz geçirgenliği ve seçicilikleri literatürde yayınlanmış membranlarla kıyaslanabilir değerlerdir.

Anahtar kelimeler: MFI, zeolit membranlar, sürekli sistem, akış sistemi, düşük sıcaklık

To my parents...

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NOMENCLATURE

- A : Alumina, Al₂O₃
- E : Ethanol, C_2H_5OH
- H : Water, H_2O
- N : Soda, Na₂O
- RT : Room Temperature
- SEM : Scanning Electron Microscopy
- S : Silica, SiO₂
- T : Tetrapropylammonium hydroxide (TPAOH), C₁₂H₂₉NO
- XRD : X-Ray Diffraction

CHAPTER 1

INTRODUCTION

Zeolites are crystalline hydrated aluminosilicates of alkali and alkaline earth elements, which contain molecular-sized pores and channels in their framework [1]. Owing to these molecular-sized pores, zeolites have been studied widely for membrane applications, as well as adsorption and catalysis. With the pore size and structure unique to each type of zeolite, zeolites are able to selectively sieve components of a mixture.

A zeolite membrane consists of a thin, selective zeolite layer on top of a thick macroporous support. The zeolite layer which is relatively thin compared to the support, functions as the membrane, where the thick and macroporous support provides mechanical strength and has very little effect on the separation [2].

Conventionally, zeolite membranes are synthesized in batch systems, by placing the support, on which the membrane will be grown, inside the synthesis solution or gel. Synthesis is done typically at high temperatures between 150 and 200°C. This batch synthesis method may cause a number of problems for industrial-scale production. The membranes used in industrial scale have shapes that provide a large surface area within a small volume, such as monoliths or shell-and-tube like structures. In such membrane geometries, it is hard to provide homogeneous synthesis conditions all through the support in batch synthesis systems. It is even hard to fill the support properly in the case of capillary-sized tubes or monoliths. In addition to this, the membranes may tend to have different thickness throughout, due to the settling of the crystals in the bulk. As a result, although there exists numerous research carried out on zeolite membranes, there actually exists only a single application using a zeolite membrane in a large-scale separation for the separation of water from various solvents by pervaporation [3].

An alternative to synthesis of the membranes in batch systems is using a continuous system. In a continuous system, much better homogeneity can be provided in terms of the synthesis conditions at different sites of the membrane, not only because all the support can be filled and no settling of crystals from the bulk occurs, but also because local depletion of nutrients and concentration gradients caused by this will be prevented [4, 5]. As a result, homogeneous conditions can be provided for the growth of a membrane on supports of various shapes and sizes. Thereby a continuous system may offer a solution to one of the major difficulties in implementing zeolite membranes to industrial scale, which is producing them with large surface area and reproducibly. The continuous system may also provide some economical advantages. In a continuous system, raw material usage can be minimized if the synthesis solution is circulated all through the synthesis duration, as was done in this study. Where in batch systems the membrane support is placed inside the synthesis solution, in a continuous system with circulation, all that is necessary will be the amount that will fill the support and a line between the entrance and the exit to provide circulation.

A few studies related to the synthesis of zeolite membranes with flow systems have been published very recently in literature. Richter et al. [5] synthesized tubular MFI type membranes at 150°C by flowing the synthesis solution slowly inside autoclaves. They renewed the synthesis solution all through the synthesis without recirculation. Pina et al. [4] synthesized tubular LTA type membranes by renewing the synthesis solution periodically using a semi-continuous approach. Tsutsumi and Satoshi [6] used a flow system in the synthesis of flat LTA membranes by heating only the substrate to be coated and flowing the synthesis solution on the substrate.

In the studies mentioned, different techniques involving the flow or renewal of the synthesis solution have been applied in the synthesis of MFI or LTA membranes. In this study, MFI type zeolite membranes were synthesized on tubular alumina supports using a continuous system, where the synthesis solution was circulated through the tubular supports. Synthesis was carried out at atmospheric pressure and at temperatures below 100°C, using clear precursor

solutions. The method suggested in this study is a novel method, and compared to the studies published, is a simpler but promising method of synthesizing zeolite membranes.

CHAPTER 2

LITERATURE SURVEY

2.1. Zeolite membranes

A membrane is a semi-permeable barrier, which separates the components of a mixture, where some of the components travel faster through the membrane than the others [7]. The component of a mixture which permeates faster through the membrane is called the permeate, whereas the component which permeates slower is called the retentate (Figure 2.1). At the end of the membrane separation, one end of the membrane is enriched in the retentate and the other is enriched in the permeate and in this way separation is achieved.



Figure 2.1. Schematic representation of a membrane with its feed, retentate and permeate sides

Almost all industrially used membranes are made of polymeric materials. The application of polymeric membranes, however, is limited to temperatures below about 200°C and to the separation of chemically inert mixtures [8]. Where high

temperatures and chemically active species exist, inorganic membranes are used. Amorphous silica membranes, dense metallic membranes and zeolite membranes are examples of inorganic membranes. Among these different types of membranes, zeolite membranes present a special class with their well-defined pore sizes.

Zeolite membranes usually consist of a thin and selective zeolite layer (0.5-100 μ m) on top of a thick macroporous support [9], although there also exist self-supported zeolite membranes, which stand on their own [10]. In supported zeolite membranes, the macroporous support provides mechanical strength to the thin zeolite layer, with small contribution to selectivity or slightly hindering the flux [2].

Since each type of zeolite, in its well-defined and unique framework structure, contains channels and cages of dimensions unique to the type of zeolite, each zeolite is able to selectively allow some molecules into its framework and reject the others, based mainly on the shape and size of the molecules. The FAU type zeolites, which include zeolites X and Y, with their supercages of 0.74 nm diameter are large-pore zeolites. The MFI type zeolites, which include ZSM-5 and silicalite-1 and are widely studied for membrane applications, are medium-pore zeolites with their channel dimensions between 0.51 – 0.56 nm. LTA type zeolite family, which includes zeolite A, is a family of zeolites with small-pores of 0.41 nm [11].

In addition to molecular sieving based on the size and shape of the molecules [12], separation in a zeolite membrane depends also on preferential adsorption [13] of mixture components on the zeolite. Where adsorption is less dominant, diffusion rate of the molecules also contributes to separation achieved in zeolite membranes [14].

The two important parameters in a membrane separation are the selectivity and the permeance through the membrane. Permeance of a gas through a membrane is defined as,

$$Permeance = \frac{Molar flux}{Driving force}$$
(2.1)

where the driving force is usually the pressure difference between the feed and permeate sides of the membranes.

There exists a trade-off between these two properties. For instance, with increasing membrane thickness, although the selectivity may increase, this increase in selectivity is usually accompanied by a decrease in flux. From an industrial point of view, a highly selective membrane with a low flux is of no use and therefore it is necessary to synthesize membranes with high selectivity accompanied by a high flux.

In expressing the separation performance, the ideal selectivity (Eq. 2.2), which is the ratio of single gas permeances, and separation factor (Eq. 2.3), which is based on the compositions of the permeate and retentate sides in mixture separations are used.

Ideal selectivity,
$$_{A/B} = \frac{\text{Permeance of A}}{\text{Permeance of B}}$$
 (2.2)

Separation factor =
$$\frac{[X_A / X_B]_{permeate}}{[X_A / X_B]_{retentate}}$$
(2.3)

Here, X_i are the fractions of the mixture components in the permeate or retentate sides. Alternatively, the separation factor can be defined as the ratio of the permeances of the mixture constituents using a log-mean transmembrane pressure difference based on partial pressures on both sides [15]. The separation factor in this study is calculated using this approach and the details of the calculation are given in Appendix C.

2.2. Description of MFI type zeolites

Zeolites are crystalline, hydrated aluminosilicates of alkali or alkaline earth elements. Within their backbone composed of SiO_4 and AlO_4 tetrahedra, which are connected through the oxygen atoms, there exist pores of molecular dimensions (0.3-1.3 nm).

MFI type zeolites are hydrophobic zeolites with a Si/Al ratio of $20 - \infty$. Silicalite-1 is the alumina-free form of MFI, whereas ZSM-5 is the name given to MFI type zeolites which have alumina in their structure. The framework of MFI contains two types of channels. These are 10-membered rings of 0.51 x 0.56 nm (straight, circular channels) and 0.51 x 0.54 nm (sinusoidal, elliptical channels) [11] shown in Figure 2.2.



Figure 2.2. MFI channel structure [17]

MFI type zeolites are the most widely used zeolites for membrane studies [9, 12, 16]. Their pore dimensions are suitable for the separation of mixtures of commercial importance, such as the xylene isomers and light hydrocarbons.

Another reason why MFI is widely used in zeolite membrane applications is because its synthesis is widely studied and therefore well-known. With its high Si/Al ratio MFI is a zeolite with high thermal and chemical stability, which also makes it attractive for industrial applications [17].

2.3. Characterization of MFI type membranes by gas permeance

In the characterization of MFI type membranes with gas permeation, the two most widely used gas pairs are N_2 -SF₆ [18, 19, 15] and the butane isomers [13, 20, 21]. Figure 2.3 shows the kinetic diameters of these gases with respect to the pores of the MFI type zeolite.

Among the two gases N₂ and SF₆, N₂ with a kinetic diameter of 0.36 nm [1] is able to pass through the zeolite's pores whereas SF₆ with a kinetic diameter of 0.58 nm [1] is excluded. As a quality criterion for their membranes, Funke et al. used a N₂/SF₆ ideal selectivity of 80 [15]. On the other hand MacDougal et al. [22] have shown that N₂/SF₆ selectivity in a defect free silicalite membrane can be as low as 4 and due to its nearly spherical shape the SF₆ molecule may be more likely to be able to pass through MFI pores than it had commonly been expected. They attributed the much higher N₂/SF₆ selectivities reported in literature to the transport of SF₆ being reduced by grain boundaries.



Figure 2.3. Kinetic diameters of test gases with respect to MFI pore size [1]

In some studies, instead of N_2/SF_6 , H_2/SF_6 selectivity is used as the quality criterion. N_2 and H_2 are both non-adsorbing gases and both can easily pass through MFI pores. The selectivity between H_2 and N_2 in the zeolite's pores would be equal to the Knudsen selectivity, which is 3.74, and the corresponding quality criterion therefore would be approximately the Knudsen selectivity times the N_2/SF_6 selectivity set as the quality criterion.

The separation of butane isomers is governed mainly by the difference in their adsorption behaviour and their diffusion mobilities [13, 23]. As these two molecules are isomers, they cannot be separated in mesopores by Knudsen diffusion, which is dependent on the molecular weight. Therefore the butane selectivity is a good way to detect the presence of mesopores in an MFI layer. Van de Graaf et al. [23] considered an ideal selectivity of 10 at room temperature or higher as a quality criterion for their membranes. Similarly, Vroon et al. [13] considered a mixture selectivity of 10 or higher at 200°C as their quality criterion.

In addition to the gas permeance and selectivities of the MFI membranes, the gas permeance before calcination is also used as a method to evaluate the continuity of the zeolite layer on the support, if a template molecule had been used in synthesis. As the template molecule remains inside the pores of the zeolite during synthesis, a continuous zeolite film with essentially no nonzeolitic pores should be impermeable to gases right after synthesis. For this purpose generally, N_2 , He -or another probe molecule that can pass through the zeolite's pores when nonoccupied- is used.

2.4. Synthesis of zeolite membranes by in-situ hydrothermal synthesis

The synthesis of zeolite membranes is commonly achieved by in-situ hydrothermal synthesis in batch systems. The support material is placed in an autoclave and the autoclave is filled with the synthesis gel [15, 18, 23] or clear solution [12, 24, 13]. The autoclave is then placed in an oven kept at the synthesis temperature and the zeolite membrane grows on the support as well as in the bulk of the synthesis solution. In the synthesis of MFI membranes, high

temperatures between 150°C and 200°C have generally been preferred [24, 15, 20]. At these temperatures, the typical thickness of the membranes are around 10-30 μ m.

Schoeman et al. [25], who synthesized submicron silicalite films on silicon wafers at 100°C, reported that the synthesis conditions that yield silicalite at higher temperatures may not be suitable for the synthesis of thinner layers at low temperatures such as 100°C, where crystallization takes place much slower. With lower crystal growth rates, and therefore the possibility of synthesizing thinner zeolite membranes, zeolite membrane synthesis at low temperatures is yet an area not sufficiently studied and discovered.

In the synthesis of MFI powder also rather high temperatures around 150°C - 200°C have usually been applied. Recently, as opposed to the more commonly encountered synthesis system involving a gel as the precursor mixture, such high temperatures and autogeneous pressure; studies have been published reporting the synthesis from clear solutions, at temperatures around 100°C and at atmospheric pressure [12, 26]. These mild synthesis conditions offer less energy consuming, and therefore lower cost and also simpler systems in large-scale synthesis [27]. In the syntheses at low temperatures, the time necessary to reach full yield was much longer compared to syntheses at the conventional high temperatures [13, 25] and submicron MFI crystals with size down to 50 nm [28] have been synthesized.

Although limited in number, in several studies, MFI membranes also have been synthesized at low temperatures [12, 26, 29]. These studies are summarized in Table 2.1.

Vroon et al. [13], among membranes synthesized at temperatures ranging from 100°C to 180°C, synthesized MFI membranes of 3.5 μ m thickness at 100°C on alumina disks. The membranes had n-C₄H₁₀ permeance of 3.8 x 10⁻⁸ mol/m².s.Pa and a n-C₄H₁₀/i-C₄H₁₀ selectivity of 131.

Ref.	Composition	Synthesis Medium	Т (°С)	Duration	Seed	Support	Film Thickness	Permeance (mol/m².s.Pa)	Selectivity
13	80SiO ₂ : 24TPAOH: 4.24Na ₂ O: 1136H ₂ O	Batch	100	2 x 6 days	-	alumina disk with 150 nm pores	3.5 µm	n-C ₄ H ₁₀ : 3.8 x 10 ⁻⁸ (RT)	$n-C_4H_{10}/i-C_4H_{10} = 131^b$ (RT)
29	80SiO ₂ : 8TPABr: 4- 28Na ₂ O: 7856H ₂ O	Batch	95	2 x 20 hrs. or 3 x 20 hrs.	100 nm silicalite	alumina disk with 1 µm pores	-	n-C₄H₁₀: 9.9-29 x 10 ⁻⁸ (RT)	$n-C_4H_{10}/i-C_4H_{10} = 17-39^a$ (RT)
12	80SiO ₂ : 9.6TPAOH: 4800H ₂ O:320EtOH	Batch	100	30 hrs.	50 nm silicalite	asymmetric alumina disks (100 nm pored top layer)	500 nm	N ₂ : 1.29 x 10 ⁻⁵	$N_2/SF_6=10^a$
								n-C₄H ₁₀ : 9.8 x 10 ⁻⁷ (RT)	n-C ₄ H ₁₀ /i-C ₄ H ₁₀ =9 ^b (RT)
								n-C ₄ H ₁₀ : 1.2 x 10 ⁻⁶ (160°C)	$n-C_4H_{10}/i-C_4H_{10} = 3^b$ (160°C)
	80SiO ₂ : 9.6TPAOH: 4800H ₂ O:320EtOH	Batch	100	17-72 hrs.	60 nm silicalite	asymmetric alumina disks (100 nm pore- top layer)	500-1100 nm	N ₂ : 53-141 x 10 ⁻⁷	$N_2/SF_6=10-22^a$
26								n-C ₄ H ₁₀ : 4.1-13.5 x 10 ⁻⁷ (RT)	$n-C_4H_{10}/i-C_4H_{10}= 1.3-9^b$ (RT)
								n-C₄H ₁₀ : 1.2 x 10 ⁻⁶ (160°C)	n-C ₄ H ₁₀ /i-C ₄ H ₁₀ =3 ^b (160°C)
5	80SiO ₂ : 2.8TPABr: 1.44Na ₂ O: 6800 H ₂ O	Continuous	150	72 hrs.	commercial ZSM-5 or nanosized MFI synthesized	asymmetric alumina tubes and capillaries (60 nm pored top layer)	30 µm	H ₂ : 4-8 x 10 ⁻⁷	H ₂ /SF ₆ ^a =22-31

Table 2.1. MFI membranes reported in literature and synthesized at low temperature or using a flow system

a: Ideal selectivity (from single gas permeances) b: Separation selectivity (binary gas mixture)

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Kang et al. [29] synthesized MFI membranes inside the pores of alumina tubes at 95°C. Using consecutively 3 or 4 synthesis steps, they obtained MFI membranes inside alumina supports that showed selectivities of 17-39 to nbutane over isobutane.

Hedlund et al. [12, 26] used a tedious synthesis procedure, where they first filled the support pores with a wax to prevent the penetration of seeds into the support. Then for charge reversal of the support a cationic polymer was adsorbed on the support and the supports were seeded with nanosized silicalite crystals by immersing them into a seed sol. On this seeded support, the membranes of thickness 500-1100 nm were grown by hydrothermal synthesis. The membranes showed high N₂ fluxes accompanied by N₂/SF₆ selectivities ranging from 10 to 22 and n-C₄H₁₀ permeances to the order of 10⁻⁶-10⁻⁷ mol/m².s.Pa and n-C₄H₁₀/i-C₄H₁₀ mixture selectivities of 1.3-9 at room temperature.

While different synthesis conditions are investigated for the synthesis of membranes with improved properties, that is with high selectivity and high permeance at the same time, still much remains to be done for the implementation of these synthesis procedures to industrial scale production. With numerous studies on zeolite membrane synthesis in lab-scale, there exists only a single membrane operation using a zeolite membrane [3].

This application implemented by Mitsui Engineering in Japan, uses LTA membranes grown on alumina tubes for the separation of water from various organic solvents by pervaporation. Morigami et al. [3] report the synthesis of these LTA membranes of 80 cm length and with a surface area of about 300 cm².

Li et al. [16] reported the synthesis of a large-area MFI membrane of 260 cm² surface area. Using 3 or 4 consecutive synthesis steps 30 μ m thick ZSM-5 membranes were synthesized. Out of the ten membranes synthesized five of them showed selectivities to hydrogen over n-butane that are higher than 27 with hydrogen permeances to the order of 10⁻⁶-10⁻⁷ mol/m².s.Pa.

With only a few studies carried out for the production of large-area membranes, the investigations focusing on the synthesis of zeolite membranes for use in industrial scale are yet limited. Synthesis of the membranes in continuous systems instead of the currently used batch systems is a method that might prove useful for industrial scale production of zeolite membranes. Apart from possible improvements in performance, such systems will have flexibility in operation with various membrane geometries and with large-area membranes.

2.5. Synthesis of zeolite membranes in continuous systems in literature

There are a few studies recently published in literature related to the synthesis of zeolite membranes in continuous systems. In these studies, the conventional zeolite membrane synthesis system, which is the autoclave with the membrane support inside, is modified to include some kind of flow of the synthesis solution over the substrate. The flow is applied in the synthesis system either by circulation or by renewal of the synthesis solution by a fresh one. This renewal was done either continuously or in periodic time intervals.

Pina et al. [4] synthesized LTA type zeolite membranes on the outer surfaces of tubular alumina supports using a semi-continuous system in which fresh gel was periodically supplied to the synthesis vessel. The fresh gel was supplied from a vessel pressurized with dry nitrogen at a pressure of 10 bar. The solution from the autoclave was removed in portions of 10 mL by pneumatic valves. By this way, at different renewal rates from once in every 13 minutes to once in every 75 minutes, they replaced the gel in the autoclave with a brand new one pumped into the autoclave from a reservoir during a synthesis duration of 5 hours. The LTA membranes synthesized showed pervaporation separation factors of 94-3603 for water/ethanol (10/90 wt%) liquid mixtures accompanied by water fluxes of 2.2-3.8 kg/h.m².

Richter et al. [5] synthesized MFI type membranes on the inner surfaces of alumina tubes and capillaries. In this study, similar to the study of Pina et al. [4], a fresh synthesis gel was supplied to the autoclave, but in this study this was done continuously. Renewal of the gel was carried out at a very low velocity of 0.25 cm/min, from a reservoir outside. Synthesis was done at 150°C for 72

hours on supports seeded with nanosized MFI. A zeolite layer of 30 μ m thickness was obtained. The membranes synthesized in different sized tubes and capillaries had H₂ permeances of 4-5 x 10⁻⁷ mol/m².s.Pa and H₂/SF₆ selectivities of 22-31, which exceed the Knudsen selectivity of 8.4 by a factor of about 3-4. In this study, compared to the runs with the synthesis in batch, the membranes synthesized with the flowing synthesis solution had smoother surfaces with more intergrown crystals.

In these two studies, a continuous or semi-continuous synthesis system was applied where the synthesis solution was renewed from a reservoir during the course of synthesis. In the study of Tsutsumi and Satoshi [6], on the other hand, the synthesis solution is continuously circulated through the support, similar to the synthesis system used in this study. In this study, LTA type zeolite layers were synthesized by circulating the liquid phase separated from the hydrogel over PTFE substrates. Only the substrates were heated to prevent zeolite formation in the bulk synthesis solution. In the runs with the static synthesis solution, by-products such as gmelinite, chabazite and faujasite were detected in addition to LTA, whereas in the runs with the circulating synthesis solution pure LTA type zeolite was obtained over the substrates.

Using flow systems is a new approach that has very recently started being used in the research on the synthesis of zeolite membranes. With a few examples using different methods involving a flow system, no membrane of high quality has yet been synthesized using a flow system.

CHAPTER 3

EXPERIMENTAL METHODS

3.1. Seed synthesis

3.1.1. Materials

In the synthesis of seed MFI crystals, tetraethylorthosilicate (TEOS, Merck, 98%), sodium aluminate (Riedel-de-Haen, %45 Na₂O, %54 Al₂O₃, 1% H₂O), tetrapropylammonium hydroxide (TPAOH, Acros, 25wt% in water) and demineralized water was used.

3.1.2. Synthesis procedure

Seeds were synthesized from a batch composition of $1 \text{ Al}_2\text{O}_3$: 1.3 Na₂O: 80SiO₂: 9.9 TPAOH: 1630H₂O: 320EtOH (A₁N_{1.3}S₈₀T_{9.9}H₁₆₃₀E₃₂₀) [30]. Sodium aluminate solution (5 wt% in water) was used as the Al₂O₃ and Na₂O source. For a 100 gram batch 15.67 grams of TPAOH (25wt% in water), 7.21 sodium aluminate solution (5 wt% in water) and the remaining water, which is 44.05 grams, was added on 33.07 grams of TEOS, in the given order. The resulting mixture was aged by stirring vigorously at room temperature for 24 hours. The initially two-phase mixture turned into a clear, homogeneous solution at the end of aging.

Synthesis of MFI powder was carried out both in a system working under atmospheric pressure with reflux and at autogeneous pressure in autoclaves. The schematic drawing of the system working under atmospheric pressure is shown in Figure 3.1.

In the system working under atmospheric pressure, the synthesis solution of 150 grams is placed in a 250 mL glass flask and the flask on a magnetic stirrer

and heater. During synthesis, the solution is stirred mildly. On top of the flask was a condenser to provide reflux. Samples were taken from the flask at various times during the course of synthesis by taking the condenser off and sucking 10 mL of the synthesis solution by means of a pipette. During synthesis the temperature was kept at $80\pm2^{\circ}$ C. The heater was adjusted at the beginning of synthesis to keep the solution at 80° C and when the samples were being taken the temperature was also checked.



Figure 3.1. Schematic drawing of atmospheric pressure system used in powder synthesis

Syntheses under autogeneous pressure were carried out in stainless steel autoclaves with 10 mL PTFE inserts and 15 mL autoclavable PTFE bottles. The autoclaves and PTFE bottles were placed in an oven preheated to 80°C. When

the autoclave or PTFE bottle was taken out of the oven, it was quenched in water and then opened to take the product.

3.1.3. Recovery of the products

The product slurries were centrifuged with a relative centrifugal force of 640g (6000 rpm) for 30 minutes. They were washed with distilled water and centrifuged for a second time. After disposing of the supernatant, the precipitated products were dried overnight at 80°C.

3.1.4. Determination of percent yield and percent crystallinity

The dried products were weighed for percent yield determination. Maximum yield was defined as the amount which would be obtained if all the silica in the synthesis solution was precipitated as product. The calculation of maximum yield is given in more detail in Appendix B. Percent Yield was then defined relative to the maximum yield, and calculated as follows;

% Yield =
$$\frac{\text{solid product in 1 gram product solution}}{\text{maximum yield out of 1 gram synthesis solution}} \times 100$$
 (3.1)

Percent crystallinity of the samples was defined based on the three characteristic peaks of MFI type zeolite at Bragg angles of 23°, 24° and 24.5° shown with asterisks in Figure 3.2.

Among all the samples obtained, the one in which the sum of the diffraction intensities of these three peaks was highest was assigned the reference with 100% crystallinity and the crystallinity of others were determined accordingly.

Hence, percent crystallinity was calculated as follows;

% Crystallinity =
$$\frac{\sum_{i=1}^{3} I_i}{\left(\sum_{i=1}^{3} I_i\right)_{ref}} \times 100$$
(3.2)


Figure 3.2. The XRD pattern of MFI and the three characteristic peaks used in percent crystallinity calculation

3.2. Membrane synthesis

3.2.1. Materials

In membrane synthesis, as silica source TEOS (Merck, 98%) or LUDOX-AS-30 (Aldrich, 30wt% colloidal suspension of SiO₂ particles in water), as alumina source sodium aluminate (Riedel-de-Haen, %45 Na₂O, %54 Al₂O₃, 1% H₂O), as soda source sodium aluminate or sodium hydroxide (Merck, pellets, max. 97%), and as template TPAOH (Acros, 25wt% in water) was used. Demineralized water was used in all syntheses.

As membrane support, α -alumina tubes from Pall Exekia were used. The tubes were cut to a length of 4.5 cm. They had inner diameter of 0.7 cm, and wall thickness of 0.15 cm. The tubes had a 200 nm pore-size layer of approximately 30 µm thickness on the inner side and a larger-pore main body. Before using, the tubes were kept in ultrasonic bath for 10 minutes, cleaned with 0.1 M HNO₃ solution, rinsed in distilled water and dried.

After cleaning, the tips of the tubes were glazed with Duncan IN1001 Envision Glaze to block the pores there. The tips of the tube were dipped in the glaze, two or three times, until an opaque green glaze layer formed on the tube. Approximately 1 cm from each side was glazed, leaving an effective membrane length of 2.5 cm and an area of 5.5 cm². The glazed tubes were dried at room temperature for a few minutes and then heat treated at 900°C for an hour to mature the glaze, with a heating rate of 1.5°C/min and an average cooling rate of 1.5°C/min.

3.2.2. Seeding

The tubes were seeded by dip-coating. The dip coating setup is shown in Figure 3.3 [31].

The seed suspension was a 0.25 wt% aqueous suspension of ZSM-5, which was synthesized with the composition $A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$ under atmospheric pressure with reflux at 80°C for 98 hours, as explained in Section 3.1.2. The seeds were put in an aqueous solution of ammonia with a pH of 8. They were stirred for 30 minutes, kept in ultrasonic bath for 10 minutes and stirred again for 30 minutes. Ultrasonication for 10 minutes was applied various times during the interval when the seed suspension was stored to redisperse the seeds that had settled.

A beaker with approximately 100 mL of seed suspension in, was placed on a large plastic syringe of 60 mL. The tube to be seeded was held still and vertically, while the beaker containing the seed suspension was slowly raised upwards so that the tube was immersed in the seed solution. This movement was maintained by pumping water from a reservoir to the syringe or from the syringe to the reservoir very slowly by means of a peristaltic pump.



Figure 3.3. Schematic drawing of the dip-coating setup

When the portion of the tube that is not glazed was fully inside the seed suspension the pump was stopped and the tube was kept inside for 10 minutes. Then the seed suspension was lowered so that the tube got out. The velocity of the suspension while going up and down was 1-1.5 cm/h. This procedure was repeated twice, reversing the tube upside down in the second time to achieve uniform coating of the tube with seeds. The seed coated tubes were kept at 150°C for 4 hours to adhere the seeds to the support surface [29].

3.2.3. Synthesis in the continuous system

Synthesis of membranes was carried out in a continuous system where the synthesis solution was circulated through the tubular supports. The schematic drawing of the system is given in Figure 3.4.



Figure 3.4.(a) Continuous synthesis setup with silicon oil bath



Figure 3.4.(b) Continuous synthesis setup without silicon oil bath



Figure 3.5. Glass module holding the membrane

The synthesis solution was kept in the reservoir, which is a 100 mL glass flask, with four entries for the condenser, for the entering stream, for the exiting stream and the last one for temperature measurement or sample taking. The membrane was held vertically inside a glass module as shown in Figure 3.5.

The lines between the reservoir and the module were Platinum-cured silicon tubings (Cole-Parmer). The Platinum-cured silicon tubings were chosen because they are resistant to high temperature (230°C) and to high alkalinity. Circulation was provided by means of a peristaltic pump, which was placed between the membrane module and the entrance to the reservoir. In some syntheses, the reservoir, the module holding the membrane and the line in between was kept in a silicone oil bath kept at the synthesis temperature (Figure 3.4.a). In this case, the temperature was measured from inside the oil bath. The oil bath was heated by the magnetic stirrer-heater that it was placed on. The synthesis solution in the reservoir was stirred mildly. In other syntheses, the reservoir was used to prevent the temperature of the synthesis solution from dropping by the time it reached the membrane. In syntheses where the silicon oil bath was not used, with a flowrate of 6 mL/min, the temperature of the synthesis solution dropped by about 10°C as it left the membrane from the top.

The synthesis solutions were prepared with batches in the range 0-1 Al_2O_3 : 0-1.3 Na_2O : 80SiO₂: 9.9-30 TPAOH: 1380-4800 H_2O : 0-320EtOH. Sodium aluminate solution (5 wt% in water) was used as the Al_2O_3 and Na_2O source in the ZSM-5 membranes. In silicalite batches, no Al_2O_3 or Na_2O was used. The resulting mixture was aged by stirring vigorously at room temperature for 24 hours as was done in seed synthesis.

The amount of synthesis solution used in membrane synthesis was 70 grams. The aged solution was placed inside the reservoir, the tube in the glass module and with the silicone tubings the line was completed. The reservoir and the module were placed inside the silicone oil bath and the circulation was started. The level of the solution in the reservoir while the line is full was marked and the amount that was lost was compensated by adding demineralized water once or twice a day from the top of the condenser. Typically 2 or 4 mL was added in

one portion, and on the whole 2-6 mL was added daily. In batches with LUDOX as the silica source this amount was low, as there was no ethanol in the synthesis solution, whereas with TEOS more water was added. At the end of synthesis, the setup was taken out of the oil bath and after waiting for a while for it to cool the membrane was taken out of the module and washed with distilled water until the pH was around 8. After washing the membranes were dried overnight at 80°C.

The membranes synthesized in the continuous system in this study are given in Table 3.1.

In the synthesis of PZC89, 90, 94 and 95, while the membranes were being synthesized, samples were taken from the synthesis solution at various times during the course of synthesis by inserting a pipette from the fourth neck of the reservoir. In these syntheses, 100 grams of synthesis solution was put in the reservoir initially. The samples taken from the synthesis solution were centrifuged with a relative centrifugal force of 640g (6000 rpm). For compositions S₈₀T_{9.6}H₁₃₈₀E₃₂₀ (PZC94) and S₈₀T_{9.8}H₄₈₀₀E₃₂₀ (PZC89), centrifugation was done for 30 minutes, for the composition $S_{80}T_{16}H_{1536}E_{320}$ (PZC90) for 60 minutes and for $S_{80}T_{30}H_{1380}E_{320}$ (PZC95) for 90 minutes. After disposing of the supernatant, the precipitated products were dried overnight at 80°C.

Membranes are calcined at 450°C for 12 hours in air in a muffle furnace with a heating rate of 0.6°C/min and an average cooling rate of 0.6°C/min to burn off the template molecules inside the MFI pores.

3.2.4. Synthesis in the batch system

Membranes were also synthesized in the batch system, that is in autoclaves. The membranes synthesized in the batch system are also given in Table 3.1. For this, stainless steel autoclaves with 30 mL PTFE inserts were used. The tubes were placed vertically inside the inserts, held inside a PTFE sheet.

Membrane	Batch Composition ^a	Synthesis Medium	Silica Source	Synthesis Temperature (°C)	Synthesis Duration (h)	Number of consecutive layers	Flowrate (mL/min)
PZC89	S ₈₀ T _{9.8} H ₄₈₀₀ E ₃₂₀	Continuous	TEOS	85 ^b	124	1	6
PZC90	$S_{80}T_{16}H_{1536}E_{320}$	Continuous	TEOS	80 ^b	72	1	6
PZC94	$S_{80}T_{30}H_{1380}E_{320}$	Continuous	TEOS	80 ^b	72	1	6
PZC95	$S_{80}T_{9.6}H_{1380}E_{320}$	Continuous	TEOS	80 ^b	114	1	6
PZC85-III	$A_1 N_{1.3} S_{80} T_{9.9} H_{1630} E_{320}$	Continuous	TEOS	80 ^b	3 X 72	3	6
PZC97-III	$S_{80}T_{16}H_{1536}E_{320}$	Continuous	TEOS	80 ^b	3 X 72	3	6
PZC98-III	$S_{80}T_{16}H_{1536}E_{320}$	Continuous	TEOS	80 ^c	76 + 101 + 93	3	6
PZC100	$S_{80}T_{16}H_{1536}$	Continuous	LUDOX	95 ^c	72	1	6
PZC101	$S_{80}T_{16}H_{1536}$	Continuous	LUDOX	95 ^c	72	1	24
PZC86-II	$A_1 N_{1.3} S_{80} T_{9.9} H_{1630} E_{320}$	Batch	TEOS	80	2 x 72	2	-
PZC91-II	$A_1 N_{1.3} S_{80} T_{9.9} H_{1630} E_{320}$	Batch	TEOS	80	2 x 72	2	-
PZC99	S ₈₀ T ₁₆ H ₁₅₃₆	Batch	LUDOX	95	72	1	-

Table 3.1. Membrane synthesis conditions

^a A: Al₂O₃, N: Na₂O, S: SiO₂, T: TPAOH, H:H₂O, E:C₂H₅OH

^b Synthesis medium placed directly on the heater, i.e. silicon oil bath was not used

^c Synthesis medium placed inside silicon oil bath kept at the synthesis temperature

Membranes are calcined at 450°C for 12 hours in air in a muffle furnace with a heating rate of 0.6°C/min and an average cooling rate of 0.6°C/min to burn off the template molecules inside the MFI pores.

3.3. Characterization of membranes

3.3.1. Phase Identification

Phase identification was made by Philips PW 1729 X-Ray Diffractometer. When analyzing tubes, the tubes were smashed to pieces and these pieces were fit inside a depression-mount holder. The powder samples were analyzed by preparing smear slides using water to disperse the zeolites. Depression mounts were not used because some samples were not enough to fill them. The conditions used for analysis of tubes and powder samples are given in Table 3.2.

	For powder	For membranes
Tube	Cu	Cu
Filter	Ni	Ni
Radiation	CuKα	CuKα
Voltage (kV)	30	40
Current (mA)	24	30
Speed (°2θ/s)	0.1	0.1
Time Constant (s)	1	1
Slit (mm)	0.2	0.2

Table 3.2. Operating conditions of X-ray diffractometer

In the analysis of tubular membranes, in order to strengthen the signals, the operating voltage and the current were increased to 40 kV and 30 mA, respectively.

3.3.2. Determination of membrane morphology

Morphology of the membranes was determined by JEOL JSM-6400 Scanning Electron Microscope. The accelerating voltage was 20 kV. The samples were coated with gold before analysis.

3.3.3. Gas permeation measurements

Membrane performances were evaluated by measuring single gas and binary gas permeation. In both, the membrane was held inside a brass module, fitted with O-rings to prevent leakage from the retentate side to the permeate side. The schematic drawing of the membrane module is given in Figure 3.6.



Figure 3.6. The membrane module used in gas permeation experiments

3.3.3.1. Single gas permeation

After synthesis, the N_2 permeances of the membranes were measured before calcination. This is a method used to assess the amount of coverage of the support with the zeolite film [32, 33]. As the template molecule is inside the pores of the zeolite after synthesis, a continuous zeolite film with essentially no nonzeolitic pores should be impermeable to gases.

After the membranes were calcined, the single gas permeances of N₂, SF₆, n- C_4H_{10} and i- C_4H_{10} through the membranes were measured and ideal selectivities of N₂/SF₆ and n- C_4H_{10} /i- C_4H_{10} were calculated by taking the ratios of single gas permeances. n- C_4H_{10} and i- C_4H_{10} permeances were measured at room temperature, 100°C, 150°C and 200°C. N₂ and SF₆ permeances were measured at room temperature only.

Single gas permeation measurements were carried out by the constant pressure-variable volume method. The schematic drawing of the permeation setup is given in Figure 3.7. The permeate side was open to atmosphere and the feed side was kept at a gauge pressure of 1 bar. The deviation of the pressure difference from 1 bar was at most 0.05 bar for N_2 and SF_6 permeation experiments. The deviation in permeation experiments with the butane isomers, on the other hand, was at most 0.2 bar. The flowrate of the permeate stream was measured by a bubble flowmeter. In high temperature measurements, the module was wrapped with a heating tape, temperature was measured from the middle of the tube and controlled by a temperature controller. The heating rate was not controlled and was about 10°C/min.

Assuming ideal gas behaviour, permeance was calculated as

$$Permeance = \frac{Molar flux}{Transmembrane Pressure Difference}$$
(3.3)

The ideal selectivity is defined as the ratio of the permeances of the two gases,

Ideal selectivity,
$$_{A/B} = \frac{\text{Permeance of A}}{\text{Permeance of B}}$$
 (3.4)



Figure 3.7. Schematic drawing of the single gas permeation setup

3.3.3.2. Binary gas permeation

The membranes were also evaluated by their separation performances of butane isomers. Measurements were done at room temperature, 100°C, 150°C and 200°C. The schematic drawing of the binary gas permeation setup is given in Figure 3.8.

The permeate side was again open to the atmosphere and the feed side was kept at a gauge pressure of 1 bar. The transmembrane pressure difference was provided by means of back-pressure valves. The flowrate of n-butane and isobutane was controlled with mass flow controllers and the retentate and permeate flowrates were measured with bubble flowmeters. In high temperature measurements, the module was wrapped with a heating tape, temperature was measured from the middle of the tube and controlled by a temperature controller, as was done in single gas permeation measurements. Permeate was analyzed by a gas chromatograph Varian CP-3800 connected online to the setup. The operating parameters for permeance measurements and the operating parameters for the gas chromatograph are given in Tables 3.3 and 3.4, respectively.

Transmembrane pressure difference	1 bar
Permeate side pressure	0.9 bar
Temperature	RT-100°C-150°C-200°C
Feed flowrate	40 mL/min
Feed composition	50 wt.% n-C ₄ H ₁₀ – 50wt.% i-C ₄ H ₁₀

Table 3.3. Operating parameters of the binary gas permeation system



Figure 3.8. Schematic drawing of the binary gas permeation setup

Column	Chromosorb WHP 80-100 mesh		
Column Temperature	30°C		
Valve Temperature	50°C		
Detector	TCD		
Detector Temperature	100°C		
Sample Flowrate	50 mL/min		
Reference Flowrate	30 mL/min		
Column pressure	10.0 psi		

Table 3.4. Gas Chromatograph operating parameters

In binary gas permeation experiments, the selectivity was calculated using a log-mean pressure difference for the two components, calculating the permeances with this log-mean pressure difference and taking the ratio of the two permeances as the separation selectivity. The calculation of the separation selectivity is shown in more detail in Appendix C.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Synthesis of MFI powder to be used as seed

Seed crystals were synthesized using the composition $A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$ [30] at 80°C under atmospheric pressure, with reflux. During synthesis, out of a 150-gram batch 10 mL samples were taken at different times, centrifuged, dried, weighed for percent yield determination and analyzed with XRD for phase identification and percent crystallinity determination.

With the same composition $A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$ and at 80°C MFI type zeolite crystals were synthesized in autoclaves, under autogeneous pressure. Again taking samples at different times during the course of crystallization yield and crystallinity were analyzed.

In both systems, a solid product was recovered after about 45 hours and all products obtained after this time were pure MFI type zeolite. XRD pattern of the products synthesized in the atmopheric pressure system at three different times during the synthesis is given in Figure 4.1. The product obtained at the end of 98 hours in the atmospheric pressure system was used as seed.

Figure 4.2 shows the percent yield and percent crystallinity with respect to time for the samples synthesized under atmospheric pressure and for the samples synthesized under autogeneous pressure. For both systems, percent yield increases in an S-shaped curve and crystallization ends at nearly 100 hours at a maximum percent yield of 70%, where the rest of the silica remained dissolved in solution. The increase of yield with respect to time follows the same pattern in both systems, indicating that crystallization behaviour is similar in the two systems.



Figure 4.1. XRD patterns of three products synthesized at 80° C under atmospheric pressure at 43 hours (a), 91 hours (b) and 115 hours (c)



Figure 4.2. Percent yield and percent crystallinity in time for syntheses under atmospheric and autogeneous pressure

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From the time solid product could be recovered from the synthesis solution, until the end of crystallization, all samples were pure MFI as determined by XRD and all of them were highly crystalline. This observation that all products recovered are crystalline is different from what is more commonly observed in the synthesis of zeolites, where a solid product is obtained starting from the beginning of synthesis and this product, amorphous at the beginning, turns crystalline as synthesis proceeds [34, 35, 36].

The major difference between our synthesis system and the systems where amorphous products appear initially is that the synthesis mixture in this study is a clear solution at the beginning of synthesis, and the more commonly encountered one is a gel.

An observation similar to ours was reported also by Gora et al. [10] who used TEOS as silica source in the synthesis of self-supported silicalite-1 membranes from clear solutions. As TEOS, after hydrolysis, provides monomeric silica to the synthesis solution, zeolites grew from an ultimately homogeneous solution and all the solid product that formed from this homogeneous solution was crystalline zeolite.

Schoeman et al. [37, 38], who investigated the initial stages in the synthesis of TPA-silicalite-1 in apparently clear precursor solutions by both ex-situ and insitu methods, observed subcolloidal particles of 3.8 nm in the precursor solution that grew to 5 nm upon heating and maintained the same size and population all through the synthesis. In addition to these subcolloidal particles, they observed a second particle population of growing size, which they attributed to the growing of silicalite crystals. The subcolloidal particle population of 5 nm size is considered as a nutrient source for the growing crystals. The mechanism through which they supply the nutrients, is either to dissolve and contribute to crystal formation as monomeric silica, or to contribute as aggregates themselves.

Our observation that all the products obtained from the clear solution using TEOS as the silica source was crystalline is in agreement with the findings of Gora et al. [10] and Schoeman et al. [37, 38]. With centrifugation, the

subcolloidal particles of 5 nm mentioned by Schoeman et al. cannot be recovered, and therefore all that was obtained as solid product was highly crystalline MFI. The slightly lower crystallinities at the beginning of synthesis are attributed to the supernatant solution that dried on the precipitated product of centrifugation. At the beginning, as the amount of solid precipitate was low, the amount of supernatant that dried on it was comparable with the amount of precipitate and therefore the crystallinity is affected more by its presence.

Gora et al. [10] commented, based on the results of their study, that this was an advantage for synthesizing a continuous membrane. In their study, when the silica source was fumed silica, which existed in the synthesis solution as a gel, the membrane grew as the gel phase on the support turned into the membrane. They reported that when the gel phase was consumed by the crystal growth, pinholes were likely to remain between the crystals as the density of the gel is smaller than the density of the crystals.

4.2. Characterization of MFI powder obtained during membrane synthesis

As MFI membranes were synthesized in the continuous system, samples were taken from the synthesis solution at different times during the course of synthesis. With the recovered solid products, yield and crystallinity in time were observed. Batch compositions used in membrane synthesis and synthesis temperatures are in Table 4.1. In all syntheses the silica source was TEOS.

Composition Code	ТРАОН	SiO ₂	H ₂ O	EtOH	EtOH mol%	Boiling point of synthesis mixture*	Synthesis temperature
C1s	9.6	80	1380	320	19%	~83°C	80°C
C2	9.6	80	4800	320	6.3%	~87°C	85°C
C3	16	80	1536	320	17%	~83°C	80°C
C5	30	80	1380	320	19%	~83°C	80°C

Table 4.1. Batch compositions and synthesis conditions used in membrane synthesis

 $*P_{atm} = 0.9 atm$



Figure 4.3. Increase of percent yield in time for four different batch compositions

The synthesis temperatures were chosen based on the boiling points of the synthesis solutions, which were determined experimentally by measuring with a thermometer. The synthesis temperature was kept slightly below the boiling point in order to avoid bubbles in the synthesis solution. The reason why the boiling points were low, was because of the ethanol introduced by tetraethylorthosilicate after hydrolysis [26]. The mole percentage of ethanol in the batches are shown in Table 4.1. The boiling points of all batch compositions were around 83°C at the ambient pressure of 0.9 atm, except for composition C2, which had a higher amount of water and therefore a boiling point of around 87°C.

With all compositions, pure MFI was obtained. The increase of yield in time with different compositions showed different behaviour as shown in Figure 4.3. As the amount of TPAOH was increased from 10 moles to 16 moles per 80 moles of SiO_2 and 1500 moles of H_2O in the batch, the rate of crystallization increased and crystallization was completed in about half the time. Further increasing the template to 30 moles did not increase the time to complete crystallization, where crystallization ended after about 50 hours for both batch compositions C3 and C5 and the rate of crystallization was even lower in C5. The approximate rates of crystallization were calculated by taking the slopes of the crystallization curves at midway in the region where the yield was increasing. The rates of crystallization were 9 and 4.5 hr⁻¹ for compositions C3 and C5, respectively. With composition C1s, the rate of crystallization was calculated as 2 hr⁻¹ and maximum yield was achieved at about 115 hours. Increasing the amount of water from 1500 moles per 80 moles SiO_2 to 4800 moles slowed down crystallization where the maximum yield was achieved in about 145 hours and the rate of crystallization with this composition was about 0.95 hr⁻¹. Among the four batch compositions, the composition with the highest ultimate yield was C3. The yield at the end of synthesis was nearly 100% whereas in other batches the yield at the end was lower than the maximum yield.

Figure 4.4 shows the increase of the yield in time with the composition C1s and with the seed synthesis composition, which are very similar except that the seed composition contains alumina and soda and C1s does not. The two compositions



Figure 4.4. Increase of percent yield in time with composition C1 and the seed synthesis composition

show similar behaviour in terms of the yield obtained in time. With the composition C1s, crystallization proceeds a little slower, which may be due to the absence of alumina and soda or due to the decrease in temperature in the silicon tubings in the membrane synthesis system.

Persson et al. [28], who studied the effect of various composition variables on the synthesis of colloidal TPA-silicalite, observed an increase of zeolite yield with time similar to ours, as the amount of TPAOH in the batch increased among batch compositions similar to C1s, C3 and C5. In their study, they observed that as the amount of TPAOH was increased from 9.6 moles to 16 and to 29 moles per 80 moles of SiO₂, 0.32 moles of Na₂O and 1536 moles of H₂O, the mass growth rate continuously increased. The difference in our study may be due to the recovery by centrifugation not being able to recover some small crystals formed from the batch composition C5, which had the highest amount of TPAOH.

In the study by Persson et al. [28], as the amount of TPAOH increased, the particle size decreased, with 300 nm in the batch with 9.6 moles of TPAOH, decreasing to 150 nm in the batch with 16 moles of TPAOH and to 100 nm in the batch with 29 moles of TPAOH. All these submicron crystals were of spherical or nearly spherical shape, as was observed in other studies as well as in ours [27, 28].

4.3. Seeding of support surfaces

The tubular alumina supports were seeded by dip-coating. The seeding step is expected to facilitate the growth of zeolites on the support [17, 12, 39]. In literature, various seeding methods have been used, such as rubbing [40], vacuum seeding [41] and dip-coating [31, 39]. Dip-coating was chosen in this study because it allowed us to coat the support with a thin and uniform layer of seed crystals [24].

The seed suspension was ultrasonicated and mixed before each use in order to redisperse the seeds that had settled. During the dip-coating process which lasts

approximately 5 hours, on the other hand, no precipitation was observed in the seed suspension.

The pH of the seed suspension was adjusted to 8. In a study by Lai et al. [39], a seed suspension pH of 8 resulted in better coverage as compared to a pH of 6. They indicated that this was because the pH of 8 is between the points of zero charge of alumina and silicalite, which are 9 and 7, respectively, and this increases the attraction between the support and the zeolite.

The tubes entered into and exited from the seed suspension very slowly (1-1.5 cm/h) in order not to let the seeds that had attached on the support surface fall and also to cause minimum disturbance in the seed suspension[31].

In another study, Kang et al. [29], after immersing the supports into the seed suspension, heated them for 1 hour at 200°C to adhere the seeds better on the support surface. In this study, the heating was done at 150°C for 4 hours.

The SEM images of the seeded support are shown in Figure 4.5. The support surface is mostly covered by spherical shaped MFI crystals of about 300 nm diameter and the seeds are quite uniform in size. As the pores of the support tubes on the inside were 200 nm, and the size of seed crystals were 300 nm, the seeds could not penetrate inside the pores and therefore coated only the inner surface of the tube.





uncoated spherical portion seed crystals Figure 4.5. Surface SEM micrographs of the seeded alumina tube

There are some portions of the support left uncoated. This is considered to be because of the roughness of the surface, or insufficient cleaning of the support before seeding. Before seeding, the tube shown in Figure 4.5 was only washed with distilled water and then glazed. The tubes used in the syntheses of the membranes were kept in ultrasonic bath for 10 minutes, cleaned with 0.1 M HNO₃ solution, rinsed in distilled water and dried before glazing, as was also described in the experimental methods section. With this cleaning procedure, a smoother and cleaner support surface was aimed and a better coverage of seed crystals is expected. The presence of uncoated portions may also be because dipping the tube only twice into the seed suspension was insufficient.

4.4. Synthesis of membranes in the continuous system and in the batch system

Using the composition $S_{80}T_{16}H_{1536}(E_{320})$ (C3), membranes were synthesized on seeded tubes in the continuous system (PZC90 and PZC100) and in the batch system (PZC99). This composition was chosen among the others because in a short time, it yielded the highest amount of zeolite, as determined by the crystallization curves given in Figure 4.3. The synthesis duration was 72 hours and the flow rate in continuous system syntheses was 6 mL/min. The synthesis variables, thickness of the membranes and their N₂ permeances before calcination are given in Table 4.2. In the synthesis of PZC99 and PZC100, LUDOX-AS-30 colloidal silica was used as silica source instead of TEOS. This allowed the increasing of the synthesis temperature from 80°C to 95°C.

Membrane	Synthesis Medium	Silica Source	Synthesis Temperature (°C)	SEM thickness (µm)	N ₂ Permeance before calcination (mol/m ² .s.Pa)
PZC90	Continuous	TEOS	80	2	10 ⁻⁶
PZC100	Continuous	LUDOX	95	2	10 ⁻¹¹
PZC99	Batch	LUDOX	95	3	10 ⁻¹²

Table 4.2. Synthesis conditions, thickness and pre-calcination N_2 permeances of the membranes prepared using the composition $S_{80}T_{16}H_{1536}(E_{320})$ (C3)



Figure 4.6. XRD patterns of (a) PZC90, (b) PZC100 and (c) PZC99. Dots represent the alumina peaks and arrows represent MFI peaks.



Figure 4.7. XRD patterns of the residual powder obtained from the synthesis of (a) PZC90, (b) PZC100 and (c) PZC99

The crystal phase grown on the supports in all syntheses was identified to be highly crystalline MFI from the XRD patterns of the membranes as well as the XRD patterns of the residual powder from the synthesis of membranes. The XRD patterns of the three membranes are given in Figure 4.6. MFI peaks at Bragg angles of 23°, 24°, 24.5° are seen, however in the pattern of PZC90 they are weak compared to the alumina support peaks. In the patterns of PZC99 and PZC100, the MFI peaks are clearly observable.

By many researchers, the crystal phase found in the residual powder is taken as evidence of the phase that forms the membrane [15, 21]. As seen in Figure 4.7, the XRD patterns of the residual powders obtained at the end of membrane syntheses show highly crystalline MFI. This, in addition to the XRD patterns of the membranes, suggests that the support surface is covered with pure MFI.

The SEM cross-section micrographs of the membranes (Figure 4.8) show thin and continuous zeolite layers. PZC90 and PZC100 have thickness of about 2 μ m, whereas PZC99 has thickness of about 3 μ m and the thicknesses are uniform through the membrane (Figure 4.8). The crystals forming the membrane are randomly oriented and the layers show good intergrowth from the cross-section micrographs. Figure 4.9 shows the surface view of the membranes. As compared to the membranes synthesized with the LUDOX-95°C system (PZC99 and PZC100), on the surface of PZC90 which was synthesized with the TEOS-80°C system there are more voids as seen in Figure 4.9. The intergrowth in PZC99 and PZC100 are much better as seen in their surface micrographs.

Comparing the two membranes prepared with the LUDOX-95°C system, in the continuous and batch systems, in PZC100, which was synthesized in the continuous system, the crystals forming the membrane are smaller, spherical, more intergrown and the layer is more homogeneous when compared to PZC99, which was synthesized in the batch system. In PZC99, in addition to the film grown, there are particles of size around 1 μ m settled on the film. The morphological differences between membranes synthesized in the continuous and batch systems will be discussed in more detail in Section 4.7.



Figure 4.8. Cross-section micrographs of (a) PZC90, (b) PZC100, with wide and closer views and PZC99 (c)



Figure 4.9. Surface micrographs of (a) PZC90, (b) PZC100 and PZC99 (c)

The N₂ permeances of the membranes were measured before calcination. PZC90, after synthesis had a N₂ permeation of 7 x 10^{-6} mol/m².s.Pa, indicating that there exists nonzeolitic pores on the membrane. PZC99 and PZC100, on the other hand, had pre-calcination N₂ permeances of 10^{-12} and 10^{-11} mol/m².s.Pa, indicating that the supports are fully covered with continuous zeolite layers. In this study the membranes with pre-calcination N₂ permeances of smaller than 10^{-11} mol/m².s.Pa were considered impermeable. This is also an accepted value in literature for He or N₂ permeance before calcination as the MFI pores are occluded by the template molecule [32, 33].

As a conclusion, with the TEOS-80°C system, as evaluated with pre-calcination N_2 permeances, the XRD patterns and SEM images, a defect-free zeolite membrane could not be synthesized, whereas with the LUDOX-95°C system, an essentially defect-free membrane was synthesized in a single synthesis step, both in the continuous and batch systems.

4.5. Effect of consecutive synthesis on membrane morphology

A commonly used method in the preparation of defect-free zeolite membranes is to use multiple synthesis steps [29, 13]. After the synthesis of the first zeolite layer, with or without calcining the layer, a second layer is synthesized using a new synthesis solution. These consecutive syntheses are carried on until the membrane becomes impermeable to N_2 or another gas chosen as the probe molecule. In this study the probe molecule used was N_2 .

Using the composition $S_{80}T_{16}H_{1536}E_{320}$ the membranes PZC97-III, PZC98-III and using the composition $A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$, PZC85-III were synthesized in the continuous system by synthesizing consecutively three layers of zeolite. In the membranes synthesized in the continuous system, 6 mL/min flowrate was used. All syntheses were carried out at 80°C, with TEOS as the silica source. PZC86-II was synthesized in the batch system with two consecutive synthesis steps using the composition $A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$ again at 80°C and with TEOS. The synthesis conditions are given in Table 4.3.

Membrane	Synthesis medium	Batch Composition	Synthesis Duration (h)	N ₂ Permeance before calcination (mol/m ² .s.Pa)	SEM thickness (µm)
PZC97-III	Continuous	$S_{80} T_{16} H_{1536} E_{320}$	3 X 72	10 ⁻⁸	4
PZC98-III	Continuous	$S_{80} T_{16} H_{1536} E_{320}$	76 + 101 + 93	10 ⁻¹¹	4
PZC85- III	Continuous	$A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$	3 X 72	10-7	30
PZC86-II	Batch	$A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$	2 X 72	10-11	7

Table 4.3. Synthesis conditions thicknesses and pre-calcination N_2 permeances of the membranes prepared with consecutive synthesis steps

PZC 97-III and PZC98-III were synthesized under the same conditions except that in the synthesis of PZC98-III silicon oil bath was used around the synthesis medium, as was explained in the experimental section. The pre-calcination N_2 permeance of PZC 97-III dropped from 10^{-5} to 10^{-8} mol/m².s.Pa after the synthesis of the third layer, whereas that of PZC 98-III dropped from 10^{-6} to 10^{-11} mol/m².s.Pa. The pre-calcination N_2 permeances of all the layers of PZC97-III, PZC98-III and also those of PZC85-III and PZC86-II are given in Table 4.4.

The cross-section of both show continuous films of thickness about 4 μ m (Figure 4.10). No indication of multilayer is seen in the film. From the surface micrograph, the films look very similar, as in both membranes the support is covered fully and the film is well-intergrown (Figure 4.11).

Mombranac	N ₂ Permeance (mol/m ² .s.Pa)					
Membranes	1 st layer	2 nd layer	3 rd layer			
PZC97-III	10 ⁻⁵	10 ⁻⁷	10 ⁻⁸			
PZC98-III	10 ⁻⁶	10 ⁻⁷	10 ⁻¹¹			
PZC85-III	10 ⁻⁵	10 ⁻⁶	10 ⁻⁷			
PZC86-II	10 ⁻⁷	10 ⁻¹¹	no 3 rd layer			

Table 4.4. The precalcination N_2 permeation of each layer for the membranes consisting of multiple layers



Figure 4.10. Cross-section micrographs of PZC97-III (a) and PZC98-III (b)



Figure 4.11. Surface micrographs of PZC97-III (a) and PZC98-III (b)

Considering these two membranes together with PZC90 (Figure 4.8.a), which is the membrane synthesized under the same conditions with a single synthesis step, after the synthesis of three layers the thickness of the membrane had increased from 2 μ m to only 4 μ m. Yet, the N₂ permeance before calcination had dropped from 10⁻⁶ to 10⁻¹¹ mol/m².s.Pa. This implies that, what was a thin zeolite layer containing nonzeolitic pores after the synthesis of a single layer, was "patched" through the synthesis of the second and third layers. The membrane after the synthesis of the third layer is still thin, however it contains much less nonzeolitic pores as indicated by the drop in the N₂ permeance.

PZC86-II, synthesized using composition $A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$ in the batch system became impermeable to N_2 after the synthesis of the second layer. The SEM cross-section of PZC 86-II shows a continuous layer of 7 µm thickness (Figure 4.12.a). From the surface, the membrane consists of well-intergrown crystals (Figure 4.12.b). Figure 4.12.c shows that there are cracks on the film, which probably occurred during calcination, either during the calcination after synthesis or the calcination in between butane permeation experiments.



Figure 4.12. The cross-section (a) and surface (b and c) micrographs of PZC86-II. In (c), a crack on the membrane surface is seen.

PZC85-III, which was synthesized with the same composition $A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$ in the continuous system had a N_2 permeance of 10^{-5} mol/m².s.Pa after the synthesis of the first layer and this permeance dropped only to 10^{-7} mol/m².s.Pa after the synthesis of the third layer, indicating that pinholes remained in the membrane layer.

The SEM images of the cross-section and surface of PZC85-III are shown in Figure 4.13. The membrane has a thickness of 30 μ m. It is homogeneous in thickness and very dense. Looking at the surface view the film looks very-well intergrown as the crystals forming the film cannot be distinguished separately from each other. It looks almost like a single crystal, as from the cross-section the appearance is very smooth. On the right bottom corner of Figure 4.13.c, which shows the cross-section of PZC85-III, there is the sign of a crystal broken, yet nowhere else is there any sign of crystal boundaries. This shows that the layer is indeed a zeolite layer and not amorphous as might be suspected regarding the unusually dense appearance and the N₂ permeance before calcination. From the surface the membrane looks like it is growing in spherical crystals, more like the growth of new material on the dense zeolite layer described, rather than the intergrowth of separate crystals (Figure 4.13.b). Apart from this, as the membrane is permeable to nitrogen before calcination, there should be pinholes in the zeolite layer.

The membrane PZC86-II, which was synthesized with the same batch composition and at the same temperature in the batch system, when compared to PZC85-III consists of crystals with a more rectangular shape, well-intergrown in each other (Figure 4.12.b). There are larger particles that settled on the film like in PZC99, which was synthesized in the batch system also. From the cross-section, unlike PZC85-III, the grain boundaries forming the membrane are observable (Figure 4.12.a). PZC86-II is much thinner, with a thickness of 7 μ m, compared to the 30 μ m-thick PZC85-III.

In the membranes PZC97-III and PZC98-III synthesized with composition $S_{80}T_{16}H_{1536}E_{320}$ the synthesis of consecutive layers resulted in N₂-impermeable membranes. In PZC85-III, which was synthesized with the composition $A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$, which contained less TPAOH and had Al_2O_3 and Na_2O ,
although the appearance in SEM images shows a well-intergrown zeolite layer, a film that is impermeable before calcination was not obtained after the synthesis



of three layers. Using the same composition, in the batch system on the other hand, a membrane that is N_2 -impermeable before calcination was obtained after the synthesis of two layers.

4.6. Effect of TPAOH amount on membrane synthesis

Membranes with a single layer were synthesized using three different amounts of TPAOH, as shown in Table 4.5. Apart from three different amounts of TPAOH, in the synthesis of PZC89, the water amount was changed. All the membranes mentioned were prepared in the continuous system using a flowrate of 6 mL/min and the silica source used in synthesis was TEOS. The analysis of the powder obtained from the syntheses was reported in Section 4.2.

Т	able 4.5	. Synthes	is c	onditions,	th	icknesses	and	l pre-calci	ination N_2 p	ermeance	s
0	of the me	embranes	pre	pared with	di	fferent ba	tch	compositi	ons		_
									N. Permeance	2	1

Membrane	Composition Code	Batch Composition	Synthesis Temperature (°C)	Synthesis Duration (h)	N ₂ Permeance before calcination (mol/m ² .s.Pa)	SEM thickness (µm)
PZC89	C2	$S_{80}T_{9.8}H_{4800}E_{320}$	85	124	not measured	3
PZC90	C3	$S_{80}T_{16}H_{1536}E_{320}$	80	72	10 ⁻⁵	2
PZC94	C5	$S_{80}T_{30}H_{1380}E_{320}$	80	72	10 ⁻⁶	8
PZC95	C1s	$S_{80}T_{9.6}H_{1380}E_{320}$	80	114	10 ⁻⁶	3

In the membranes PZC95, PZC90 and PZC94, the TPAOH amount was increased starting from 9.6 to 16 and finally to 30. In all, continuous films were obtained, looking at the SEM cross-section images (Figure 4.14). PZC95 and PZC90 had thickness of 3 and 2 μ m, respectively. As the TPAOH amount was increased to 30 moles, the zeolite layer became as thick as 8 μ m. From the surface micrographs, PZC95 consists of crystals of around 500 nm, PZC90 of crystals about 300 nm and PZC 94 of smaller crystals, such that the crystals cannot be distinguished in the SEM image (Figure 4.15). Intergrowth is better in PZC94 that it is in PZC95 and PZC90, regarding the voids observable in PZC95 and PZC90. Persson et al. [28] who synthesized MFI powder with similar compositions, observed that the crystal size decreased with increasing TPAOH amount in the batch.



Figure 4.14. Cross-section micrographs of PZC89 (a),PZC90 (b),PZC94 (c),and PZC95 (d)



Figure 4.15. Surface micrographs of PZC89 (a), PZC90 (b), PZC94 (c), and PZC95 (d)

Wong et al. [42] also reported that as TPAOH amount was increased zeolite growth became faster. They worked with higher amounts of H_2O and lower amounts of TPAOH per silica as compared to this study and that of Persson et al. [28]. They observed that as they increased the amount of TPAOH in the batch, intergrowth was improved but the crystals forming the membrane became larger and more rectangular in shape.

The membrane PZC89, synthesized with the composition C2, which contains more water than the other compositions, is a layer of about 3 μ m thickness. The coverage is good, as seen from the surface view, but voids are also seen between the crystals forming the film. Apart from the smaller crystals of about 500 nm forming the intergrown layer, there are larger, twinned crystals of about 1 μ m that are probably settled on the membrane from the bulk.

As given in Table 4.5, the membranes PZC90, PZC94 and PZC95 were permeable to N_2 after the synthesis of only a single layer, before calcination. (The N_2 permeance of PZC89 could not be measured.) This shows that although continuous layers are observed by SEM images, there exists considerable amount of nonzeolitic pores in the membrane layers.

4.7. Evaluation of film morphologies

The MFI membranes in literature are prepared mostly at higher temperatures ranging from 150-180°C [24, 15, 20]. The membranes prepared at such high temperatures have different appearance when compared to the membranes prepared in this study and also the membranes prepared at lower temperatures in literature. The films synthesized at high temperatures usually tend to be thicker, composed of larger and rectangular or coffin-shaped crystals. The powder synthesized at high temperatures also has these shapes. MFI powder synthesized at temperatures around 100°C, on the other hand, has spherical shape [28, 27]. Similarly, in MFI membranes synthesized at such low temperatures, the crystals forming the membranes are usually more globular rather than edged [12], as was observed in this study also.

Thin membranes of $0.5 - 3.5 \mu m$ have been synthesized at temperatures around 100°C in literature [12, 13]. Schoeman et al. [25], who prepared TPA-silicalite-1 films on single crystal silicon wafers at 100°C reported that the synthesis at high temperatures and low temperatures necessitated different synthesis variables to form a continuous zeolite film mainly due to the lower crystal growth rates.

In the single study on the synthesis of MFI membranes in a flow system [5], synthesis was done at 150°C and the films obtained had a thickness of 30 μ m, and the film consists of rectangular shaped crystals intergrown in each other with a columnar structure from the cross-section view. Regarding the synthesis conditions and the membrane obtained, although a flow system was used, this study is quite different from ours.

The membranes synthesized in the continuous system, except the 30 μ m-thick membrane PZC85-III, had thicknesses of 2-8 μ m. The films consist of crystals of round shape, intergrown in each other, similar to the membranes synthesized at temperatures around 100°C in literature.

When we compare the membranes synthesized in the continuous and batch systems, the membranes synthesized in the continuous system are composed of smaller crystals intergrown in each other. In specific, we can compare the two membranes PZC99 and PZC100. PZC99 was synthesized in the batch system and PZC100 in the continuous system. PZC100 consists of smaller crystals of more uniform size and more intergrown appearance as compared to PZC99. Similarly, PZC86-II consists of larger crystals with shapes approaching rectangular, which are not observed in any of the membranes synthesized in the continuous system.

During the course of zeolite membrane synthesis, zeolites can grow either on the surface of the support, or they can grow in the bulk solution. Both can contribute to the growing of the zeolite layer, since as well as the zeolite layer growing directly on the support – or the seed layer on the support – zeolite crystals or precursors to zeolite crystal formation, which are forming in the bulk, may deposit on the growing zeolite layer and form a part of the zeolite film. Nakazawa et al. [43] who investigated the early stages of MFI film formation in their studies suggested two routes in film formation. In one of the routes, the gel layer that formed on the substrate grew to yield a zeolite layer. And in the other route, the particles, be it gel or crystalline, deposited on the growing film. They observed in some of the MFI films they grew, an oriented layer adhered tightly to the substrate and on top of that layer a randomly-oriented layer more weakly adhered. They commented that the oriented layer may be due to the film that grew directly on the support and the randomly oriented layer on top due to the crystals deposited from the bulk.

In a batch system, both routes can equally contribute to film formation. On the other hand, in a system where the synthesis solution is flown over the support, the deposition of material from the bulk solution is very little or none at all, as the flow sweeps away any particle that had attached yet weakly on the film surface or any particle that can potentially attach on the film. Tsutsumi and Satoshi [6] who studied the synthesis of LTA membranes by the typical batch method and by the circulated solution method, which is similar to the method used in this study, reached a similar conclusion. In their study, they observed LTA films consisting of cubic shaped LTA crystals when they synthesized the films with the batch method. When the circulated solution method was used, on the other hand, the crystals forming the film were globular and smaller than those in the batch method. They argued that the globular shape of the crystals as well as their smaller sizes might be due to the flowing of the synthesis solution over the film. As the solution continuously flew over the substrate, it hindered the β -cages from combining into a cube, rendering the zeolite crystals smaller and rounded shaped.

The more intergrown appearance and the smaller crystals forming the membranes synthesized in the continuous system in this study can also be attributed to the flow, preventing attachment of particles from the bulk onto the membrane. As the flow prevented clinging of particles – amorphous or crystalline – onto the zeolite layer, the membranes grown in the continuous system ended up more homogeneous as compared to the ones grown in the batch system. Compared to the batch system, more of what grows as the

membrane came from what actually grew on the support. Clinging of building units that will form the zeolite, or the zeolite crystals that formed in the bulk was much less in the continuous system, and therefore the crystals forming the film were smaller. Also the films were more homogeneous and intergrowth was more, as the majority – if not all – of the membrane growth came from the same source, that is the growth of the zeolite onto the film on the support. On the contrary, in the batch system, in addition to the growth on the film that exists on the support, the building units, amorphous material and crystals from the bulk had the chance to settle on the growing film. As a result, growing of the membrane on the support went on from these various sources, resulting in a membrane with more varied properties.

This is indeed an advantage of the continuous system. Considering the case where, unlike the batch system where settling of crystals or smaller building units also takes place, the growth of the zeolite membrane in the continuous system is mainly due to the growth that takes place directly on the support, this can make possible the fine tuning of membrane properties like synthesis of preferentially oriented membranes as observed by Nakazawa et al. [43] or membranes consisting of monomodal sized crystallites as observed in this study.

4.8. Gas permeation properties of the membranes

All the membranes that were impermeable to N₂ before calcination were evaluated with gas permeances. In addition to these membranes, PZC97-III and PZC85-III, which had pre-calcination N₂ permeances of 10^{-8} and 10^{-7} mol/m².s.Pa, respectively were also calcined and evaluated with gas permeances. The four membranes PZC89, PZC90, PZC94 and PZC95, which had N₂ permeances of $10^{-6} - 10^{-7}$ mol/m².s.Pa before calcination were not calcined for gas permeation testing.

The gas pairs N₂ - SF₆ and n-C₄H₁₀ - i-C₄H₁₀ are two pairs widely used in the evaluation of MFI membrane performances. MFI type membranes show selectivity for N₂ over SF₆ because N₂ with a kinetic diameter of 0.36 nm [1] diffuses easily through the zeolite's pores whereas the bulkier SF₆ molecule with a kinetic diameter of 0.58 nm [1] is excluded. Funke et al. used a N₂/SF₆ ideal

selectivity of 80 as a quality criterion for their membranes [15]. On the other hand Macdougal et al. [22] have claimed that N_2/SF_6 selectivity in a defect free silicalite membrane can be as low as 4, and that higher N_2/SF_6 selectivities reported in literature are attributed to the transport of SF₆ being reduced by grain boundaries.

Selectivity between two butane isomers is another commonly used means of evaluating MFI type membranes [13, 23, 26]. These two molecules, being isomers, cannot be separated in mesopores by Knudsen diffusion. Where both isomers fit in MFI pores, the selectivity between them is governed by their diffusion mobilities [13, 23]. Van de Graaf et al. [23] considered an ideal selectivity of 10 at room temperature or higher as a quality criterion for their membranes. Similarly, Vroon et al. [13] considered a mixture selectivity of 10 or higher at 200°C as their quality criterion. The selectivity for these isomers varies with temperature since at room temperature more is adsorbed but the adsorbed molecules move slower and as temperature increases the amount adsorbed gets less but the adsorbed molecules move faster. As the change in these properties with varying temperature follow different trends for the two isomers, selectivity as a function of temperature [14].

In Table 4.6 the N₂ permeances and N₂/SF₆ selectivities of the membranes synthesized in both the continuous and batch systems are shown. All membranes except PZC85-III showed selectivities over the Knudsen selectivity of 2.28. PZC85-III, despite its thick and dense structure contained nonzeolitic pores as it was permeable to N₂ before calcination also. Among the membranes synthesized in the continuous system, the ones synthesized with the LUDOX-95°C system showed higher selectivities of 11 and 9.1, compared to the ones synthesized with the TEOS-80°C system. Among these membranes PZC100 and PZC101, PZC100 was synthesized using a flowrate of 6 mL/min and PZC101 with 24 mL/min in the continuous system.

Membrane	Synthesis medium	N ₂ Permeance (mol/m ² .s.Pa)	SF ₆ Permeance (mol/m ² .s.Pa)	N_2/SF_6
PZC85-III	Continuous (6 mL/min)	8.28 x 10 ⁻⁷	5.38 x 10 ⁻⁷	1.6
PZC97-III	Continuous (6 mL/min)	3.84 x 10 ⁻⁷	7.18 x 10 ⁻⁸	5.3
PZC98-III	Continuous (6 mL/min)	3.58 x 10 ⁻⁷	7.30 x 10 ⁻⁸	4.9
PZC100	Continuous (6 mL/min)	4.38 x 10 ⁻⁷	3.95 x 10 ⁻⁸	11
PZC101	Continuous (24 mL/min)	2.25 x 10 ⁻⁷	2.46 x 10 ⁻⁸	9.1
PZC86-II	Batch	4.03x 10 ⁻⁷	5.71 x 10 ⁻⁸	7.1
PZC91-II	Batch	9.03 x 10 ⁻⁷	1.14 x 10 ⁻⁷	7.9
PZC99	Batch	3.42 x 10 ⁻⁷	1.26 x 10 ⁻⁸	27

Table 4.6. N_2 permeances and N_2/SF_6 selectivities of the membranes

When membranes synthesized using the same composition in the continuous and batch systems are compared with each other, the membranes PZC86-II and PZC91-II, had higher N_2/SF_6 selectivities of 7.0 and 7.9, respectively, compared to PZC85-III, whose N_2/SF_6 selectivity was only 1.6. Similarly, PZC99 has a selectivity of 27, which is higher than the selectivities of the two membranes synthesized in the continuous system, using the LUDOX-95°C system.

For N_2 and SF_6 permeances, higher selectivities in the membranes synthesized in autoclaves did not result in much lowered permeances, which is a compromise in membrane processes. All membranes had N_2 permeances to the order of 10^{-7} mol/m².s.Pa.

In Table 4.7 the $n-C_4H_{10}$ permeances and $n-C_4H_{10}/i-C_4H_{10}$ ideal selectivities and mixture selectivities of the membranes synthesized in both the continuous and batch systems are shown. The membranes PZC97-III and PZC98-III, synthesized with the TEOS-80°C system showed selectivities slightly higher than the Knudsen selectivity, in both ideal selectivity and mixture selectivity,

Table 4.7. n-C ₄ H ₁₀ permeances and n-C ₄ H ₁₀ /i-C ₄ H ₁₀ selectivities (ideal and mixture) of the membrane	s
(a) Membranes synthesized in the continuous system	

Mombrano	n-C4	H ₁₀ permean	ce (mol/m².s	Ideal selectivities				
Membrane	RT	100°C	150°C	200°C	RT	100°C	150°C	200°C
PZC97-III	3.12E-07	-	-	2.29E-07	1.9	-	-	3.0
PZC98-III	2.31E-07	-	-	2.11E-07	1.9	-	-	3.0
PZC100	1.66E-07	5.17E-07	5.79E-07	4.21E-07	5.8	7.7	10.6	10.6
PZC101	1.06E-07	4.24E-07	4.81E-07	4.01E-07	70.7	17.5	47.6	71.4
Mombrano	n-C	H ₁₀ permean	ce (mol/m².s	.Pa)	Bir	nary mixture	selectivities	S
Membrane	n-C RT	H ₁₀ permeand 100°C	ce (mol/m².s 150°C	.Pa) 200°C	Bir RT	nary mixture 100°C	selectivities 150°C	s 200°C
Membrane PZC97-III	n-C RT 1.92E-07	H ₁₀ permeand 100°C -	ce (mol/m ² .s 150°C -	.Pa) 200°C -	Bir RT 1.5	nary mixture 100°C -	selectivitie: 150°C -	s 200°C -
Membrane PZC97-III PZC98-III	n-C 2 RT 1.92E-07 1.77E-07	H ₁₀ permeand 100°C - 1.77E-07	ce (mol/m ² .s 150°C - -	.Pa) 200°C - 9.54E-08	Bir RT 1.5 2.3	ary mixture 100°C - 2.1	selectivities 150°C - -	s 200°C - 1.4
Membrane PZC97-III PZC98-III PZC100	n-C 2 RT 1.92E-07 1.77E-07 3.57E-08	H ₁₀ permeand 100°C - 1.77E-07 2.07E-07	ce (mol/m².s 150°C - - 2.52E-07	.Pa) 200°C - 9.54E-08 2.12E-07	Bir RT 1.5 2.3 4.3	nary mixture 100°C - 2.1 5.9	selectivitie 150°C - - 6.4	200°C - 1.4 6.1

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(b) Membranes synthesized in the static system

Mombrano	n-C₄	H ₁₀ permean	ce (mol/m².s	Ideal selectivities					
Membrane	RT	100°C	150°C	200°C	RT	100°C	150°C	200°C	
PZC86-II	1.13E-07	-	-	2.52E-07	6.9	-	-	7.5	
PZC91-II	6.24E-07	-	-	5.37E-07	1.6	-	-	3.1	
PZC99	1.05E-08	2.29E-07	3.06E-07	2.90E-07	17.8	69.4	261.5	66.7	
Mombrano	n-C₄	H ₁₀ permean	ce (mol/m².s	.Pa)	Binary mixture selectivities				
Membrane	RT	100°C	150°C	200°C	RT	100°C	150°C	200°C	
PZC86-II	1.31E-07	-	-	-	1.6	-	-	-	
PZC99	5.53E-09	4.67E-08	1.25E-08	1.53E-08	6.6	11.2	6.4	6.1	

indicating the presence of nonzeolitic pores in addition to the zeolite pores. As in N_2/SF_6 selectivities, the membranes synthesized with the LUDOX-95°C system, on the other hand, showed higher selectivities, indicating much less nonzeolitic pores.

The ideal selectivities of PZC100 synthesized in the continuous system with a flowrate of 6 mL/min, was 5.8 at room temperature increasing to 10.6 at 150°C and 200°C, which is over the quality criterion accepted by various researchers [13,23]. The ideal selectivities of PZC101, which was synthesized using a higher flowrate of 24 mL/min, were higher. At room temperature the selectivity was 70.7, showing a minimum of 17.5 at 100°C and increasing to 71.4 at 200°C.

The mixture selectivities of these two membranes, on the other hand, were similar. The mixture selectivity of PZC100 was 4.3 at room temperature, and around 6 at higher temperatures of 100, 150 and 200°C. The mixture selectivity of PZC101 was 7.7 at room temperature and around 7 at higher temperatures of 100, 150 and 200°C.

PZC99, synthesized in the batch system, showed ideal selectivities to n- C_4H_{10} over i- C_4H_{10} , which increased from 17.8 at room temperature to 262.5 at 150°C and dropped back to 66.7. Although, especially the selectivity of 262.5 at 150°C was quite high compared to other selectivities in this study and also the ones reported in literature, the mixture selectivities of this membrane were also similar to the membranes PZC100 and PZC101, synthesized in the continuous system. The selectivity was 6.6 at room temperature, showed a maximum at 11.2 and dropped back to 6.1 at 200°C.

Considering all the membranes synthesized in the continuous system, all except PZC85-III showed selectivities higher than the Knudsen selectivities. The membranes synthesized in the LUDOX-95°C system show higher selectivities both to N_2 over SF₆ and to n- C₄H₁₀ over i- C₄H₁₀, compared to the ones synthesized in the TEOS-80°C system.

Considering the membranes synthesized in the continuous system, some of the selectivities were lower than the ones synthesized in the batch system and some

were similar values. Regarding the morphological differences observed, the differences in selectivities can be attributed to the two membranes having different morphologies, and not necessarily the membranes synthesized in the continuous system having more defects or nonzeolitic pores.

4.9. Comparison of the membranes synthesized in this study and the membranes reported in literature

Figure 4.16 shows the N_2 permeance and N_2/SF_6 ideal selectivities of membranes reported in literature and the membranes prepared in this study. Similarly in Figure 4.17, the $n-C_4H_{10}$ permeance and $n-C_4H_{10}/i-C_4H_{10}$ ideal selectivities of the membranes at room temperature are shown. The plots are given with the selectivity on one axis and the permeance of the faster permeating component on the other, as these two properties are what define a membrane.

Data in literature form a wide distribution in the plots of selectivity versus permeance for both gas pairs. All the data from literature belong to membranes synthesized in batch systems mostly at temperatures higher than 150°C. The membranes synthesized at temperatures lower than 100°C are indicated with different symbols. As the permeance-selectivity pair for these gas pairs are dependent on membrane thickness and morphology, and these in turn are dependent on the synthesis conditions, comparing the membranes synthesized in this study with the membranes synthesized at low temperatures will be more suitable.

Looking at the permeation data for the N_2/SF_6 pair, the membranes synthesized in this study, in both continuous and batch systems, are comparable to the membranes synthesized in batch systems reported in literature. The permeances are moderate and the selectivities are around 10 for the membranes synthesized in the continuous system. The membranes from literature included in this plot are mainly synthesized at temperatures higher



Figure 4.16 - Gas permeation for N_2 -SF₆ pair of membranes from this study and from literature

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Figure 4.17 - Gas permeation at room temperature for $n-C_4H_{10}$ - $i-C_4H_{10}$ pair of membranes from this study and from literature

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than 150°C. The only membranes synthesized at temperatures close to ours are those of Hedlund et al [12, 26], synthesized at 100°C, with support masking, that is by filling the supports before synthesis and then burning off the material in the supports after synthesis. The membranes were seeded with 50 nm silicalite by dip-coating the supports previously coated by a cationic polymer to provide better attaching of the seeds on the support. By this way, they were able to synthesize membranes with N₂ fluxes of around 10⁻⁵ mol/m².s.Pa. The selectivities of these membranes were between 8 and 22. As was reported by Macdougal et al [22], higher N₂/SF₆ selectivities are not necessarily an indication of a better membrane but could be a function of grain boundaries in the membrane layer.

The only MFI membranes synthesized in a flow system in literature are those synthesized by Richter et al. [5] by renewing the synthesis solution at a slow rate. It was reported that these membranes had H_2/SF_6 selectivities of 22-31 and H_2 permeances of 4.0-4.7 x 10⁻⁷ mol/m².s.Pa. To compare these values with those in this study, we can consider that in MFI pores N₂ and H₂ are separated by Knudsen diffusion, as they can both easily pass through the pores. With the Knudsen selectivity of 3.74, the H_2/SF_6 selectivities and H_2 permeances correspond to N₂/SF₆ selectivities of 6-8 and N₂ permeances of 1-1.25 x 10⁻⁷ mol/m².s.Pa. In this study, membranes with higher selectivity and higher permeance have been prepared. In addition to this, the membranes in this study have been prepared at a much lower temperature (95°C compared to 150°C) and were much thinner (2-3 µm compared to 30 µm).

Looking at the permeation data for the $n-C_4H_{10}/i-C_4H_{10}$ pair, the membranes synthesized in this study are again of comparable selectivity with many of the membranes reported in literature. The permeances of the membranes synthesized in the continuous system are higher than most of the membranes in literature. PZC101, which was synthesized in the continuous system with a higher flowrate of 24 mL/min, showed an ideal selectivity of 70.7 at room temperature accompanied with a flux of 10^{-7} mol/m².s.Pa. The low temperature reports from literature again include the membranes synthesized by Hedlund et al. [12, 26] by support masking, and the membranes synthesized by Kang et al [29] inside the pores of alumina tubes. With two different approaches in synthesis, in these studies, membranes of $n-C_4H_{10}$ permeance similar to those in this study were reported with selectivities ranging between 9-37.

It must be considered that among many MFI membranes reported in literature, very few are synthesized at temperatures below 100°C as in this study. In comparing the gas permeation results of the membranes, this factor was also taken into account. The membranes synthesized at low temperatures are generally thinner than those synthesized at higher temperatures. This results, not only in thinner membranes, which shows itself as higher permeances, but probably also in different film morphologies, which affect the selectivities.

Considering that these membranes are the first MFI type membranes synthesized in a continuous system with circulation of the synthesis solution, therefore, it is concluded that the method used in this study is promising for the synthesis of zeolite membranes. Apart from the practical and economical advantages the method will possibly have in large-scale synthesis, the different synthesis mechanism discussed can provide other advantages such as the possibility of synthesizing preferentially oriented membranes or membranes consisting of monomodal sized crystallites.

CHAPTER 5

CONCLUSION

In this study, thin MFI type membranes (2-4 μ m) were synthesized on tubular alumina supports at temperatures of 80-95°C and at atmospheric pressure using a continuous system where the synthesis solution is circulated through the membrane during synthesis. The membranes prepared using this method were found to be comparable with membranes prepared in the conventional static system in autoclaves.

The membranes prepared using colloidal silica (LUDOX) as the silica source at 95°C showed better gas separation performance when compared to the membranes prepared using monomeric silica (TEOS) as the silica source at 80°C. Using the LUDOX-95°C system, membranes that are N₂-impermeable before calcination were synthesized after only a single synthesis step, whereas with the TEOS-80°C system, this took three consecutive synthesis steps. The membrane synthesized with the composition $S_{80}T_{16}H_{1536}$ using the LUDOX-95°C system in the continuous system with a flowrate of 6 mL/min, when compared to the membrane synthesized with the same composition and at the same temperature in the static system, was thinner and more homogeneous. The two membranes synthesized using flowrates of 6 and 24 mL/min in the continuous system showed similar selectivities for the gas pairs N₂-SF₆ and the butane isomers. Both were comparable to the membrane synthesized in the static system in their butane isomer mixture selectivities.

The effect of batch composition on the zeolite film properties was investigated. It was seen that increasing the TPAOH amount in the batch resulted in faster crystallization and smaller crystals forming the film. With the highest TPAOH amount used, in the composition $S_{80}T_{30}H_{1536}E_{320}$, a 8 µm-thick film was obtained whereas in all other compositions the film thicknesses were around 2-3 µm.

Increasing the amount of water in the batch resulted in slower crystallization and larger crystals.

The membranes prepared in the continuous system in this study were of comparable quality with the membranes reported in literature synthesized under similar conditions, such as low temperatures, but in the conventional batch system. The method suggested therefore is considered to be a simple and promising method for the synthesis of zeolite membranes.

RECOMMENDATIONS

Thin and continuous MFI membranes have been synthesized on the inner surface of tubular alumina supports in a continuous system. In addition to what has been done in this study, suggestions on further work to be done are as follows:

- Synthesis can be done using higher flowrates. As very high flowrates have the possibility of sweeping away the seeds on the support, a low flowrate for the first layer and a higher flowrate in the second layer can be applied.
- Membranes can be prepared with consecutive layers using different compositions for each layer. For instance, after synthesizing the first layer with the composition $S_{80}T_{16}H_{1536}(E_{320})$ (used in the synthesis of PZC90, PZC98-III, PZC100, etc.) or $A_1N_{1.3}S_{80}T_{9.9}H_{1630}(E_{320})$ (used in the synthesis of PZC85-III), a second layer can be synthesized with the composition $S_{80}T_{30}H_{1380}(E_{320})$ which has a high growth rate, yields small crystals and a thick zeolite layer (8 µm, in PZC95). The second layer composition can be used to fill non-zeolitic pores with its high growth rate and the small crystals it forms.
- After a dip-coating step and the synthesis of the zeolite layer, before synthesizing a second layer an intermediate seeding step can be performed just like the one performed initially and the second layer can be synthesized after this second seeding step.
- Synthesis can be performed on more complex support geometries such as monoliths, and on larger supports.
- Other zeolite membranes can also be prepared using this continuous system.

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APPENDIX A

CALCULATION OF SYNTHESIS RECIPE FROM A BATCH COMPOSITION

Materials used:

Sodium aluminate: Riedel-de-Haen, 44% Na₂O, 55% Al₂O₃, 1% H₂O (by weight) Tetraethylorthosilicate ($C_8H_{20}O_4Si$): Merck, 98%, 208.3 g/mol

Tetrapropylammonium hydroxide ($C_{12}H_{29}NO$): Acros, 25 wt% in water, 203.4 g/mol

Deionised water (H₂O): 18.015 g/mol

Batch composition: $A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$

1 mole $AI_2O_3x \frac{101.957 \text{ gr}}{1 \text{ mole}} = 101.957 \text{ gr} AI_2O_3$

Sodium aluminate composition: 44% Na₂O, 55% Al₂O₃, 1% H₂O

For 101.957 grams of Al₂O₃,

101.957 gr $Al_2O_3x \frac{100 \text{ gr sodium aluminate}}{55 \text{ gr } Al_2O_3} = 185.376 \text{ gr sodium aluminate}$

In 185.376 grams of sodium aluminate,

 $185.376 \text{ gr sodium aluminate} \times \frac{44 \text{ gr Na}_2\text{O}}{100 \text{ gr}} \times \frac{1 \text{ mole}}{61.979 \text{ gr Na}_2\text{O}} = 1.316 \text{ mol Na}_2\text{O}$

 $185.376 \text{ gr sodium aluminate} \times \frac{1 \text{ gr } \text{H}_2\text{O}}{100 \text{ gr}} \times \frac{18.015 \text{ gr}}{1 \text{ mole } \text{H}_2\text{O}} = 33.395 \text{ gr } \text{H}_2\text{O}$

In 5 wt% sodium aluminate solution,

185.376 gr sodium aluminate $\times \frac{100 \text{ gr solution}}{5 \text{ gr}} = 3707.520 \text{ gr solution}$

In 3707.520 gr sodium aluminate solution,

3707.520 gr sodium aluminate soln. × $\frac{95 \text{ gr H}_2\text{O}}{100 \text{ gr soln}}$ = 3522.144 gr H₂O

80 mole SiO₂x
$$\frac{1 \text{ mole TEOS}}{1 \text{ mole SiO}_2} \times \frac{208.3 \text{ gr}}{1 \text{ mole TEOS}} \times \frac{100}{98} = 1700.408 \text{ gr TEOS} (98\%)$$

9.9 mole TPAOHx $\frac{203.4 \text{ gr}}{1 \text{ mole}} = 2013.660 \text{ gr}$ TPAOH

 $2013.660 \text{ gr TPAOH} \times \frac{100 \text{ gr TPAOH}(25\%)}{25 \text{ gr TPAOH}} = 8054.640 \text{ gr TPAOH}(25\text{wt}\%)$

In 8054.640 gr TPAOH (25 wt%),

8054.640 gr TPAOH (25%) × $\frac{75 \text{ gr H}_2\text{O}}{100 \text{ gr}}$ = 6040.980 gr H₂O

1630 mole H_2O + 2 x 80 mole H_2O for the hydrolization of TEOS* = 1790 mole H_2O ,

1790 mole $H_2O \times \frac{18.015 \text{ gr}}{1 \text{ mole } H_2O} = 32246.850 \text{ gr } H_2O$

32246.850 – 6040.980 (from TPAOH) – 3522.144 (from sodium aluminate solution)-

33.395 (from sodium aluminate) = $22650.331 \text{ gr H}_2\text{O}$

*TEOS hydrolysis reaction: $C_8H_{20}O_4Si + 2 H_2O = SiO_2 + 4 C_2H_5OH$

3707.520 gr 5wt% sodium aluminate 17004.082 gr TEOS 8054.640 gr TPAOH (25 wt% in water) 22650.331 gr deionised water

+

51416.573 gr

100 gram basis:

7.21 gr 5 wt% sodium aluminate solution33.07 gr TEOS (98%)15.67 gr TPAOH (25 wt% in water)44.05 gr deionised water

APPENDIX B

CALCULATION OF MAXIMUM YIELD

Composition: $S_{80}T_{16}H_{1536}E_{320}$ 100 gram basis: 7.74 gr 5 wt% sodium aluminate solution 35.50 gr TEOS (98%)

16.82 gr TPAOH (25 wt% in water)

47.29 gr deionised water

In 100 gram synthesis solution,

 $35.50 \text{ gr TEOS} \times \frac{1 \text{ mole}}{208.3 \text{ gr}} \times \frac{1 \text{ mole SiO}_2}{1 \text{ mole TEOS}} = 0.1704 \text{ mole SiO}_2$ $0.1704 \text{ mole SiO}_2 \times \frac{60.088 \text{ gr}}{1 \text{ mole SiO}_2} = 10.24 \text{ gr SiO}_2$

In one unit cell of MFI, there exist 4 moles of SiO₂ and 96 moles of TPA.

 $0.1704 \text{ mole SiO}_2 \times \frac{4 \text{ mole TPAOH}}{96 \text{ mole SiO}_2} \times \frac{203.4 \text{ gr}}{1 \text{ mole TPAOH}} = 1.44 \text{ gr TPAOH}$

From 100 grams of synthesis solution, the maximum yield that can be achieved is,

 $10.24 \text{ gr SiO}_2 + 1.44 \text{ gr TPAOH} = 11.68 \text{ gr silicalite}^*$

So, the maximum yield is 11.68%.

*In the calculation of maximum yield from ZSM-5 samples prepared using the composition $A_1N_{1.3}S_{80}T_{9.9}H_{1630}E_{320}$ also, only SiO₂ and TPAOH is used as in the above example, since alumina and soda were very little in amount.

APPENDIX C

CALCULATION OF SEPARATION SELECTIVITY IN BINARY GAS MIXTURES

Permeance of A,

$$\frac{\mathbf{P}_{A}}{\Delta \mathbf{P}_{transmembrane}} = \frac{\mathbf{J}_{A}}{\Delta \mathbf{P}_{transmembrane}}$$
(1)

where,

 J_{A} is the flux of A

 $\Delta P_{\text{transmembrane}}$ is the transmembrane pressure difference calculated as will be shown below

$$J_{A} = \frac{P_{atm}}{R \cdot T \cdot S_{mem}} \cdot y_{A} \cdot \left(\frac{\Delta V}{\Delta t}\right)$$
(2)

where,

 P_{atm} is the atmospheric pressure in Pa R is the universal gas constant (8.314 J/mol.K) T is the temperature in K S_{mem} is the membrane surface area in m² y_A is the mole fraction of A in the permeate side

 $\left(\frac{\Delta V}{\Delta t}\right)$ is the total flowrate in the permeate side

$$\Delta P_{\text{transmembrane}} = \Delta P_{\text{log-mean}} = \frac{\left(P_{\text{A}}^{\text{feed}} - P_{\text{A}}^{\text{permeate}}\right) - \left(P_{\text{A}}^{\text{retentate}} - P_{\text{A}}^{\text{permeate}}\right)}{In\left(\frac{P_{\text{A}}^{\text{feed}} - P_{\text{A}}^{\text{permeate}}}{P_{\text{A}}^{\text{retentate}} - P_{\text{A}}^{\text{permeate}}}\right)}$$
(3)

where,

 $\mathsf{P}^{\scriptscriptstyle i}_{\scriptscriptstyle A}$ is the partial pressure of A in the feed, permeate or retentate

Inserting equation (2) and (3) into (1) to get $P_{A},\,$

Selectivity = $\frac{P_{A}}{P_{B}}$

Sample Calculation for PZC100

Permeate flowrate, P: 1.40 mL/min Retentate flowrate, R: 38.6 mL/min Feed flowrate, F: 1.40 + 38.6 = 40.0 mL/min

Feed composition: 50% n-butane, 50% isobutane Permeate composition:67% n-butane, 33% isobutane Retentate composition:

$$F \cdot \mathbf{X}_{_{i-C4,F}} = P \cdot \mathbf{X}_{_{i-C4,P}} + R \cdot \mathbf{X}_{_{i-C4,R}}$$

$$x_{_{i-C4,R}} = \frac{F \cdot x_{_{i-C4,F}} - P \cdot x_{_{i-C4,P}}}{R}$$

$$X_{i-C4,R} = \frac{(40) \cdot (0.50) - (1.40) \cdot (0.33)}{38.6} = 0.506$$

 $S_{mem} = 5.5 \times 10^{-4} m^2$ $P_F = P_R = 1.7 atm$ $P_P = 0.9 \text{ atm}$ T = 297 K

Isobutane flux in the permeate side:

$$J_{i-C4} = \frac{0.9 \text{ atm}}{(0.082 \text{ L.atm/mol.K}) \cdot (297 \text{ K}) \cdot (5.5 \times 10^{-4} \text{ m}^{2})} \cdot (0.33) \cdot (1.40 \times 10^{-3} \text{ L/min})$$
$$\cdot \left(\frac{1 \text{ min}}{60 \text{ s}}\right) = 5.158 \times 10^{-4} \text{ mol/m}^2.\text{s}$$

Similarly the n-butane flux in the permeate side is calculated as,

 $J_{n-C4} = 1.052 \times 10^{-3} \text{ mol/m}^2.s$

The partial pressures of isobutane and n-butane on the permeate and retentate sides are,

$$\begin{split} P_{i\text{-}C4,P} &= 0.30 \text{ atm} \\ P_{n\text{-}C4,P} &= 0.60 \text{ atm} \\ P_{i\text{-}C4,R} &= 0.91 \text{ atm} \\ P_{n\text{-}C4,R} &= 0.89 \text{ atm} \\ P_{i\text{-}C4,F} &= 0.90 \text{ atm} \\ P_{n\text{-}C4,F} &= 0.90 \text{ atm} \end{split}$$

The transmembrane pressure difference is then,

 $\Delta P_{\text{transmembrane,i-C4}} = \frac{(0.90 - 0.30) - (0.91 - 0.30)}{\text{ln} \left(\frac{0.90 - 0.30}{0.91 - 0.30} \right)} = 0.605 \text{ atm} \times \frac{1 \text{Pa}}{0.9869 \times 10^{-5} \text{ atm}} = 61755 \text{ Pa}$

Similarly $\Delta P_{transmembrane,n-C4}$ is calculated as 29434 Pa.

The permeances of isobutane and n-butane in the permeate side are then calculated as,

$$\underline{P}_{i-C4} = \frac{5.158 \times 10^{-4} \text{ mol/m}^2 \text{s}}{61755 \text{ Pa}} = 8.35 \times 10^{-9} \text{ mol/m}^2 \text{.s.Pa}$$

$$\underline{P}_{n-C4} = \frac{1.052 \times 10^{-3} \text{ mol/m}^2 \text{s}}{29434 \text{ Pa}} = 3.57 \times 10^{-8} \text{ mol/m}^2 \text{.s.Pa}$$

And the selectivity is then,

$$\alpha = \frac{3.57 \times 10^{-8}}{8.35 \times 10^{-9}} = 4.3$$

APPENDIX D

CALIBRATION OF MASS FLOW CONTROLLERS



Figure D.1. Calibration of the mass flow controller for n-butane



Figure D.2. Calibration of the mass flow controller for isobutane

APPENDIX E

CALIBRATION OF GAS CHROMATOGRAPH FOR N-BUTANE AND ISOBUTANE



Figure E.1. Gas chromatograph calibration for n-butane



Figure E.2. Gas chromatograph calibration for isobutane



Figure E.3. Sample chromatogram (27.2% isobutene – retention time: 0.431 s, 72.8% n-butane – retention time: 0.483 s)

APPENDIX F

XRD PATTERNS OF MEMBRANES PZC89, PZC94, PZC95, PZC85-III, PZC86-II, PZC97-III AND PZC98-III



Figure F.1. XRD pattern of PZC89



Figure F.2. XRD pattern of PZC94



Figure F.3. XRD pattern of PZC95



Figure F.4. XRD pattern of PZC85-III


Figure F.5. XRD pattern of PZC86-II



Figure F.6. XRD pattern of PZC97-III



Figure F.7. XRD pattern of PZC98-III

APPENDIX G

XRD PATTERNS OF MFI POWDER SYNTHESIZED AT ATMOSPHERIC AND AUTOGENEOUS PRESSURE TO BE USED AS SEED



Figure G.1. XRD pattern of the powder obtained after 43 hours in the atmospheric pressure system (PZC65)



Figure G.2. XRD pattern of the powder obtained after 50 hours in the atmospheric pressure system (PZC66)



Figure G.3. XRD pattern of the powder obtained after 75 hours in the atmospheric pressure system (PZC67)



Figure G.4. XRD pattern of the powder obtained after 91 hours in the atmospheric pressure system (PZC68)



Figure G.5. XRD pattern of the powder obtained after 98 hours in the atmospheric pressure system (PZC69)



Figure G.6. XRD pattern of the powder obtained after 115 hours in the atmospheric pressure system (PZC70) $\,$



Figure G.7. XRD pattern of the powder obtained after 142 hours in the atmospheric pressure system (PZC71)



Figure G.8. XRD pattern of the powder obtained after 47 hours in the autogeneous pressure system (PZC52) $\,$



Figure G.9. XRD pattern of the powder obtained after 67 hours in the autogeneous pressure system (PZC53)



Figure G.10. XRD pattern of the powder obtained after 117 hours in the autogeneous pressure system (PZC54)



Figure G.11. XRD pattern of the powder obtained after 162 hours in the autogeneous pressure system (PZC55) $\,$

APPENDIX H

XRD PATTERNS OF THE MFI POWDER OBTAINED DURING THE SYNTHESES OF THE MEMBRANES PZC89, PZC90, PZC94 AND PZC95



Figure H.1. XRD pattern of the powder obtained from the synthesis of PZC89, after 30.5 hours



Figure H.2. XRD pattern of the powder obtained from the synthesis of PZC89, after 48 hours



Figure H.3. XRD pattern of the powder obtained from the synthesis of PZC89, after 53.5 hours



Figure H.4. XRD pattern of the powder obtained from the synthesis of PZC89, after 71 hours



Figure H.5. XRD pattern of the powder obtained from the synthesis of PZC89, after 79.5 hours



Figure H.6. XRD pattern of the powder obtained from the synthesis of PZC89, after 101.5 hours



Figure H.7. XRD pattern of the powder obtained from the synthesis of PZC89, after 124 hours



Figure H.8. XRD pattern of the powder obtained from the synthesis of PZC89, after 144 hours



Figure H.9. XRD pattern of the powder obtained from the synthesis of PZC89, after 151 hours



Figure H.10. XRD pattern of the powder obtained from the synthesis of PZC89, after 168 hours



Figure H.11. XRD pattern of the powder obtained from the synthesis of PZC90, after 47 hours



Figure H.12. XRD pattern of the powder obtained from the synthesis of PZC90, after 51 hours



Figure H.13. XRD pattern of the powder obtained from the synthesis of PZC90, after 54 hours



Figure H.14. XRD pattern of the powder obtained from the synthesis of PZC90, after 72 hours



Figure H.15. XRD pattern of the powder obtained from the synthesis of PZC94, after 46.5 hours



Figure H.16. XRD pattern of the powder obtained from the synthesis of PZC94, after 67.5 hours



Figure H.17. XRD pattern of the powder obtained from the synthesis of PZC94, after 71.5 hours



Figure H.18. XRD pattern of the powder obtained from the synthesis of PZC95, after 45.5 hours



Figure H.19. XRD pattern of the powder obtained from the synthesis of PZC95, after 62.5 hours



Figure H.20. XRD pattern of the powder obtained from the synthesis of PZC95, after 70.5 hours



Figure H.21. XRD pattern of the powder obtained from the synthesis of PZC95, after 87 hours



Figure H.22. XRD pattern of the powder obtained from the synthesis of PZC95, after 94 hours



Figure H.23. XRD pattern of the powder obtained from the synthesis of PZC95, after 114 hours

APPENDIX I



XRD PATTERN OF THE SEEDED ALUMINA TUBE

Figure I.1. XRD pattern of the seeded alumina tube

Authors	N ₂ Permeance (mol/m ² .s.Pa)	N_2/SF_6	n-C4H ₁₀ Permeance (mol/m ² .s.Pa)	n-C₄H ₁₀ / i- C₄H ₁₀
	6.00E-07	138	9.00E-09	14
Courses 1. February 1.1. and Nable D.D.	1.00E-06	299		
Coronas, J., Faiconer, J. L., and Noble, R.D.,	9.00E-07	196	7.00E-09	1
Composite Membranes" AIChE Journal 43, 1997 p	1.20E-06	259	1.10E-08	1.1
1797-1812	1.20E-06	66	5.00E-08	1
1757 1012.	1.00E-07	15	2.00E-08	2.3
	4.00E-08	6	8.00E-09	1.1
Xomeritakis, G., Nair, S., Tsapatsis, M., "Transport properties of alumina-supported MFI membranes made by secondary (seeded) growht", Microporous and Mesoporous Materials, 38, 2000, p. 1-73.			4.22E-08	28
Lai, R., Gavalas, G.R., "Surface seeding in ZSM-5 membrane preparation", Industrial and Engineering Chemistry Research, 37, 1998, p. 4275-4283.			7.40E-10	92
 Hedlund, J., Noack, M., Kölsch, P., Creaser, D., Caro, J., Sterte, J., "ZSM-5 membranes synthesized without organic templates using a seeding technique", Journal of Membrane Science, 159, 1999, p. 263-273. 			5.00E-11	1.25
Lassinanti, M., Jareman, F., Hedlund, J., Creaser, D.,	3.90E-07	4.4		
Sterte, J., "Preparation and evaluation of thin ZSM-5	1.70E-07	4.4		
membranes synthesized in the absence of organic	1.20E-07	12		
template molecules"Catalysis today,67,2001,109-119	1.20E-07	12		
	9.00E-09	8		
Kalıpçılar H., Çulfaz, A., " Role of water content of clear	3.00E-09	38		
synthesis solutions on the thickness of silicalite layers	1.63E-07	1630		
grown on porous alumina supports", Microporous and	1.61E-07	77		
mesoporous materials, 52, 2002, p. 39-54.	1.26E-07	1050		
	2.00E-08	195		

Table J.1. N_2 permeance, N_2/SF_6 selectivity, n-butane permeance and n-butane / isobutane selectivity of the membranes reported in literature, which are referred to in Figures 4.16 and 4.17

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Table J.1. continued

Authors	N ₂ Permeance (mol/m ² .s.Pa)	N ₂ /SF ₆	n-C4H ₁₀ Permeance (mol/m².s.Pa)	n-C ₄ H ₁₀ /i- C ₄ H ₁₀
			3.00E-08	100
			1.30E-07	3.2
Versen ZAED Keizen K. Dungengef All Versusi			4.50E-08	7.5
Vroon, Z.A.E.P., Keizer, K., Burggraaf, A.J., Verweij,			5.20E-08	2.1
membranes on porous supports" Journal of Membrane			1.71E-07	1.15
Science 144 1998 n 65-76			3.80E-08	131
			2.70E-08	85
			1.10E-08	48
			6.70E-09	74
Hedlund, J., Jareman, F., Bons, A., Anthonis, M., "A masking technique for high guality MFI membranes".	1.29E-05	8	1.00E-06	9
Journal of Membrane Science, 222, 2003, p. 163-179.	8.80E-06	22		
Kang B.S., Gavalas, G.R., "Intrapore synthesis of			9.90E-08	37
silicalite membranes at temperatures below 100°C",			2.90E-07	17
Industrial and Engineering Chemistry Research, 41, 2002, p. 3145-3150.			1.70E-07	32
Li Y., Zhang, X., Wang, J., "Preparation for ZSM-5 membranes by a two-stage varying-temperature			1.80E-08	12
synthesis", Separation and Purification Technology, 25, 2011, p. 459-466.			5.00E-09	2
Oonkhanond, B., Mullins, M.E., "The preparation and			5.20E-10	1.2
analysis of zeolite ZSM-5 membranes on porous			6.10E-10	1.7
alumina supports", Journal of Membrane Science, 194, 2001, p. 3-13.			1.03E-09	1.9
Bonhomme, F., Welk, M.E., Nenoff, T.M., "CO ₂	1.10E-07	28		
selectivity and lifetimes of high silica ZSM-5 membranes", Microporous and mesoporous materials,	1.40E-07	70		
66, 2003, p. 181-188.	1.60E-07	53		

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Table J.1. continued

Authors	N ₂ Permeance (mol/m ² .s.Pa)	N_2/SF_6	n-C4H ₁₀ Permeance (mol/m ² .s.Pa)	n-C ₄ H ₁₀ /i- C ₄ H ₁₀
Yan, Y., Davis, M.E., Gavalas, G.R., "Preparation of zeolite ZMS-5 membranes by in-situ crystallization on porous alpha-Al ₂ O ₃ ", Industrial and Engineering Chemistry Research, 34, 1995, p. 1652-1661.			7.50E-09	18.4
Algieri, C., Golemme, G., Kallus, S., Ramsay, J.D.F.,	4.60E-06	13.9		
"Preparation of thin supported MFI membranes by in	3.78E-07	11.8		
situ nucleation and secondary growth" Journal of	2.16E-06	10.8		
membrane science. 47. 2001. pp 127-134	2.80E-06	13.7		
Tuan, V.A., Falconer, J.L., Noble, R.D., "Alkali-Free ZSM-5 Membranes: Preparation Conditions and Separation Performance", Industrial and Engineering Chemistry Research, 38, 1999, p. 3635-3646	2.00E-08	56		
Nomura, M., Yamaguchi, T., Nakao, S., "Transport phenomena through intercrystalline and intracrystalline	2.00E-07	3.7		
pathways of silicalite zeolite membranes", Journal of membrane science, 187, 2001, p. 203-212.	5.00E-08	11.7		
Gump C.J. "Experimental configuration and adsorption	8.30E-07	240		
effects on the permeation of C4 isomers through ZSM- 5 zeolite membranes" Journal of membrane science	4.30E-07	310		
173. 2000. pp 35-52	3.80E-08	19		
Algieri C., Bernardo, P., Golemme, G., Barbieri, G., Drioli, E., "Permeation properties of a thin silicalite-1 (MFI) membrane", Journal of membrane science, 222, 2003, p. 181-190.	4.60E-06	8.56		

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Authors	N ₂ Permeance (mol/m ² .s.Pa)	N_2/SF_6	n-C4H ₁₀ Permeance (mol/m².s.Pa)	n-C ₄ H ₁₀ /i- C ₄ H ₁₀
	6.56E-07	19.3		
	5.51E-07	15.6		
	7.96E-07	12.8		
	2.52E-07	8.9		
Arruebo, M., Coronas, J., Menéndez, M., Santamaría,	3.35E-07	14.9		
J., "Separation of hydrocarbons from natural gas using	2.14E-07	5.7		
silicalite membranes", Separation and Purification	2.37E-07	7.1		
Technology, 25, 2001, p. 275-286.	7.41E-07	7.1		
	3.19E-07	21.2		
	1.10E-07	27.5		
	1.40E-07	70		
	1.60E-07	53.3		
Piera, E., Brenninkmeijer, C.A.M., Santamaría, J.,	2.10E-07	5.1		
Coronas, J., "Separation of traces of CO from air using MFI-type zeolite membranes", Journal of membrane	1.70E-07	33		
science, 201, 2002, p. 229-232.	4.80E-07	95		
Li G., Kikuchi, E., Matsukata, M., "ZSM-5 zeolite membranes prepared from a clear template-free	1.25E-07	12.5		
solution", Microporous and mesoporous materials, 60, 2003, p. 225-235.	4.00E-08	8		
	2.20E-06	105		
Funke, H.H., Frender, K.R., Green, K.M., Wilwerding,	2.50E-06	83		
J.L., Sweitzer, B.A., Falconer, J.L., Noble, R.D.,	3.80E-06	81		
"Influence of adsorbed molecules on the permeation	2.21E-06	92		
properties of silicalite membranes", Journal of	6.39E-07	90		
membrane science, 129, 1997, p. 77-82.	6.40E-07	102		

Table J.1. continued

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Authors	N ₂ Permeance (mol/m ² .s.Pa)	N ₂ /SF ₆	n-C4H ₁₀ Permeance (mol/m ² .s.Pa)	n-C₄H ₁₀ /i- C₄H ₁₀
	8.30E-07	1.5		
	4.00E-07	7.1	1.10E-07	6.9
	9.00E-07	7.9	6.20E-07	6.9 1.6 1.9
This work	3.80E-07	5.3	3.10E-07	1.9
	3.60E-07	4.9	1.20E-07	1.9
	3.40E-07	27	8.00E-09	5.5
	4.40E-07	11	1.70E-07	5.8
	2.25E-07	9.1	8.00E-09	5.5

Table J.1. continued

APPENDIX K

RAW DATA OF BİNARY MİXTURE PERMEATİON EXPERİMENTS WİTH PZC99

Time	Time Temperature		Stream	Flowrate	Compos (%	sition)	Compos (%,norm	sition alized)
(min)	(°C)			(mL/min)	isobutane	n- butane	isobutane	n- butane
-	RT	44360	F	(mL/min) isobutane n-butane isobutane n-butane 40.2 48.7 52.6 48.1 51.9 41.4 51.0 50.5 50.2 49.8 42.7 50.1 51.2 49.5 50.5 42.9 49.9 51.6 49.2 50.8 0.12 26.7 70.6 27.4 72.6 37.5 - - - - 0.2 26.8 71.5 27.3 72.7 41.2 - - - - 0.19 26.7 71.5 27.2 72.8 43.1 - - - -				
-	RT	44361	F	41.4	51.0	50.5	50.2	49.8
-	RT	44362	F	42.7	50.1	51.2	49.5	50.5
-	RT	44363	F	42.9	49.9	51.6	49.2	50.8
40	RT	44371	Р	0.12	26.7	70.6	27.4	72.6
40	RT		R	37.5	-	-	-	-
55	RT	44372	Р	0.2	26.8	71.5	27.3	72.7
55	RT		R	41.2	-	-	-	-
115	RT	44373	Р	0.19	26.7	71.5	27.2	72.8
115	RT		R	43.1	-	-	-	-
55	100	44374	Р	1.08	21.9	76.7	22.2	77.8
55	100		R	44.2	-	-	-	-
85	100	44375	Р	1.12	21.7	77.2	21.9	78.1
85	100		R	41	-	-	-	-
110	100	44376	Р	-	21.6	75.9	22.2	77.8
110	100		R	-	-	-	-	-
120	100	44377	Р	1.43	21.6	76.1	22.1	77.9
120	100		R	43.5	-	-	-	-
130	100		Р	2.69	-	-	-	-
130	100		R	42.6	-	-	-	-
140	100		Р	1.07	-	-	-	-
10	150	44449	Р	0.48	28.4	65.7	30.2	69.8
10	150		R	38.1	-	-	-	-
15	150		Р	-	-	-	-	-
15	150		R	37.6	-	-	-	-
50	150	44452	Р	0.5	22.1	75.2	22.7	77.3
50	150		R	37.8	-	-	-	-
75	150	44455	Р	0.36	24.2	73.1	24.9	75.1

Table K.1. Temperature, flowrates and compositions with respect to time in the binary mixture permeation experiments with PZC99

75	150		R	37.2	-	-	-	-
90	150	44456	Р	0.31	25.6	71.6	26.3	73.7
90	150		R	36.1	-	-	-	-
100	150	44457	Р	0.24	27.2	70.5	27.8	72.2
100	150		R	-	-	-	-	-
105	150	44458	Р	-	28.3	69.4	29.0	71.0
105	150		R	-	-	-	-	-
45	200	44459	Р	0.46	30.8	69.2	30.8	69.2
45	200		R	37.8	-	-	-	-
70	200	44460	Р	0.29	27.2	71.4	27.6	72.4
70	200		R	36.7	-	-	-	-
95	200	44461	Р	0.49	28.1	69.5	28.8	71.2
95	200		R	31.2	-	-	-	-
125	200	44462	Р	0.68	28.2	69.2	29.0	71.0
125	200		R	37.4	-	-	-	-

Table K.1. Temperature, flowrates and compositions with respect to time in the binary mixture permeation experiments with PZC99 (cont.d)



Figure K.1. Change of n-butane composition with time in mixture permeation experiments at room temperature (PZC99)





experiments at room temperature (PZC99)























APPENDIX L

ZSM-5 PDF CARD

etr 48	akis (Tet H116 N4 0	raprop 196 Si	ylammon 96	ium)	Silic	ate Hydro	xide				Ze	olite.	ZSM-S	i.				
adi ali ef:	ation : bration: von Ball Collecti	CuKa moos, lon of	R. Simulat	ed XR	D Pow	Lambda d-CutOff der Patte	: 1.5418 : rns For Z	I/: eolites ()	Filter Ic(RIR) 1984)									
yst ell ef:	em: Ortho Paramete (Reno 19	orhombi ers= 983), B	c() 19.949 utterwo	20.0 rth	96 1 Londo	13.428 90 on, Englar	.G.: Pmnb .00 90.0 d.6th	(62) 0 90.00	1	Z= mp=								
X=	2.030 Dm	Commun 1=	1cation Mwt=	6581	.56	Vol(RC)=	5383.22	F (30	=999.9	(.0006,34)							
a= ef:		n	wB=			ey≈		Sign:	2	1=								
12	Reflectio	ons.	Radi	ation	: CU_	1.540598.	Stro	ng Lines:	3.85/G	3.83/G 3	.72/	G 11.2/G	11.1	L/G	3.6	5/G 3.76/G	9.97/G	10.0/G
# 1223455657889901011111111111111111111111111111111	$ \begin{array}{c} d(\lambda) \\ 111.14000 \\ 9.9740 \\ 9.97430 \\ 9.97440 \\ 9.97430 \\ 8.0450 \\ 7.44380 \\ 0.99740 \\ 7.4380 \\ 0.99740 \\ 7.4380 \\ 0.99740 \\ 7.4380 \\ 0.9940 \\ 9.97430 \\ 0.9940 \\ 0.99$	$ \begin{smallmatrix} I & \{ f_{5} \\ f_{5} \\ f_{2} \\ f_{$	$\begin{smallmatrix} 1 & \{var\} \\ 1 & \{1, 1, 2, 3, 9, 3, 7, 3, 1, 6, 4, 3, 2, 2, 1, 1, 1, 1, 2, 1, 7, 2, 6, 4, 1, 2, 3, 9, 3, 7, 3, 1, 6, 4, 3, 2, 1, 1, 1, 1, 1, 2, 1, 7, 2, 6, 1, 1, 1, 1, 2, 1, 7, 2, 6, 1, 1, 1, 1, 1, 2, 1, 7, 2, 6, 1, 1, 1, 1, 1, 2, 1, 7, 2, 6, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1,$	h10201222120113031202213240431423121424141354013021532	k01021101220010313023122304113143031203214303224111133003133	2-Theta 7,9303 8,7930 8,7930 9,069 9,068 10,989 11,8829 9,048 10,989 12,494 13,895 14,767 14,884 15,808 15,970 16,504 15,498 15,970 16,504 17,728 17,772 19,284 15,970 16,504 17,772 19,284 15,970 19,284 15,970 19,284 15,970 19,284 19,927 19,285 20,756 20,756 20,756 21,756 22,155 21,756 22,155 22,155 22,155 22,2380 23,083 23,987 23,986 23,987 23,986 23,987 23,986 23,987 23,986 23,987 23,986 23,987 23,986 23,987 23,986 23,987 23,986 23,987 23,986 23,987 23,986 23,987 24,987 24	Theta $3,9565$ 3,9565 4,397 4,5354 4,5944 5,9244 5,9244 6,9444 6,9445 6,9445 6,9444 7,2946 6,9444 7,2945 8,252 8,6442 9,9642 9,9642 10,3788 10,4288 10,4288 11,5542 12,777 12,777	1 (2d) 0.04488 0.04712 0.05132 0.055132 0.055132 0.05525 0.06722 0.07063 0.07752 0.07752 0.07752 0.08752 0.09552 0.10245 0.10245 0.10245 0.11453 0.12444 0.124484 0.13434 0.13434 0.14355 0.14339 0.14355 0.14455 0	#); 55; 55; 66; 56; 66; 66; 66; 66	$\begin{array}{c} d(X)\\ 3,334250\\ 3,34250\\ 3,3$	1(fi	x) 214219111112111121111111111111111111111	LOG403163214214354630311540665275465158030248827556184	¥000650075626255457457457652047050757575468085774280355707	140301417213040211033423344232514404410055401003442322	$\begin{array}{c} 2-\text{Thetal}\\ 226, 5395\\ 226, 5521\\ 226, 5915\\ 226, 5521\\ 226, 7914\\ 227, 4211\\ 227, 428\\ 227, 4211\\ 227, 428\\ 227, 4211\\ 227, 428\\ 228, 23830\\ 229, 2228\\ 229, 9322\\ 229, 932\\ 229, 9322\\ 229, $	Theta 5 13.2686 13.2686 13.2687 13.2687 13.412 13.395 13.412 13.710 13.7287 13.7287 14.023 14.1023 14.1023 14.1023 14.1023 14.1023 14.1023 14.1023 14.1023 14.1023 14.1023 14.1023 14.1023 15.155 15.155 15.157 17.3302 17.3302 17.3302 17.3302 17.597 17.597 17.597 17.597 18.0228 18.023 19.024	1/(28)4 0.148910 0.448910 0.55036 0.155056 0.155056 0.155056 0.155056 0.155056 0.155056 0.155394 0.155784 0.155784 0.155784 0.155785 0.15689 0.155785 0.166451 0.166456 0.166956 0.166956 0.166956 0.166956 0.166956 0.166956 0.166956 0.166956 0.16955 0.166956 0.16955 0.19402 0.19402 0.19402 0.19403 0.20403 0.204
54>	3.4420	13 1	14	4 5	3 2	25.864	12.932	0.14526	110>	2.3020		$\begin{array}{ccc}1&1\\1&1\end{array}$	30	8	16	39.099 40.265	19.550	0.21720