Thin Films of Molecular Sieves
- Synthesis and Applications -

Jonas Hedlund

October 1998

Luleå University of Technology
Department of Chemical and Metallurgical Engineering
Division of Chemical Technology
Abstract

A novel method, the seed film method, for the synthesis of thin molecular sieve films was developed. Basically, the method consists of a three-step procedure. In the first step, a support surface is modified to facilitate attachment of pre-synthesized colloidal molecular sieve seed crystals. The modified support is immersed in a sol of seed crystals in the second step. In the third step, the seeded support is hydrothermally treated in a precursor solution or gel to induce growth of the seeds into a dense film with a thickness controlled by the duration of the hydrothermal treatment. Ultra thin molecular sieve films, i.e. with a thickness < 0.1 µm, were synthesized for the first time in this work. Thin, dense and continuous films and thicker films (up to 3.5 µm) were synthesized as well. The films were characterized by Scanning electron microscopy (SEM), X-ray diffraction (XRD), gas adsorption, variable angle of incidence spectroscopic ellipsometry (VASE) and Fourier transform infra red spectroscopy (FTIR). The versatility of the method was demonstrated by the successful preparation of films of a number of molecular sieves such as silicalite-1, ZSM-5 and NA on various supports such as silicon, quartz, alumina, carbon and gold. The orientation of the crystals constituting molecular sieve films is of major importance for stability and performance in various applications. This topic was thus studied in detail for films synthesized by the novel method. The preferred orientation of the crystalline material constituting the films was found to be dependent on the seed size, seed amount, film thickness and the habit of grown seed crystals. The preferred orientation can thus be controlled to one desired for a specific application by an appropriate choice of the synthesis parameters. Since additional synthesis parameters are available when using the seed film method, more freedom is introduced to the system compared to the normal synthesis route denoted direct crystallization where no seeds are used. The utilization of molecular sieve films in a variety of novel applications such as sensors, membranes and membrane reactors has enormous potential, since molecular sieves are selective for differences in size, shape and properties of molecules. Thus, all these different types of selectivity are "built in" for the specific application. In the present work, silicalite-1 films with a thickness of 80 and 220 nm on silicon wafers were evaluated as optical gas sensors. The amount of condensed vapor in the films, which is a function of the concentration in the surrounding fluid, was measured by VASE. Sorption isotherms at room temperature of water, toluene, 1-propanol and n-hexane were recorded. The films were evaluated in a membrane application as well. ZSM-5 films with a thickness of 1.5 µm were crystallized on a porous α-alumina support without the use of organic template molecules. The membranes were not calcined prior to the permeation experiments in order not to induce formation of cracks in the film. The flux in single gas experiments decreased in the series H2O, H2, CO2, O2, N2 and CH4, i.e. the flux decreased with increasing kinetic diameter of the molecules. The difference in flux between each molecule was about 1 order of magnitude which indicated the high quality of the membranes. The measured separation factors for binary (feed volume ratio 1:1, 105°C and Δp=0) mixtures of N2/SF6 and H2/i-C4 were 99 and 66, which is much larger than expected for Knudsen diffusion and higher than previously reported for similar membranes.
This dissertation is based on the work contained in the following papers, referred to in the text by Roman numbers (I-IX).

I Synthesis of ultra thin films of molecular sieves by the seed film method  
Jonas Hedlund, Brian J. Schoeman and Johan Sterte  
Presented at the 11th International Zeolite Conference in Seoul, Korea and published in  
H. Chon, S.-K. Ihm and Y.S. Uh (Editors), Progress in Zeolites and Microporous  

II Thin zeolite NA films by the seed film method  
Jonas Hedlund, Elena Babouchkina and Johan Sterte  
Presented at the 12th International Zeolite Conference in Baltimore, USA and accepted  
for publication in the proceedings.

III Controlling the preferred orientation in silicalite-1 films synthesized by seeding  
Jonas Hedlund, Svetlana Mintova and Johan Sterte  
Accepted for publication in Microporous and Mesoporous Materials.

IV ZSM-5 films prepared from template free precursors  
Svetlana Mintova, Jonas Hedlund, Valentin Valtchev, Brian J. Schoeman and Johan  
Sterte  
Accepted for publication in Journal of Materials Chemistry.

V Control of the preferred orientation in MFI films synthesized by seeding  
Jonas Hedlund  

VI Preparation and characterization of hollow fibers of silicalite-1  
Valentin Valtchev, Brian J. Schoeman, Jonas Hedlund, Svetlana Mintova and Johan  
Sterte  

VII Continuous films of zeolite ZSM-5 on modified gold surfaces  
Svetlana Mintova, Jonas Hedlund, Brian Schoeman, Valentin Valtchev and Johan Sterte  
Chemical Communications, 1997, 15-16.

VIII Vapor Adsorption in Thin Silicalite-1 Films Studied by Spectroscopic Ellipsometry  
Robert B. Bjorklund, Jonas Hedlund, Johan Sterte and Hans Arwin  

IX Evaluation of ZSM-5 membranes synthesized in the absence of organic template  
molecules  
Jonas Hedlund, M. Noack, P. Kölsch, Derek Creaser, J. Caro and Johan Sterte.  
Submitted to Journal of Membrane Science.
CONTENTS

1 INTRODUCTION..........................................................................................................................1
  1.1 Background ............................................................................................................................1
  1.2 Scope of the present work .....................................................................................................2

2 A BRIEF DESCRIPTION OF ZEOLITES ......................................................................................3
  2.1 General description ..............................................................................................................3
  2.2 Properties of the zeolites used in this work ..........................................................................3
  2.3 Crystallographic aspects .......................................................................................................4

3 CONVENTIONAL ZEOLITE SYNTHESIS .....................................................................................5

4 SYNTHESIS OF ZEOLITE FILMS AND MEMBRANES- AN OVERVIEW ...................................6
  4.1 Zeolite crystals embedded in a non-zeolite matrix .............................................................6
  4.2 Non supported films ..........................................................................................................6
  4.3 Supported films synthesized by direct crystallization .........................................................7
  4.4 Supported films synthesized by the vapor phase method ....................................................7
  4.5 Supported films synthesized by methods employing seeding ..............................................8
  4.6 Crack formation in zeolite films ..........................................................................................8
  4.7 Film formation mechanisms for the MFI-system by direct synthesis .................................9

5 APPLICATIONS FOR MOLECULAR SIEVE FILMS ................................................................11
  5.1 Zeolite membranes ..........................................................................................................11
  5.2 Sensors ..............................................................................................................................14

6 SYNTHESIS OF FILMS BY THE SEED FILM METHOD .............................................................16
  6.1 Seed synthesis .....................................................................................................................16
  6.2 Substrate modification .........................................................................................................16
  6.3 Seed adsorption ..................................................................................................................17
  6.4 Film growth .........................................................................................................................18

7 CHARACTERIZATION OF THE FILMS .....................................................................................19
  7.1 Scanning electron microscopy and X-ray elemental analysis ..............................................19
  7.2 X-ray diffraction .................................................................................................................19
  7.3 Dynamic light scattering ......................................................................................................20
  7.4 Gas adsorption ....................................................................................................................21
  7.5 Permeation measurements ..................................................................................................21
  7.6 Ellipsometry ........................................................................................................................22
  7.7 Infra red spectroscopy .........................................................................................................22

8 PROPERTIES OF FILMS SYNTHESIZED BY THE SEED FILM METHOD .............................23
  8.1 Seed adsorption ..................................................................................................................23
  8.2 Film crystallization ..............................................................................................................24
  8.3 Synthesis of films in the absence of organic template molecules ..........................................26
  8.4 Preferred orientation ..........................................................................................................27
  8.5 Growth model .....................................................................................................................30

9 APPLICATIONS.........................................................................................................................32
  9.1 Sensors ................................................................................................................................32
  9.2 Membranes .......................................................................................................................32

10 CONCLUSIONS .......................................................................................................................34

11 FUTURE WORK .......................................................................................................................35

12 ACKNOWLEDGMENTS .............................................................................................................36

13 REFERENCES ..........................................................................................................................37
1 INTRODUCTION

1.1 Background

A molecular sieve is a structure that is able to separate molecules on a size basis [1]. Zeolites belong to the wider group of molecular sieves and about 100 zeolite structure types are known today [2]. Most of them are synthetic and numerous recipes for the synthesis of zeolites in the powder form are given in the literature [3]. Synthetic zeolite is widely used for separation of gas mixtures, for example water removal from various gases. The prevailing separation methods to utilize zeolites today are batch processes relying on adsorption in pellets at high pressure and/or low temperature followed by desorption at low pressure and/or high temperature. Continuous processes using membranes for separation are preferable economically. However, zeolite membrane synthesis is technically more challenging than the synthesis of powder, and currently good zeolite membranes are not yet commercially available. Due to the potential for the use of zeolite films in sensor and membrane applications, considerable synthesis efforts has been conducted in the last decade, but still significant improvements are necessary. To obtain a fast response of a zeolite sensor or high flux through a zeolite membrane it is preferable that the zeolite film is ultra thin [4], i.e. thinner than 100 nm. Dense films without cracks or pinholes are necessary in membrane applications, whereas this is not necessary for most sensor applications. Thin and dense zeolite films may be difficult to synthesize by the conventional method where the substrate is treated directly in a molecular sieve precursor solution. The film thickness for dense films is often several tenths of μm leading to low fluxes through membranes and slow responding sensors. Furthermore, the growth of zeolite films may be dependent on the substrate [5] when the conventional method is used. The preferred orientation and the size of the crystals constituting the film affects the crack formation mechanisms in films [6]. In addition, the preferred orientation affects the separation performance of the film since the channel system varies in different directions of the zeolite crystals, making control of the preferred orientation and size of the crystals important parameters to master.
1.2 Scope of the present work

The scope of this work covers the development of a method for the synthesis of truly ultra thin (< 100 nm) and thin\(^1\) zeolite films on various substrates with control of the preferred orientation of the crystals constituting the films and the use of the films in sensor and membrane applications. A further objective was to characterize the films by conventional methods used in thin film and zeolite science (e.g. SEM, XRD, gas adsorption, permeation measurements, IR-spectroscopy and ellipsometry). This work was also aimed at creating a base for initiating joint projects with experts in different application areas such as the sensor and membrane field for assessment of the usefulness of the materials.

\(^1\) In the zeolite field, zeolite films as thick as 10-40 µm are in some cases [7-11] denoted as thin. The thickest film synthesized in the present work was 3.5 µm.
2 A BRIEF DESCRIPTION OF ZEOLITES

2.1 General description

Zeolites are crystalline porous aluminosilicates with a three-dimensional network of \([\text{SiO}_4]^{4-}\) and \([\text{AlO}_4]^{5-}\) tetrahedra. The tetrahedra are linked in the corners and share all oxygen atoms. For each aluminum atom in the framework, one charge equivalent from a non-framework cation must balance the charge of the framework. The chemical composition of zeolites may be expressed as:

\[
\frac{M_{n}^{+} \cdot \text{AlO}_2^{-} \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}}{n}
\]

where

- \(M\) = counterion
- \(n\) = counterion valency
- \(x\) = silicon / aluminum ratio \(\geq 1\)
- \(y\) = content of hydrate water

The counterion may be a metal cation or an ammonium or alkylammonium cation. The non-framework metal cations are, if located within a channel, exchangeable and give the zeolite its ion-exchange capacity. Alkylammonium cations which are incorporated during synthesis are often impossible to remove by cation-exchange. The pore diameter is determined by the crystal structure in each zeolite. Pore diameters in known zeolites are between ca 0.3 and 1 nm [2]. Vapors such as water vapor condense readily in the narrow zeolite channels. Zeolites often have catalytic properties, and these properties can be modified by exchanging non-framework cations, or by incorporating other cations than aluminum, such as titanium, in the framework during synthesis. The zeolites used in this work are silicalite-1, ZSM-5 and NA. Zeolites are divided in structure type groups according to their structure. Silicalite-1 and ZSM-5 have the same structure and belong to the MFI type group whereas NA belongs to the LTA type group.

2.2 Properties of the zeolites used in this work

The difference between silicalite-1 and ZSM-5 is the aluminum content. Silicalite-1 contains only small amounts of, or no aluminum at all, whereas ZSM-5 has a silica/alumina ratio of 5-100 [3]. The Al-content in ZSM-5 renders the framework charged and more hydrophilic than the framework in silicalite-1. Silicalite-1 it thus an effective adsorbent for...
organic molecules whereas ZSM-5 is less effective in this respect. ZSM-5 has, on the other hand, catalytic properties due to its acidic sites, and can be used e.g. to convert methanol to aromatics. The catalytic properties are in some cases undesired. If the purpose is to separate compounds from each other, catalytic properties of the zeolite may be detrimental since new (undesired) compounds may form. The framework of zeolite NA contains more aluminum (silica/alumina ratio 2-7 [3] ) than ZSM-5 and zeolite NA is thus more hydrophilic than ZSM-5. Hence, zeolite NA preferentially adsorbs water in water containing organic solutions.

2.3 Crystallographic aspects

The MFI channel system is shown in Figure 1. The straight elliptical channels running in the b-direction have the dimensions $5.3 \times 5.6 \ \text{Å}$ and the sinusoidal channels running in the a-direction have the dimensions $5.5 \times 5.1 \ \text{Å}$ [2]. The colloidal silicalite-1 crystals used in this work are $90^\circ$ rotational intergrowths with a common c-axis, which from this point will be referred to as twin crystals or twins for convenience. When there is a difference in size of the intergrown crystals, as in Figure 1, the larger crystal is referred to (in this work) as the mother and the smaller as the daughter crystal. A few of the pinacoids and one dome are depicted in the figure as well. The indices of the daughter crystal are depicted with a ´. Note that the daughter's a-axis runs in the same direction as the mother's b-axis.

Figure 1. The MFI channel system and a silicalite-1 twin crystal. The crystallographic axes of the mother crystal is depicted.

Zeolite NA belong to the LTA group and has only straight, almost circular, intersecting channels with a diameter of $4.1 \ \text{Å}$ [2]. The colloidal zeolite NA crystals used in this work are cube shaped, and the lattice is cubic. All pinacoids are thus equivalent and belong to the $\{100\}$ form.
3 CONVENTIONAL ZEOLITE SYNTHESIS

Zeolites are crystallized at hydrothermal conditions, often using a high temperature and pressure and the product is obtained in the form of powder. A common procedure is to mix the components, transfer the mixture (synthesis gel) to an autoclave and heat the autoclave for a certain time. The pressure in the autoclave is autogenous, and depends on the composition of the mixture and the temperature in the oven. It is not unusual to use temperatures as high as 200°C, which causes the pressure to rise to high levels, particularly if the mixture contains volatile compounds such as ethanol. Pure ethanol has a vapor pressure of approximately 30 bar at 200°C. It can be more convenient to synthesize the zeolite at for instance 100°C at atmospheric pressure and under reflux if possible. The composition of the synthesis mixture, the temperature and the synthesis time determines which zeolite phase will form and its properties such as the crystal size and habit. The synthesis mixture contains a silica source such as colloidal SiO₂ or tetraethoxysilane (TEOS) and an aluminum source such as aluminum isopropoxide or aluminum sulfate. Sodium is often added as sodium hydroxide or may be supplied with the SiO₂ sol. In a conventional zeolite synthesis, a gel is formed upon mixing the chemicals. Large crystals, typically several microns, with a broad size distribution are often obtained due to the heterogeneous character of the gel. However, it is also possible to synthesize zeolite crystals from clear solutions. A narrow size distribution can often be obtained in clear systems due to the homogeneity of the bulk solution and its low viscosity. Colloidal (size 1-1000 nm) zeolite crystals can be obtained from clear solutions [12] or larger (but still colloidal) crystals can be synthesized from synthesis gels seeded with (smaller) colloidal seeds [13].

A crucial component in zeolite synthesis is the templating agent. A molecule or ion is considered to be a template or crystal-directing agent if, upon its addition to the reaction mixture, crystallization of a specific zeolite structure that could not be formed in the absence of the agent is favored [3]. Examples of templates are the tetramethylammonium (TMA) ion or the tetrapropylammonium (TPA) ion. These ions can be added as hydroxides or bromides. The template molecules are blocking the pores, and can be removed by methods such as calcination or in some cases, by ion exchange. Calcination entails heating the as-synthesized zeolite in air, to a temperature high enough (often 400°C) to decompose and remove the organic template molecules by oxidation to CO₂ and H₂O.
4 SYNTHESIS OF ZEOLITE FILMS AND MEMBRANES - AN OVERVIEW

This section gives a few examples of approaches to zeolite film synthesis reported in the literature where numerous papers treating the subject can be found. The latter part of the section deals with crack formation and proposed film growth mechanisms. Several methods can be distinguished for the preparation of non-continuous and continuous zeolite films and layers [14]. However, for the synthesis of continuous zeolite films, only three main routes can be found in the literature; the method of direct crystallization (most frequently used), the vapor phase method and methods utilizing seeds.

4.1 Zeolite crystals embedded in a non-zeolite matrix

Several reports have appeared, describing methods in which zeolite crystals are embedded in a non-zeolite matrix. If the intention is to use the resulting composite in a separation process, gaps between the matrix and the zeolite would obviously be detrimental. Furthermore, clogging of the zeolite pores by the non zeolite matrix may be a problem. An example is given by Geus et al. [15] where large ZSM-5 crystals were attached to α-alumina membranes and dip coated with a γ-Al₂O₃ sol and subsequently calcined at 500 °C to demonstrate the usefulness of the dip-coating technique. However, the resulting ZSM-5 / alumina film was not gas tight (since γ-alumina is not gas tight) or free of cracks. In a related study [16], silicalite-1 crystals were embedded in other matrices such as silica gel, yttria-stabilized zirconia and lead-boron glaze. Large (about 80 µm in length) silicalite-1 crystals were embedded in a metal matrix by an elegant method [17]. The crystals were attached to a conducting lacquer (cathode) and subsequently embedded in a Ni or Ag foil by reducing metal ions to metal at the cathode from a bath containing metal ions by a simple galvanic process. The cathode was dissolved in a solvent prior to permeation experiments. The membranes were found to be stable up to 650 K. However, the net zeolite area accessible for permeation in a membrane was only about 1/100 cm².

4.2 Non supported films

Zeolite membranes can be manufactured as free standing films and a few recent examples of this approach have been reported. Oriented zeolite films were synthesized at the interface between two fluid phases [18]. One phase was a clear aqueous phase which contained TPA, sodium hydroxide and large silica particles (on the bottom of the autoclave).
The other phase was an organic fluid or air. The crystals in the films synthesized at the water-air interface were oriented with their b-axes perpendicular to the film surface. The films were not continuous but divided in several pieces. Using a similar approach, ZSM-5 films were synthesized on the interface between an aqueous synthesis solution and mercury [19]. The films in this example were between 25-100 µm thick and the crystals were oriented with the b-axes perpendicular to the mercury surface on the mercury side. Non supported zeolite films have to be quite thick to obtain sufficient mechanical strength for membrane applications. Low fluxes are thus obtained for this type of membrane due to the high resistance through the thick microporous film.

4.3 Supported films synthesized by direct crystallization

If a support, which may be porous, is used to provide mechanical strength, the zeolite film can be thinner and will possess less resistance for mass transport in membrane applications. Commonly used porous supports are ceramic and metallic ones. The term direct crystallization refers (in this thesis) to synthetic approaches where the substrate is treated directly (or after cleaning) with a molecular sieve precursor solution. Numerous papers dealing with this synthesis approach are available in the literature. Most of the work treating zeolite membranes reported so far have concerned the MFI system. For instance, ZSM-5 films were grown on fused silica glass supports [20]. The crystals in the films were oriented with the b-axis perpendicular to the substrate surface and the size of the crystals could be controlled between 500 nm and 30 µm. Another example is the synthesis of perfectly oriented (b-axis perpendicular to the substrate surface) silicalite-1 films on silicon wafers [21]. The thickness of the films could be controlled between 200 and 500 nm. This approach has been used in our lab as well, and films with thickness between 180 and 1000 nm could be synthesized [22]. However, it was difficult to synthesize thin films with no pinholes.

4.4 Supported films synthesized by the vapor phase method

In the vapor phase method developed by Xu et al. [23], the support is first covered with a parent aluminosilicate gel. The amorphous gel is treated in an autoclave for several days with vapors of the organic amine template molecule necessary to transform the parent gel into a zeolite film. A ferrierite film and a film consisting of a mixture of ZSM-5 and ferrierite was synthesized on alumina supports and tested in permeation experiments [7, 8]. A mordenite membrane on a porous alumina support was also synthesized and tested [24]. The thickness of
the zeolite films in these membranes were between 10-40 µm. In a later work, MFI films with thickness between 10-100 µm were synthesized on alumina supports [25]. So far, films thinner than 10 µm have apparently not been prepared using this method.

4.5 Supported films synthesized by methods employing seeding

A silicalite-1 seed sol and a boehmite suspension were subjected to film casting to produce porous supports approximately 2 cm in diameter and 1-2 mm thick [26]. The porous support containing seeds was treated in a silicalite-1 precursor solution. Zeolite films with a thickness of 0.75-2 µm were formed on top of the mesoporous support and the membranes were tested in permeation experiments. A thin zeolite A film was synthesized by seeding a glass substrate with colloidal (200-300 nm) zeolite A crystals [27]. The substrate was dipped in a sol of the crystals, dried and calcined. The procedure was repeated three times to increase the amount of adsorbed zeolite. The seeded substrate was treated in a synthesis solution in order to form a dense zeolite A film. This work is related to work reported by our group [28] which is described in more detail in paper II. Masuda et al. synthesized a zeolite A film on the outer surface of an alumina tube [29]. The hydrothermal treatment was repeated several times to increase the film thickness. When the substrate was treated with a slurry of crushed zeolite or alumina prior to hydrothermal treatment, the film thickness increased more. The final film thickness was in the range 10-50 µm.

4.6 Crack formation in zeolite films

If zeolite films are to be utilized in membranes, a key goal is to avoid crack formation. Independent of method, a considerable fraction of the films are synthesized in the presence of organic template molecules. The template molecules are trapped inside the zeolite channels after synthesis, and must be removed to expose the zeolite channels for guest molecules. The removal of template molecules is often realized by calcination which entails heating the sample in air to temperatures exceeding 400 °C. The calcination following the film synthesis often introduces cracks in the zeolite film which are detrimental in a membrane application. The effect of the calcination process on large MFI single crystals has been studied in detail by Geus et al. [30]. The authors recommend calcining supported polycrystalline MFI membranes with a slow heating rate of 1°C/min. to a maximum temperature of 400°C.

Since the changes in the unit cell dimensions are different in different directions of MFI crystals, i.e. a shrinkage in the a-direction and an expansion in the b-direction upon template
removal [2] the orientation of the crystals constituting MFI-films is probably of major
importance in the crack formation process. This fact was addressed by den Exter et al. [6] who
studied how the crack formation in silicalite-1 films depended on the preferred orientation of
the crystals in the films.

4.7 Film formation mechanisms for the MFI-system by direct synthesis

A few growth models for MFI films synthesized by direct synthesis, i.e. without the use
of seeds, have been proposed in the literature.

# In the proposed model by the group of van Bekkum [31] a gel layer is formed on silicon
substrates in the first step in the synthesis of MFI-films. The interior of the gel layer does not
contain any TPA molecules according to FTIR measurements [21]. However, TPA molecules
adsorb on the gel-solution interface in a close packed monolayer. Since the TPA molecules
must be located in a channel in the zeolite, only nuclei oriented with their bc-planes (straight
channels, see Figure 1) or their ac-planes (sinusoidal channels) in the plane of the gel-solution
interface can form. MFI-crystals grow faster in the ac-plane than in the bc-plane and crystals
oriented with the ac-plane parallel to the substrate surface will therefore win the competition
for nutrients and survive an Ostwald ripening process. Most of the crystals will thus be
oriented with the b-axis perpendicular to the substrate surface. If a more dilute synthesis
solution is used, no gel layer is formed and the crystals become randomly oriented. On metal
substrates [32], the crystals became oriented with their c-axes directed close to perpendicular
to the substrate surface.

# In the growth model proposed by Okubo et al. [33], a gel layer is first formed on the
substrate. The gel layer contains TPA as measured with XPS (compare with above). The gel
layer grows in thickness and spherical particles of about 10 nm in diameter appear on the
layer. At this point, the growth can follow two routes. In route A, nucleation occurs within the
gel layer and crystals grow out from the layer. In route B, the spherical particles on the gel
layer aggregate, since they are able to move randomly over the surface (according to the
suggested mechanism) and the aggregates subsequently fuse to form crystals. The crystals
constituting the film become oriented with their a- or b-axes perpendicular to the substrate
surface. However, the authors state that the model is preliminary and open for discussion.
Kiyozumi et al. [19] synthesized MFI films on a mercury surface. According to their model, nucleation occurs predominantly on the mercury surface, but nuclei formed in the bulk of the synthesis solution should be attracted to the surface by the high surface tension. The nuclei in contact with the mercury orient with the ac-plane parallel to surface since the largest surface is influenced most by the surface tension. Other nuclei become randomly oriented. The nuclei grow to form a film and the crystals are oriented with their b-axes perpendicular to the mercury surface on the mercury side and randomly oriented on the solution side.

In the work of Tricoli et al. [18] unsupported silicalite-1 films were synthesized at the interface of two fluids. A growth model was not proposed, but the authors mention that it appears as if the zeolite nuclei are oriented at the interface and thus oriented (b-axes perpendicular to the substrate surface) zeolite films form in accordance with the model by Kiyozumi et al.
5 APPLICATIONS FOR MOLECULAR SIEVE FILMS

Potential use of molecular sieve films has been proposed in a number of application areas [34]. Two such areas of particular interest are membranes and sensors.

5.1 Zeolite membranes

A membrane is a barrier which is capable of separating components in a gas or liquid stream through a driving force such as a gradient in pressure, chemical potential or electric potential. Most of the membrane processes are based on an applied pressure difference across the membrane. Classical examples of the use of man made membranes are the desalination of sea water, dialysis of blood, and the separation of uranium isotopes. Membranes can be divided in two groups, organic and inorganic. Because of their unique stability, inorganic membranes, as opposed to organic ones, can be used for high temperature and high pressure separation processes as well as in catalytic membrane reactors. Inorganic membranes can in turn be divided into two main categories, porous membranes and dense membranes. Dense inorganic membranes, such as palladium membranes, have a number of rather severe limitations and the only remaining alternative for use at elevated temperatures is thus porous inorganic membranes. To obtain high selectivity, the pore size must be small. Zeolites being porous inorganic compounds with well defined pores of molecular dimensions should be ideal for this purpose, see Figure 2.

Zeolite membranes have the potential for use at elevated temperatures, to exhibit high selectivity and, if the zeolite film is thin, high flux can be obtained. Not only the size and
shape of the molecules in the mixture to be separated are important, but also differences in adsorption strength, due to the fact that surface diffusion may be the prevailing transport mechanism in the narrow zeolite pores. Several recent review articles treating zeolite membranes [14, 35-37] and describing the state of the art are available. Zeolite membranes can be manufactured as free standing films and a few examples have been reported, see section 4.2. However, the zeolite film must be relatively thick to obtain mechanical strength and low fluxes are obtained for this type of membrane. A thin zeolite film offers less resistance but requires a porous support to attain mechanical strength. Commonly used porous supports are ceramic and metallic ones.

Zeolite films can also be used as a component in membrane reactors [38]. In catalytic membrane reactors, catalysis and separation is performed simultaneously, which enhances the conversion in equilibrium limited reactions. Furthermore, two unit operations are combined into one and the plant can be simplified significantly by using membrane reactors. Numerous industrial processes are limited by equilibria, such as ammonia and methanol synthesis, water-gas shift, (de)hydrogenations (see Figure 3) and isomerisations [39]. Other processes such as oxidation reactions are highly exothermic and low feed concentrations are necessary to ensure effective product selectivity and temperature control, oxygen can be supplied in a controlled manner through a membrane to the reactor.

Figure 3. A conceptual membrane reactor for the dehydrogenation of ethylbenzene to styrene.
Several studies of MFI membranes on stainless steel supports [39-42] have been reported in the literature. These studies all dealt with similar membranes, i.e. a 40 µm thick silicalite-1 membrane on a porous stainless steel support. The main advantage with stainless steel supports is that a gas tight sealing between the support and the membrane test facility can be obtained in a straightforward manner. However, the difference in thermal expansion coefficient between the support and the zeolite may introduce problems. Furthermore, the pore size of the support is considerably larger ( > 1 µm) than the pores in alumina supports. Thicker zeolite films are thus necessary in order to close the large pores.

The most commonly used membrane support for zeolite films is meso- or macroporous alumina membranes, which are commercially available in different forms and well described in the literature. The advantage with porous alumina supports is that they are available with well defined pore sizes in a wide range, starting at approximately 5 nm (γ alumina). The thermal expansion coefficient of zeolite match better with alumina than with stainless steel. The disadvantage of alumina is that gas tight sealing at elevated temperatures is not as straightforward as in the case with stainless steel supports.

In two interrelated studies, membranes with approximately 10 µm thick ZSM-5 films were synthesized on α-alumina disks [43, 44]. The best membrane had a permselectivity (calculated from single gas experiments) for hydrogen/isobutane of 151 at room temperature and a transmembrane pressure difference of 1.27 atm. In another study, silicalite films with a thickness of about 10 µm, were synthesized on the inner side of γ alumina tubes [10]. The permselectivity (calculated from single gas experiments ) for hydrogen/isobutane was reported to be as high as 1100 at room temperature. However, the separation factor for a hydrogen/isobutane mixture was only about 10. In contrast to the high separation factors reported in the studies above, no separation of binary and ternary mixtures of aromatic hydrocarbons was obtained by Baertsch et al. [45]. They used membranes consisting of silicalite-1 films with a thickness of 2-10 µm on the inside of γ-alumina tubes. The mixture permeated through the membrane with the same rate as the slowest component in single gas experiments, and no separation was observed. The authors explain this behavior with single file transport through the membrane.

Although a substantial amount of work has been performed in the zeolite membrane field, sometimes with very successful results, improvements in both the synthesis procedure and the understanding of the diffusion mechanisms are necessary in order to fully utilize the
potential of zeolite membranes. The zeolite film thickness in all known membrane studies is too large, often several tenths of micrometers, leading to low fluxes. Armor [4] states that the thickness of the working layer in the membrane should be as thin as 100 nm, i.e. ultra thin. With decreasing zeolite film thickness, higher flux is obtained. A decreasing film thickness makes defects such as pinholes in the zeolite film more difficult to avoid. The calcination step is often detrimental to the membranes due to crack formation in the zeolite film. This step may possibly be avoided by synthesizing the films in the absence of organic template molecules, which may be a challenging synthesis task.

In some cases, no separation of mixtures is obtained, although expected from single gas permeation results. This is attributed to single file diffusion and novel measures must be taken to avoid such phenomena. The solution may be zeolite films consisting of small, randomly oriented crystals, forcing diffusing molecules to jump between neighboring crystals, thus enabling passage of faster diffusing species.

5.2 Sensors

A chemical sensor is a device constructed to give a response that is related to the quantity of a chemical compound or a group of compounds. Different chemical sensors are realized depending on the measured physical parameter. Sensors can be divided into thermal, mass, electrochemical and optical ones [46]. Optical sensors are based on an optical response when compounds adsorb on a sensor surface. The optical response can be related to a change in optical density or index of refraction which can be used to determine the concentration of the adsorbing species in the surrounding gaseous or liquid phase. In order to be effective, the chemical sensing component of the sensor, often a thin film on the sensor surface, must exhibit some adsorption selectivity to different compounds.

By reflecting polarized light against a surface, information about the surface properties can be recorded by measuring the change in the polarization of the reflected light. This technique is called ellipsometry [47], see Figure 4. Zeolite films, with channels of molecular dimensions, together with the possibility to tailor the chemical environment inside the channels, possess a considerable potential for use in sensors. It is not necessary for one sensor to be able to distinguish all chemical compounds from each other, since it is possible to combine several sensors with different characteristics in an array which in turn is able to detect and distinguish all compounds. Other techniques where zeolite films can be used are in surface acoustic wave (SAW) [48] and quartz crystal microbalance (QCM) [49] devices which are
mass sensors. Pyroelectric detectors which are thermal sensors have also been modified with thin zeolite layers [50].

Figure 4. An optical sensor using a thin zeolite film and ellipsometry.
6 SYNTHESIS OF FILMS BY THE SEED FILM METHOD

In the zeolite film synthesis method developed in this work, the substrates are first modified to facilitate adsorption of seed crystals. Gold substrates are silanized to render the surface negatively charged. Negatively charged substrates such as silicon wafers and silanized gold substrates are charge-reversed by adsorption of cationic polymer molecules. Zeolite seed crystals are subsequently adsorbed by means of electrostatic adsorption on the surface of the modified support from a sol. The seeded support is finally treated with a zeolite precursor solution in order to grow the seed crystals into a dense film. The development of the method for synthesizing thin films of various zeolites on a variety of substrates was reported in a number of publications (I-VII). Films of MFI type (I, III-IX) as well as LTA type films (II) were synthesized. The supports used were polished silicon (100) single crystals (I, III, VIII), polished alumina (001) wafers (II), polished quartz (001) wafers (IV), carbon fibers (VI) and gold sputtered silver discs (VII). Parameters influencing the preferred orientation of the crystals constituting the films were studied in detail (III, IV, V). Films were evaluated in sensor applications (VIII) as well as in membrane applications (IX).

6.1 Seed synthesis

Discrete colloidal monodisperse seed crystals of the zeolite are synthesized in clear homogeneous solutions and purified by repeated centrifugation and re-dispersion [12]. The solids content and the pH of the seed sol are adjusted. The pH of the sol was in the range 10 to 10.5 in order to maintain a negative surface charge on the colloidal crystals. The quality of the sol is important to obtain a monolayer adsorption. Aggregates in the sol will form islands of multilayer adsorption on the substrate.

6.2 Substrate modification

The substrates were cleaned using suitable methods, depending on the particular substrate. In the case of silicon, quartz and alumina substrates (I-V, VIII-IX), the cleaning procedure is described in Table 1. The purpose of this procedure is to clean the surface [51] and render it more hydrophilic.
Table 1. Cleaning procedure for silicon, quartz and alumina substrates.

<table>
<thead>
<tr>
<th>Cleaning step*</th>
<th>Composition+</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetone</td>
<td>Ultrasound for 5 minutes</td>
</tr>
<tr>
<td>2</td>
<td>$5\text{H}_2\text{O} : 1\text{H}_2\text{O}_2 : 1\text{NH}_3$</td>
<td>Boiling for 5 minutes</td>
</tr>
<tr>
<td>3</td>
<td>$6\text{H}_2\text{O} : 1\text{H}_2\text{O}_2 : 1\text{HCl}$</td>
<td>Boiling for 5 minutes</td>
</tr>
</tbody>
</table>

* Water rinsing between each step.
+ Composition in parts by volume of $\text{H}_2\text{O}$, 30% $\text{H}_2\text{O}_2$, 25% $\text{NH}_3$ and 37% $\text{HCl}$.

Gold substrates (VII) were rinsed and subsequently silanized by treatment with a solution of γ-mercaptopropyl trimethoxysilane in methanol. The silane was subsequently hydrolyzed in a dilute hydrochloric acid solution. After this treatment, the modified gold substrate resembles a SiO$_2$ surface with a negative charge, see Figure 5 [52].

![Figure 5. A silanized gold surface.](image)

The negatively charged substrates were treated with a cationic polymer solution (Berocell 6100 or Redifloc 4150, Akzo Nobel AB, repeating unit $[\text{CH}_2\text{CHOHCH}_2\text{N(CH}_3)_2]^+ \cdot 50.000$ g/mole, pH 8.0) to introduce a positive surface charge. Excess polymer solution was rinsed from the substrates prior to seed adsorption using a 0.1M ammonia solution.

### 6.3 Seed adsorption

The positively charged substrates were transferred to the zeolite sol to electrostatically adsorb the negatively charged colloidal zeolite crystals. The contact time with the seed sol was 1 h in the early work but since a shorter time proved to be sufficient, only 5 minutes was used in the later work. The sequence charge reversal-seed adsorption was in some cases (II, III, V) repeated to increase or to control the amount of adsorbed seeds.
6.4 Film growth

The seeded substrates were treated in a clear precursor solution (I-III, VII-VIII) or in a synthesis gel (IV, IX) to grow the seed crystals into a dense film. In some cases, both clear solutions and gels were used (V, VI). When crystals simultaneously form in the bulk of the synthesis solution, the nutrients are consumed by the crystals growing in the bulk as well as by the seed crystals on the substrate. Eventually, the crystal growth in the bulk and on the substrate ceases and a fresh synthesis solution can be used (II, III, V) to further increase the film thickness.
7 Characterization of the Films

7.1 Scanning electron microscopy and X-ray elemental analysis

A Philips XL 30 scanning electron microscope (SEM) equipped with an LaB₆ emission source played a central role in the characterization of the films. Film thickness and film morphology were determined from images recorded with the SEM. The amount of seed crystals was in some cases estimated by IMQUANT image analysis software from Link. The preferred orientation of the seed crystals and in some cases of the crystals constituting the film was determined from images. Better resolution is obtained with an LaB₆ emission source compared with a conventional Tungsten emission source, and tiny features which may be impossible to detect by a conventional W-SEM may be visible in an LaB₆ SEM [53]. An Oxford Ge X-ray detector with a super atmospheric thin window (ATW) attached to the SEM was used for energy dispersive X-ray analysis (EDX) of a few samples. Due to the relatively large sampling area of approximately 1 (µm)² for the EDX technique, the use of this method was limited to analysis of the relatively thick films of the zeolite membranes (IX) and to the analysis of powders.

7.2 X-ray diffraction

X-ray diffraction (XRD) was used extensively for the characterization of the zeolite films. XRD data were recorded with a Philips PW 1710-00 powder diffractometer in the early work (I, VI, VII). In the later work (II-V and VIII-XI), XRD data were collected with a Siemens D5000 powder diffractometer, which was in some cases equipped with thin film accessories.

In classical powder diffractometry the sample is illuminated by an X-ray beam and the intensity of X-rays emerging from the sample is recorded as a function of deflection (2θ). The deflection is dependent on the d-spacing within the crystals according to Bragg's law. The relative intensity of a certain X-ray peak is dependent on the orientation of the crystals within the sample. When analyzing powders, care is taken to avoid preferred orientation of the crystals. However, crystals in films may be oriented and the intensities of the recorded peaks may deviate significantly from the intensities expected from a sample with randomly oriented crystals. This phenomenon can be used to determine the orientation of the crystals in a film. In order to obtain a number that describes the preferred orientation of the films, CPO(X)/(Y)
(Crystallographic Preferred Orientation based on the (X) peak and the (Y) peak) was defined in the following way [54]:

\[
\text{CPO}(X)/(Y) = \frac{I_s^{(X)} / I_p^{(Y)} - I_s^{(Y)} / I_p^{(X)}}{I_s^{(X)} / I_s^{(Y)}}
\]

where \( I \) refers to the intensity of a peak (counts/step), whereas \( P \) and \( S \) refer to the powder reference and film sample respectively. The powder reference must consist of the same phase and should have similar crystal size etc. as the material in the film and the crystals in the powder should have no preferred orientation. The diffractogram from the powder reference and the film samples must be recorded with the same settings to enable comparisons. Any appropriate peak or combination of peaks can be chosen to describe the orientation of the crystals constituting the film. With this definition, a value of \( \text{CPO}(X)/(Y) = 1 \) means that the X-peak dominates over the Y-peak in the film sample due to preferred orientation. For instance, if \( \text{CPO}(h\ 0\ 0)/(Y) = 1 \), where \( (Y) \) is any other peak, all crystals in the film are oriented with the a-axes perpendicular to the substrate surface. If \( \text{CPO}(X)/(Y) = 0 \), the crystals are oriented as in the powder (randomly) in this respect. If \( \text{CPO}(X)/(Y) = -\infty \), the crystals are oriented in the opposite way. \( \text{CPO}(X)/(Y) \) was suitable to plot versus the film thickness to monitor the change in preferred orientation as a function of film thickness (III-V).

7.3 Dynamic light scattering

Particle size analysis by dynamic light scattering (DLS) was performed with a Brookhaven Instruments ZetaPlus on the seed sols used in this work and, in some cases, on synthesis solutions after synthesis. The ZetaPlus is equipped with a 4 mW diode laser. The sol under investigation is illuminated by the laser and the particles in the sol scatter light. The detector measures the scattered light from the particles at an angle of 90° from the incident laser beam. The random motion of the particles cause fluctuations in the scattered light intensity. From these fluctuations, it is possible to calculate the diffusion coefficient for the particles. If the viscosity of the sol is known, the hydrodynamic particle size distribution can be calculated, assuming spherical particles. The particle size distribution obtained is intensity-weighted. Another important fact is that the intensity of the scattered light is proportional to the particle diameter raised to the power of six, which makes DLS measurements very sensitive to particle aggregation.
7.4 Gas adsorption

Gas adsorption data at liquid nitrogen temperature on calcined seeds and films was recorded with a Micromeritics ASAP 2010. Nitrogen adsorption measurements were used for powder samples and krypton adsorption data were collected on the films. Kr-adsorption is more sensitive than N₂-adsorption and was thus more suitable to analyze the small amounts (<1 mg) of zeolite in the films. The BET or the Langmuir-equation was used to calculate the surface area. The BET-equation is only valid for multilayer adsorption on solid surfaces with pores considerable larger than the adsorbed molecule. Despite the fact that zeolites are microporous, the surface area obtained from the BET-equation can still be used for comparison and is conventionally used in zeolite science in that way. The film thickness was calculated from the BET-surface area of the film using the BET-surface area determined from zeolite powder, the density of the zeolite and the geometric area of the film as a reference (I, VII). In one case (VIII), the Langmuir equation was used (which should be more correct since a monolayer of adsorbed gas is assumed in the model for the equation), since the adsorption isotherms were found to be of Langmuir type, which is expected for zeolites.

7.5 Permeation measurements

Permeation measurements were performed on membranes prepared using the seed film method (IX). The membrane was mounted in a stainless steel permeation cell, see Figure 6. A rubber O-ring was pressed directly against the film to obtain a gas tight connection. Single gas permeation measurements were performed in the static mode, i.e. the increase in pressure on the permeate side was used to calculate the flux of the permeating gas. When binary mixtures were used, the flow of the gases on the feed side were controlled by mass flow controllers and a sweep gas was used on the permeate side. The pressure was controlled by back pressure regulators. A gas chromatograph was used to measure the composition of the permeating mixture. These experiments were performed at the Institute for Applied Chemistry in Berlin.
7.6 Ellipsometry

Ellipsometric measurements were performed on a variable angle spectroscopic ellipsometer (VASE) from J. A. Woollam Co (I, VIII). Ellipsometry measures the complex reflectance ratio, $\rho = \tan \psi \exp(i\Delta)$ where $\psi$ and $\Delta$ are the ellipsometric angles [47]. Ellipsometry is an indirect technique and it is necessary to develop an optical model in order to fully interpret the results. The model used in the earliest work (I) was a single layer of quartz and void in an effective medium layer on an infinitely thick silicon substrate. The experimental spectra were fitted to this model in order to obtain film thicknesses and void volume fractions which represented the pores in the zeolite. In the latter work (VIII), the amount of condensed vapor in the void volume (the channel system) was also included in the model. These experiments were performed at the division of Applied Physics at Linköping University.

7.7 Infra red spectroscopy

A few FTIR measurements (VI) were performed with a Perkin Elmer 2000 FTIR spectrometer. The adsorption bands characteristic for the MFI-type molecular sieves at 450, 550 and 1220 cm$^{-1}$ were recorded on selected samples.
8 PROPERTIES OF FILMS SYNTHESIZED BY THE SEED FILM METHOD

8.1 Seed adsorption

The SEM image in Figure 7 (a) shows 350 nm silicalite-1 crystals on a silicon wafer after the first seed adsorption. The seeds form approximately half a monolayer on the surface. If the seed coverage after the first adsorption is low, repeated polymer and seed adsorption can improve the seed coverage of the substrate. This was utilized in the preparation of silicalite-1 films on silicon wafers (III, V) where the preferred orientation of the crystals in the films as a function of the seeding density was investigated, see Table 2. Figure 7 (b) and (c) show the monolayer and the bi-layer of 350 nm seeds obtained after two and four adsorption steps, respectively. The solids content of the sol and the crystal size affects the amount of seeds adsorbed in the adsorption step. Small crystals are more readily adsorbed than large ones which can be seen in Table 2.

Table 2. Conditions for seed adsorption (III).

<table>
<thead>
<tr>
<th>Seed size (nm)</th>
<th>Number of adsorption steps</th>
<th>Approximate seed coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1</td>
<td>monolayer</td>
</tr>
<tr>
<td>60</td>
<td>2</td>
<td>bi-layer</td>
</tr>
<tr>
<td>160</td>
<td>1</td>
<td>half monolayer</td>
</tr>
<tr>
<td>160</td>
<td>2</td>
<td>monolayer</td>
</tr>
<tr>
<td>160</td>
<td>4</td>
<td>bi-layer</td>
</tr>
<tr>
<td>350</td>
<td>1</td>
<td>half monolayer</td>
</tr>
<tr>
<td>350</td>
<td>2</td>
<td>monolayer</td>
</tr>
<tr>
<td>350</td>
<td>4</td>
<td>bi-layer</td>
</tr>
</tbody>
</table>

Figure 8 (a) shows a monolayer of 45 nm silicalite-1 crystals obtained after one adsorption step. This figure should be compared with Figure 7 (a) where only half a monolayer of 350 nm crystals was obtained after one adsorption step. The area fraction of the substrate covered with seeds was estimated by image analysis. For instance, in Figure 7 (a) the estimated fraction of area covered by zeolite was 49 % and in (b) the fractional coverage was 76 %. In the case of NA films on alumina substrates (II), multiple adsorption steps were used as well. The objective was to improve the seeding density since thin dense films are more readily synthesized from a monolayer, see below. After the first seed adsorption, 40% of the substrate surface was covered, whereas 65 and 80% of the surface was covered after the second and third adsorption, respectively.
Figure 7. Approximately half a monolayer (a), a monolayer (b) and a bi-layer (c) of seed crystals with a size of 350 nm on silicon wafers.

Figure 8a. SEM image showing 45 nm silicalite-1 crystals on a silicon wafer after one adsorption step.
Figure 8b. SEM image showing the silicalite-1 film after 10 h of crystallization.

8.2 Film crystallization

After seed adsorption, calcination can be performed (I, IV, IX) or omitted. For instance, if seeds containing organic template molecules are used, the template can be removed prior to a film synthesis where no organic template molecule is used in order to obtain a system completely free of template molecules. A membrane synthesized in that way does not need to be calcined. Calcination following seeding does not appear to affect MFI films. However, it was found detrimental to calcine the alumina wafers seeded with NA-crystals, since no film formed in that case upon hydrothermal treatment (II).

Crystallization was performed after seeding by hydrothermal treatment in a zeolite precursor solution. The same hydrothermal treatment conditions were used for most (a gel was also used in paper VI) silicalite-1 films, only the duration was varied. The molar composition of the synthesis solution was 3TPAOH : 25SiO₂ : 1500H₂O : 100EtOH and the temperature was 100°C. Reflux boiling and atmospheric pressure were used. After a certain crystallization
time, the seed crystals grow to form a continuous film. The size of the seeds and the seed coverage determine the time required to obtain a continuous film. Figure 8 (b) shows an SEM image of the film obtained after 10 h of crystallization using the seeded silicon wafer shown in Figure 8 (a). This film is about 80 nm thin and almost dense. However, when starting from half a monolayer of 350 nm seeds as in Figure 7 (a) more than 24 h of crystallization is needed to obtain dense films (III). If the hydrothermal treatment is continued, an increase in film thickness is obtained. The maximum film thickness that can be obtained in one step is determined by the composition of the synthesis solution. Crystals simultaneously grow in the bulk of the synthesis solution and when the limiting nutrient is consumed, both the film and the crystals in the bulk cease to grow. Figure 9 (a) shows an SEM side view image of the film obtained after 3 days of crystallization, using the seeded silicon wafer shown in Figure 8 (a).

![Figure 9 a. A silicon wafer with a 530 nm silicalite-1 film obtained after 3 days of crystallization.](image)

![Figure 9 b. A silicon wafer with a 1200 nm silicalite-1 film obtained after 3+3 days of crystallization.](image)

After this time, both the 530 nm film and the crystals in the bulk cease to grow. However, it is possible to treat the film obtained after the first crystallization with a fresh synthesis solution to increase the film thickness. Figure 9 (b) shows a SEM side view image of the film obtained after a further crystallization period for 3 days in a fresh synthesis solution. After this time, the film reached a thickness of 1200 nm.

In some cases, the film thickness was determined by several methods such as SEM, Krypton-adsorption and VASE with similar results (I). This fact is clearly demonstrated in Table 3 where it is shown that the film thickness as measured with different methods are similar and increase linearly with synthesis time.
The film thickness determined by SEM is the thickness at one small part of the sample. However, almost no variation in film thickness is obtained when analyzing several parts of the same sample with the microscope. The film thickness obtained by VASE is determined from an area of a few square millimeters of the sample, depending on the size of the light beam. Finally, the film thickness obtained from Kr-adsorption data is based on the whole sample. The fact that all methods give similar results, indicates that a film with constant thickness over the entire substrate was produced. A good agreement between film thickness obtained from SEM and Kr-adsorption data was also obtained in the case of ZSM-5 films on gold surfaces (VII).

In the synthesis of NA films on alumina (II), it was crucial to avoid temperature fluctuations when moving the sample from the exhausted synthesis solution to a fresh one in order to increase the film thickness in a second hydrothermal treatment step. If temperature fluctuations occurred, major parts of the film could peel off completely, leaving the bare substrate (a polished alumina wafer) exposed. Several hydrothermal treatment steps could be used without any film peeling if temperature fluctuations were avoided by preheating the fresh synthesis solution. After completed synthesis the films seemed to by stable and could withstand several hours of ultrasonic treatment without any peeling. The interactions between the film and the substrate are not yet understood in detail.

### 8.3 Synthesis of films in the absence of organic template molecules

The main advantage of zeolite films synthesized in the absence of organic template molecules is that calcination of the as-synthesized membranes is no longer necessary to render the pore system accessible for guest molecules. Since the method developed includes seeding
of the substrates, it is possible to use a synthesis solution where no zeolite is formed in the absence of seeds. This alternative is ruled out when using the method of direct synthesis since the surface not is seeded in this case. This possibility was explored (IV, V, IX) to synthesize ZSM-5 films by seeding the substrates with TPA-silicalite-1 seeds. The seeded supports were calcined and subsequently treated in a synthesis gel with the molar composition 28Na₂O : Al₂O₃ : 100SiO₂ : 4000H₂O at a temperature of 180 °C under autogenous pressure. The growth of the seed crystals could be followed in this case as well. However, the early stages in the film formation process were difficult to monitor since a gel layer seemed to cover the growing crystals on the support. In some cases, the gel layer could be removed by prolonged ultrasound treatment in a 0.1 M ammonia solution after which the growing crystals on the support appeared. If the location of the seeds can be controlled, it should be possible to control the location of the film. For instance, the film penetration depth into a porous alumina support may be limited if seeds larger than the pores are used.

8.4 Preferred orientation

The preferred orientation of the crystals in a film can in some cases be evaluated directly from SEM images. For instance, in Figure 7 (a) and 10 (a) it can be seen that most of the mother crystals are oriented with the b-axes perpendicular to the substrate surface, whereas the intergrown twins have their a-axes perpendicular to the substrate surface. However, when a continuous film has formed, as in Figure 10 (b), the crystals have lost their normal morphology due to sterical hindrance during growth, see section 8.5. It is now more difficult to evaluate the orientation of the crystals, but when comparing Figure 10 (a) and (b) it would seem that most of the crystal faces seen in (b) are perpendicular to the a-axes of the intergrown twin crystals. One feature readily seen in SEM images of samples seeded in the same way is that the number of exposed crystal faces per unit area decreases with increasing film thickness, see 10 (a) and (b). This is probably a result of a competitive growth mechanism. The phenomenon can be seen even more clearly in Figure 4 in paper III.
If thin film XRD accessories are used, diffraction data with good quality can be obtained from relatively thin films. XRD is an excellent tool to evaluate the preferred orientation of the crystals in the films. A simple example is the NA films (II). Pattern (a) in Figure 11 was obtained from a powder sample with randomly oriented NA crystals. Some of the major peaks are indexed by using a reference pattern.

Pattern (b) is from a 280 nm thick NA film and is dominated by \{h 0 0\} peaks which was the case for the XRD pattern from the adsorbed seed crystals as well. This means that the \{h 0 0\}
planes of the adsorbed seed crystals and the crystals constituting the film are oriented parallel\textsuperscript{2} to the substrate surface. This is not surprising, since the seeds in this case are cube shaped and thus are adsorbed in a "flat" manner with the pinacoids facing the substrate surface. The situation is more complicated in the case of MFI films for several reasons:

1. The MFI system is orthorhombic (or even monoclinic after calcination) which is a system with less symmetry than the cubic NA system.

2. The habit of the MFI crystals is more complicated, see Figure 1, than the habit of the cube shaped NA crystals and different habits are possible [15]. The habit of MFI crystals is determined by the hydrothermal treatment conditions.

3. The MFI seeds used in this work are twin crystals with different directions of the a- and b-axes in the mother and daughter crystals.

![Figure 12. CPO (501)/(133) as a function of film thickness for MFI films synthesized by using different hydrothermal treatment conditions.](image)

\textsuperscript{2} If a normal θ:2θ scan is used (Bragg-Brentano configuration), only X-rays diffracting from crystal planes which fulfill the Bragg law and are oriented \textit{parallel} to the substrate surface will be detected. In most of the present work, θ was kept at 1° (grazing incidence) for intensity reasons which leads to planes that are more and more tilted from the substrate surface are detected when 2θ is increasing (detector scan), the deviation is 2θ/2-θ°. However, the peaks dominating when analyzing MFI-films when a grazing incidence and a detector scan was used were found to dominate when a normal θ:2θ scan was used as well (the intensity was lower in the latter case) and thus the deviation could be neglected in this case.
Despite the more complicated system, the preferred orientation could be evaluated in this case as well by XRD (III-V). Figure 12 shows CPO (501)/(133) as a function of film thickness for two types of MFI films. It illustrates the large difference in preferred orientation that can be obtained by using different hydrothermal treatment conditions and also that the preferred orientation is a function of film thickness. Moreover, the preferred orientation was found to be influenced by the crystal size and seeding density (III).

8.5 Growth model

A growth model for zeolite films synthesized by the seed film method based on the SEM and XRD data from a vast number of experiments (I-V) was proposed. A crucial assumption in the model is the absence of secondary nucleation or attachment of crystals formed in the bulk of the synthesis solution (except for the formation of multiple intergrown crystals and hillocks [55] on the mother crystals when synthesizing silicalite-1 films). The mechanism can be summarized as follows:

# Most of the seed crystals are adsorbed in a "flat" manner. In the case of cube shaped NA crystals this means that they will be preferentially oriented with the \{1 0 0\} pinacoids parallel to the substrate surface. In the case of MFI twin crystals it means that the b-axes of the mother crystals will be perpendicular to the substrate surface. However, the crystals will not be perfectly aligned, especially in the latter case. A distribution around the preferred orientation will always exist.

# The seed crystals grow in all directions upon hydrothermal treatment until a dense film has formed, whereafter growth in the lateral direction is restricted by neighboring crystals.

# The growth of the crystals in the film is competitive, i.e. crystals oriented with the fastest growing direction perpendicular to the substrate surface will be able to grow both perpendicular to the substrate surface and in the lateral direction. These crystals will dominate in thick films and the number of crystal faces per unit area will decrease with increasing film thickness.
# The fastest growing direction of the seed crystals is dependent on the hydrothermal treatment conditions.

The growth mechanism results in MFI films with most of the crystalline material oriented with the b-axes perpendicular to the substrate surface in thin films. This orientation would probably be more emphasized if seeds with no intergrowths [56] were used. However, the utilization of flat seeds was not explored in the present work. The hydrothermal treatment conditions determine which crystals that will dominate in thicker films due to competitive growth (V). When silicalite-1 films were synthesized, most of the crystalline material became oriented with the a-axes directed perpendicular to the substrate surface in thick films since growth of the intergrown daughter crystals were favored in the synthesis solution. On the other hand, when the ZSM-5 films free of organic template molecules were synthesized, most of the crystalline material became oriented with the c-axes directed at an angle of approximately 35 ° to the substrate surface in thick films since elongated (longest in the c-direction) crystals with no intergrowths are formed in this system. No change in preferred orientation with film thickness was encountered for the NA films, probably since the crystals were very oriented from the beginning in this case. The growth model developed in the present work is similar although much more detailed compared to the models depicted by Kiyozumi et al. [19] and Lai et al. [57].
9 APPLICATIONS

9.1 Sensors

Zeolite films manufactured by the seed film method were evaluated and tested as optical sensors in cooperation with the division of Applied Physics at Linköping University which has considerable experience in sensors based on optical principles. Thin films of silicalite-1 were synthesized on polished silicon supports (VIII). It was found that films with 250 nm thickness and thinner were suitable for studies using the VASE technique. Thus, two films with approximately 80 nm thickness and two films with approximately 250 nm thickness were used to investigate the use of the films as optical sensors. It is interesting to note that the void volume for zeolites often are estimated from the maximum liquid volume determined from adsorption data of different guest molecules. When using VASE (VIII), the void volume was first determined from the VASE data when the film was in an atmosphere of dry nitrogen at room temperature. Vapor of a particular gas was introduced at a certain partial pressure and the amount of condensed gas was determined from the VASE data based on the change in refractive index when liquid molecules replaced nitrogen in the pores. Adsorption isotherms for vapors of water, toluene, 1-propanol and hexane were recorded. It was then directly evident that only a fraction of the pores could be filled with liquid of certain gases such as water, whereas other gases such as hexane were able to fill the pores almost completely with condensed vapors. All recorded data except the water isotherms for the silicalite-1 films was found to be in good agreement with corresponding data from powder samples reported in the literature. A possible explanation for the discrepancy of the adsorption isotherm for water was proposed.

9.2 Membranes

ZSM-5 membranes (IX) were synthesized in the same way as the ZSM-5 films on quartz supports (IV), i.e. without the use of organic template molecules. The hydrothermal treatment time of the seeded substrate was 10 h which resulted in a film thickness of approximately 1.5 µm on the α-alumina support in accordance with the results when using polished quartz wafers. The preferred orientation on a microscopic scale of the crystals in the membrane seemed to be similar to the one in the films on flat quartz supports when comparing SEM images at high magnification, i.e. the c-axes were directed close to perpendicular to the
substrate surface. However, the surface roughness of the alumina support makes the crystals appear to be randomly oriented on a macroscopic scale when analyzed with X-ray diffraction. The membrane was not calcined prior to the permeation experiments. It was mounted in the permeation cell after drying at room temperature and subsequently heated to 120 °C at a pressure less than 10^{-4} mbar for 16 h. These conditions were found sufficient to remove most of the adsorbed molecules but mild enough in order not to induce cracks in the film. The flux in single gas experiments decreased in the series H2O, H2, CO2, O2, N2, CH4, i.e. with increasing kinetic diameter of the molecules. The difference in flux between each molecule in the series was almost 1 order of magnitude which indicated a high quality membrane. Molecules larger than CH4 permeated with similar flux, independent of their kinetic diameter, indicating that for these larger molecules, a non-selective permeation path through defects in the zeolite film dominated at a transmembrane pressure difference of 1 bar. However, the flux of these larger molecules was relatively low, less than 1/10 000 of the flux for H2O. Separation factors for binary mixtures (molar ratio 1/1) of N2/SF6 and H2/i-C4 at a transmembrane pressure difference of 1.5 bar and a temperature of 105 °C were 110 and 76, respectively, i.e. values far beyond Knudsen separation factors. On the other hand, when the transmembrane pressure difference was 0 bar, n-butane and i-butane permeated with the same flux through the membrane independent of the composition of the feed at 105 °C. This behavior is indicative of mass transport governed by adsorption and subsequent surface diffusion through the channels in the zeolite. The reported results (IX) were compared with results from related studies. It seems that the fluxes generally were lower and the separation factors for hydrogen/i-butane mixtures were higher than reported by other groups on similar membranes. These findings were ascribed to the presence of fewer defects and non-desorbed species in the channel system. The preferred orientation of the crystals in the film may also have reduced the flux, since no channels run along the c-axis and the molecules must diffuse in a tortuous path through the crystals in the film.
10 CONCLUSIONS

The novel procedure for the preparation of thin molecular sieve films developed in this work can be used to synthesize ultra thin and thin films of silicalite-1, ZSM-5 and NA on various substrates such as silicon, quartz, alumina, carbon and gold. The method seems to be rather insensitive to the chemical properties of the substrate surface since it is applicable to such a variety of substrates. Furthermore, a variety of synthesis solutions can be used for the synthesis of dense films, including synthesis solutions where no zeolite is formed unless seeds are added. The final film thickness can be controlled from approximately 80 nm and upwards by choosing the appropriate seed crystal size and hydrothermal treatment condition. A further degree of control of the final film thickness can be achieved by growth of the film in several steps. The preferred orientation of the crystals constituting the films can be controlled and altered to some extent.

Films produced by the novel method are of great potential interest for use in sensors, membranes, catalysis, electrochemistry, etc. Hollow fibers of zeolite as the only constituent can be synthesized by calcining a zeolite film deposited upon carbon fibers. The films have been evaluated in sensor and membrane applications with successful results.
11 Future Work

The interaction between the seeds and the substrate as well as between the film and substrate is not yet understood and work aimed at clarifying this important topic has already started. The template free precursor approach seems to be an elegant route to synthesize membranes with a low defect density. This approach has to be explored in greater detail for the ZSM-5 system but more importantly for other zeolites such as NA and Y since cracks seem to form easier in the latter cases. One envisioned project at the division aims at the development of synthesis methods for thin zeolite films effective for high temperature separation/catalytic reaction applications. The permeation properties of zeolite films will be investigated which will in turn support efforts to refine the synthesis methods to improve control of the film properties. In the long term the project may lead to the development of a zeolite membrane suitable for a catalytic application. Another project concerning membranes is aimed at studying how to avoid the formation of cracks in zeolite membranes and how these cracks can be repaired after they are formed.
12 ACKNOWLEDGMENTS

First of all, I sincerely thank my advisor and friend professor Johan Sterte for his support, inspiring enthusiasm and many ideas during this work. It has been a privilege to work in his group and it will be nice to go on working in the group in the future. I also thank professor Brian Schoeman, who is an expert in zeolite synthesis, for all discussions, ideas and help in the first part of my work. I hope he will visit us frequently in the future. I am thankful to professor Valentin Valtchev and Dr. Svetlana Mintova for their contribution to important parts of this work. I thank Dr. Derek Creaser for his help concerning the Noble English Language and also for his scientific help and I hope that the cooperation which we have started will continue in the future with great success. I thank Dr. Robert Bjorklund in Linköping for his cooperation. I hope we will go on with this and reach new, interesting results in various fields. I thank Dr. Jürgen Caro, Dr. Manfred Noack and Dr. Peter Kölsch in Berlin for their cooperation. I hope we will go on synthesizing and evaluating more and even better membranes. I am very thankful to Dr. Elena Babushkina for her help. I thank Miss Vania Engström. I hope we will have the opportunity to continue our work together in the future. I thank Miss Magdalena Lassinanti, Mr. Olle Niemi, Mr. Kurt Dyhr, Miss Lubomira Tosheva, Miss Qinghua Li, Mrs. Boreana Michailova, Mrs. Ingrid Granberg for your companionship and discussions. I also thank all my other colleagues here at the department of Chemical and Metallurgical Engineering and hope we will have a nice future together.

Financial support from the Swedish Research council for Engineering Sciences (TFR) and the Carl Trygger foundation is acknowledged. I am indebted to my parents who never stopped me when performing crazy experiments in my childhood. Last, I want to thank my Erja, whom I love and to whom I dedicate this work, for her courageous support during the last decade or so.
13 REFERENCES

Synthesis of ultra thin films of molecular sieves by the seed film method
Thin zeolite NA films by the seed film method
Jonas Hedlund, Elena Babouchkina and Johan Sterte
Presented at the 12th International Zeolite Conference in Baltimore, USA and accepted for publication in the proceedings.
Controlling the preferred orientation in silicalite-1 films synthesized by seeding
Jonas Hedlund, Svetlana Mintova and Johan Sterte
Accepted for publication in Microporous and Mesoporous Materials
ZSM-5 films prepared from template free precursors
Svetlana Mintova, Jonas Hedlund, Valentin Valtchev, Brian J. Schoeman and Johan Sterte
Accepted for publication in Journal of Materials Chemistry.
Control of the preferred orientation in MFI films synthesized by seeding
Jonas Hedlund
Submitted to Journal of Porous Materials
Preparation and characterization of hollow fibers of silicalite-1
Valentin Valtchev, Brian J. Schoeman, Jonas Hedlund, Svetlana Mintova and Johan Sterte
Continuous films of zeolite ZSM-5 on modified gold surfaces
Svetlana Mintova, Jonas Hedlund, Brian Schoeman, Valentin Valtchev and Johan Sterte
Chemical Communications, 1997, 15-16.
Vapor Adsorption in Thin Silicalite-1 Films Studied by Spectroscopic Ellipsometry
Robert B. Bjorklund, Jonas Hedlund, Johan Sterte and Hans Arwin
Evaluation of ZSM-5 membranes synthesized in the absence of organic template molecules
Jonas Hedlund, M. Noack, P. Kölsch, Derek Creaser, J. Caro and Johan Sterte.
Submitted to Journal of Membrane Science.