

**Synthesis and Characterization of Thin MFI-type
Zeolite Layer on Porous Alumina Substrates**

BY

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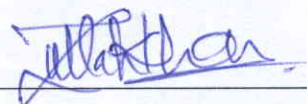
DEANSHIP OF GRADUATE STUDIES

This thesis, written by TURKI NABIEH BAROUD under the direction of his thesis advisor and approved by his thesis committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE in MECHANICAL ENGINEERING**.

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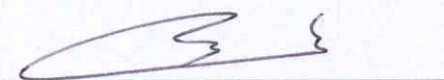
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THIS WORK IS DEDICATED TO MY LATE

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NABIEH MOHAMMAD BAROUD

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RODINA ALI MAGRABI

AND TO MY WIFE

ASMA ZAINYAMANI

(MAY ALLAH BE PLEASED WITH THEM)

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THESIS ABSTRACT (ENGLISH)

Name: Turki Nabieh Mohammad Ali Baroud

Title: Synthesis and Characterization of Thin MFI-type Zeolite Layer on Porous Alumina Substrates

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The most commonly used and commercially available membranes utilized for water desalination are made of polymeric materials. Due to their limitation and low performance in harsh environment such as high temperature and corrosive medium, ceramic-based membranes constitute a viable alternative. MFI is a particularly interesting inorganic zeolite structure with pores' size close to the kinetic diameter of many industrially important molecules. Controlled thickness, defect-free layer and preferential crystal orientation are still the main challenges with zeolite membrane fabrication.

In this research work, fabricating MFI zeolite membranes was performed using two techniques, in-situ crystallization and secondary growth. With the in-situ crystallization method, MFI zeolite crystals were directly grown on the substrates by subjecting the substrate to a hydrothermal treatment in the synthesis solution. Processing parameters such as hydrothermal treatment temperature and duration were varied. In the secondary growth method, MFI zeolite layer was synthesized by microwave assisted secondary growth, from microwave derived seeds deposited on α -Al₂O₃ substrate by either dip-coating or spin-coating before being exposed to the synthesis solution and subjected to a

microwave thermal treatment. The synthesized MFI zeolite layers were analyzed with X-ray diffraction (XRD) and scanning electron microscope (SEM) for their surface properties, coverage and the orientation of the zeolite crystals.

It is worth noting that the morphology of MFI zeolite membrane/layer was strongly influenced by several parameters. Albeit the simplicity of the in-situ crystallization technique, the combination of leaching and lack of continuity of the zeolite layer made this technique inadequate. Continuous MFI zeolite thin layer, defect free, with good morphology was grown on porous alumina substrate using secondary growth technique with the assistance of microwave irradiation at 160°C for 2h. Two seeding methods were used; namely dip-coating and spin-coating. The spin-coating technique showed promising results in term of the ability to reach a level of uniform seeds distribution on the top of the alumina substrate leading to formation of a closed packed seeding layer, in addition to a short process time compared to dip-coating technique.

To our knowledge, this is the first published work using spin-coating technique for seeding porous alumina substrate with MFI-zeolite nano-sized crystals. The uniform morphology of MFI zeolite layer was enhanced as the number of seeding runs was increased, and the orientation of the grown crystals was controlled with their crystallographic preferred orientation (CPO) (1 0 1). MFI zeolite layer was calcinated at very low heating and cooling rates of 1°C/min at 500°C for 6 hours. After calcination, the chemical analysis performed using energy dispersive spectroscopy (EDS) confirmed the diffusion of aluminum ions into the zeolite layer.

However, the results revealed that using three seeding layers with a thickness of about 120 nm was sufficient to prevent the diffusion of the aluminum ions towards the top surface of MFI zeolite crystals.

MASTER OF SCIENCE DEGREE

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THESIS ABSTRACT (ARABIC)

الاسم : تركي نبيه محمد علي بارود

الموضوع: تصنيع وتشخيص طبقة من مادة إم إف آي زيولاليت الخالص على قاعدة مسامية سيراميكية من مادة الألومينا.

القسم: الهندسة الميكانيكية.

التاريخ: رجب ١٤٣٣ هـ - مايو 2012م

تشكل الأغشية المصنعة من المواد البوليمرية أغلب الأغشية المتوفرة في معالجة وتحلية المياه ونظراً لقصور أدائها في بعض التطبيقات التي تصاحبها درجات حرارة عالية أو محيط مساعد على التآكل أصبحت الحاجة ملحة لخيارات أخرى تزيد من كفاءة هذه الأغشية. وتعتبر الأغشية السيراميكية خياراً ملائماً جداً خصوصاً لما تمتلك من صفات مثل الثبات الحراري والكيميائي تجعلها تنافس بقوة الأغشية البوليمرية. أحد أنواع هذه الأغشية السيراميكية الغير عضوية هي مادة (MFI-zeolite) والتي تتميز على غيرها من الأغشية السيراميكية بانتظام وتوحد إنتشار المسامات وكذلك صغر مساحة هذه المسامات في حدود (0.5 nm) مما يجعلها مادة واعدة في كثير من تطبيقات الفصل والمعالجة. وما زال استخدام مثل هذه المادة في تصنيع طبقات فاعلة مع إمكانية التحكم في سمكها وإتجاهات مجموعات الكريستال المكونة للطبقات مع خلوها من التشققات محل تحدي وخطوة تحتاج إلى دراسة علمية وتجارب عديدة.

تم التركيز في هذه الرسالة العلمية على تصنيع طبقة من مادة (MFI-zeolite) وذلك من خلال استخدام تقنيتين مختلفتين الأولى تسمى (In-situ Crystallization) والأخرى تسمى تقنية (Secondary Growth). نظراً لأن تقنية (Secondary Growth) تتطلب خطوة مهمة جداً ألا وهي خطوة توزيع مجموعة الكريستال النانوية (البذور) على سطح القاعدة السيراميكية تهيئة لها لكي تنمو ونظراً لأن هذه الخطوة لها التأثير الواضح والأهمية القصوى في تشكل وجودة الطبقة المتكونة، قامت هذه الدراسة باستخدام تقنيتين هما (Dip-coating) و (Spin-coating) من أجل الوصول إلى مستوى فائق من التحكم في مواصفات هذه الطبقة.

تشير النتائج التي تم التوصل إليها وتحليلها باستخدام أجهزة دقيقة ومتقدمة مثل جهاز (X-ray Diffraction)
(Scanning Electron Microscope) و (Scanning Electron Microscope) أن الطبقات التي تم تصنيعها باستخدام تقنية
(Secondary Growth) باستخدام المايكرويف من أجل التسخين الحراري لمدة ساعتين ودرجة حرارة 160°C
إلى إمكانية الحصول على طبقة متصلة ومتجانسة عالية الجودة من مادة (MFI-zeolite) على سطح القاعدة
السيراميكية. مع القدرة على التحكم باتجاه نمو مجموعات الكريستال النانوية من خلال عملية (Spin-coating)
حيث أثبت النتائج أن الانتقال من حالة النمو العشوائي إلى حالة النمو المنتظم في الاتجاه المفضل للكريستال (١٠١)
يتم بعد إعادة عملية (Spin-coating) ثلاث مرات لمحلول تركيز البذور فيه (1wt.%) لبذور من مادة (MFI-
zeolite) حجمها (89 nm). وحتى يتم تفعيل هذه الطبقة لتصبح جاهزة لإستخدامها في التطبيقات المختلفة تم إزالة
المادة العضوية- التي أستخدمت سابقا في صناعة التركيب الداخلية لمادة الزيولايت- وذلك بعد تسخين الطبقة عند
درجة (500°C) بمعدل تسخين منخفض ($1^{\circ}\text{C}/\text{min}$) لمدة خمسة ساعات. ونظراً لتعكس ردات الفعل أثناء
التسخين بين القاعدة السيراميكية من مادة الألومينا وطبقة مادة (MFI-zeolite) مما قد يؤدي إلى تشققات على
السطح بالإضافة إلى أن نتائج ((Energy-dispersive X-ray spectroscopy (EDS) أظهرت أن أيونات
الألمونيوم من القاعدة السيراميكية تستطيع النفاذ أثناء عملية التسخين العالية لتصبح جزءا من الكريستال المكون. لكن
النتائج العملية أثبتت أن (٣) طبقات من البذور هو ما يعادل (120 nm) كافية لتشكيل حاجزاً منيعاً أمام هذه النفاذية
مع إنعدام وجود التشققات على سطح الطبقة مما يؤكد جودة الطبقة المصنعة لتصبح جاهزة لإستخدامها في تطبيقات
مختلفة.

درجة الماجستير في العلوم
جامعة الملك فهد للبترول والمعادن
الظهران ، المملكة العربية السعودية
رجب ١٤٣٢ هـ

CHAPTER 1 INTRODUCTION

Water is an abundant natural resource that covers three quarters of the earth's surface. However, only 3% of all water sources are potable. About 25% of worlds' population does not have access to satisfactory quality and quantity of freshwater and 110countries face sever water problems even countries that do not face water shortage may have to tackle the problem of fresh water scarcity in the near future [1]. According to Stockholm International Water Institute, 47% of world population will be living in areas of high water stress. Hence the impact of this will be affecting every country in the world, including the developed, unless they reduce demand and develop additional water sources. However, many regions in the world such as Arabian Gulf, the Mediterranean Sea and the Caribbean depend mostly on ground and seawater desalination to meet their water demand. This limitation in the water supply source has forced these countries to become increasingly dependent on desalination. The main producers in the Gulf region are the United Arab Emirates with 26% of the worldwide seawater desalination capacity, Saudi Arabia with 23%, of which 9% can be attributed to the Gulf region and 13% to the Red Sea, and Kuwait with less than7% from the total production [3].

1.1 Water desalination

Water desalination is the process of removing salt and other minerals from water to make the water suitable for drinking or irrigation (Fig.1). No single desalination technology is considered a panacea for producing potable water. Most technologies use either thermal or membrane processes, however other technologies exist and many more are under

development. Desalination technologies need to be chosen based on site specific conditions including salt content, accessibility to engineering and construction services, and the quality of water needed by the end user. Often, maintenance requirements for a given technology will determine the type of system chosen for desalination plants. The economics of desalination varies from country to country, depending upon the cost of energy and capital as the main factors of production and the type of desalination process used. Desalination methods can be classified under two broad headings: Phase change processes (thermal processes) and Single phase (Membrane processes). While in the Gulf region thermal processes (MSF: multi-stage flash; MED: multi effect distillation) account for 90% of the production, the main process in Spain depends on reverse osmosis (RO) membranes with 95% of all plants [4].

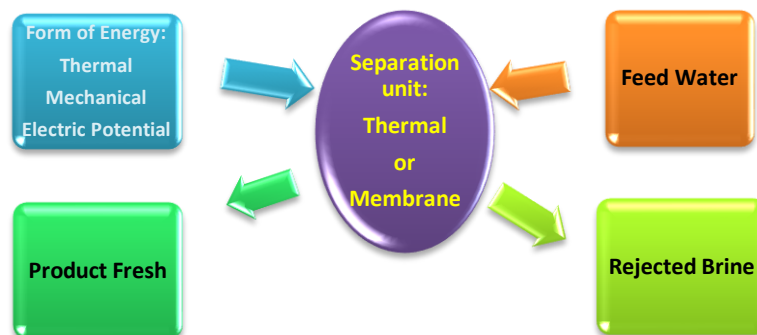


Figure 1 Definition of desalination process

1.1.1 Phase change processes (Thermal Method)

The thermal separation technique includes two main categories; the first is evaporation followed by condensation of the formed water vapor and the second involves freezing

followed by melting of the formed water ice crystals. The former process is the most common in desalination and nearly at all cases it coupled with power generation units, which may be based on steam or gas turbine. The most commonly used thermal methods and their time of adoption for desalination: multi-effect distillation (MED, 1900), multistage flash (MSF, 1950) and vapor compression (VC, 1940) [4]. Figure 2 shows a simplified schematic of a Multistage-flash unit (MSF) technique. The incoming seawater passes through the heating stage(s) and is heated further in the heat recovery sections of each subsequent stage. After passing through the last heat recovery section, and before entering the first stage where flash-boiling (or flashing) occurs, the feed water is further heated in the brine heater using externally supplied steam. This raises the feed water to its highest temperature, after which it is passed through the various stages where flashing takes place. The vapor pressure in each of these stages is controlled so that the heated brine enters each chamber at the proper temperature and pressure (each lower than the preceding stage) to cause instantaneous and violent boiling/evaporation. The freshwater is formed by condensation of the water vapor, which is collected at each stage and passed on from stage to stage in parallel with the brine. At each stage, the product water is also flash-boiled so that it can be cooled and the surplus heat recovered for preheating the feed water. Because of the large amount of flashing brine required in an MSF plant, a portion (50% to 75%) of the brine from the last stage is often mixed with the incoming feed water, recirculated through the heat recovery sections of the brine heater, and flashed again through all of the subsequent stages. A facility of this type is often referred to as a "brine recycle" plant. This mode of operation reduces the amount of water-conditioning chemicals that must be added, and can significantly affect operating costs. On the other

hand, it increases the salinity of the brine at the product end of the plant, raises the boiling point, and increases the danger of corrosion and scaling in the plant. In order to maintain a proper brine density in the system, a portion of the concentrated brine from the last stage is discharged to the ocean. The discharge flow rate is controlled by the brine concentration at the last stage.

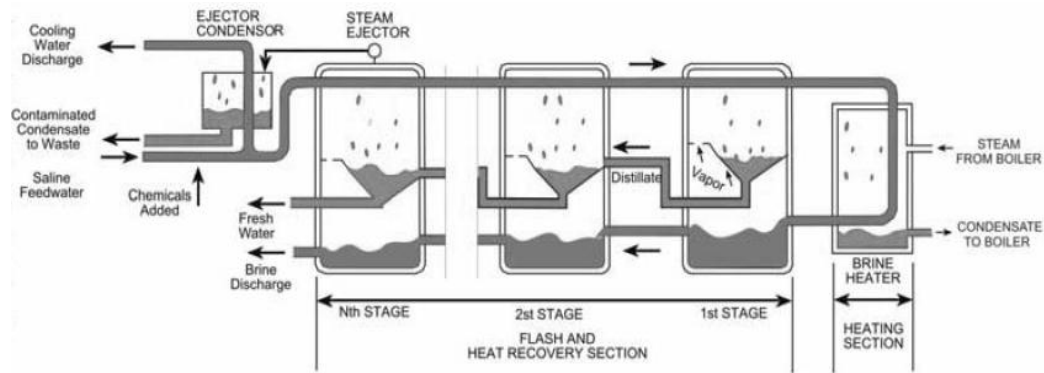


Figure 2 Schematic of Multistage Flash Unit

1.1.2 Single phase (Membrane Method)

Based on the Preferential Sorption-Capillary Flow Model Loeb and Sourirajan developed cellulose acetate membrane for seawater desalination, the announcement of Loeb-Sourirajan membrane in 1960 opened up the golden era of research and development activities on membrane technologies [6]. Reverse Osmosis membrane RO is currently the state-of-the-art desalination technology. The preference for membrane systems, specifically RO, over other techniques is due in part to the development in last 50 years of membranes with higher recovery rates and lower pressure needs, making them more efficient to operate [7]. Membrane can be defined as a selective barrier between two

phases, the term selective being inherent to a membrane or a membrane process. Transport through the membrane takes place when a driving force is applied to the components in the feed. In most membrane process, the driving force is a pressure difference or a concentration difference across the membrane. Various pressure-driven membrane processes can be used to concentrate or purify a dilute solution. The characteristic of these processes is that the solvent is the continuous phase and the concentration of the solute is relatively low. The particle or molecular size and chemical properties of the solute determine the pore size and pore size distribution necessary for the membrane employed. In addition, the membrane can be classified According to their structure into various processes. These processes are Microfiltration, Ultrafiltration, Nanofiltration and Reverse Osmosis. The principle of different processes is illustrated in figure.3. Because of the applied pressure, the solvent and various solute molecules permeate through the membrane, whereas other molecules or particles are rejected to various extents dependent on the structure of the membrane.

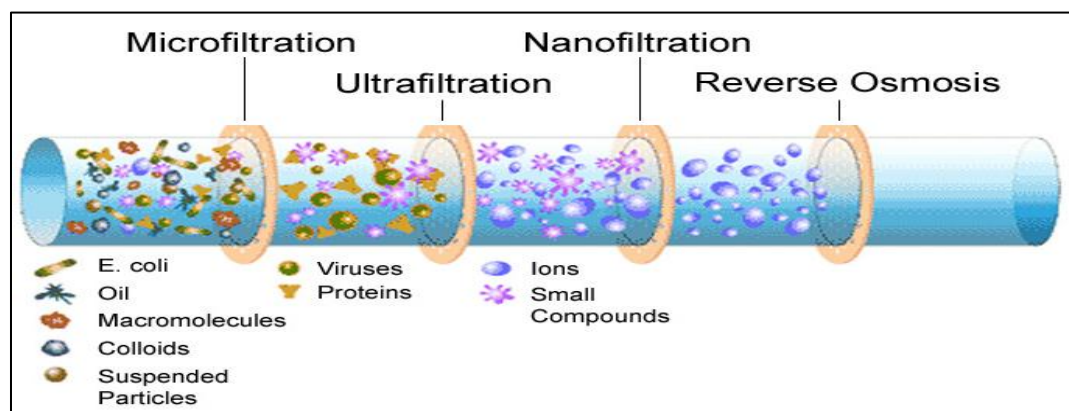


Figure 3 Principles of membrane separation

1.2 RO membrane

Desalination by RO requires the use of an osmotic membrane (i.e., one that allows water to pass through it at much higher rates than dissolved salts). Osmotic membranes occur naturally in living organisms everywhere. The osmotic membrane also is referred to as a semipermeable membrane because of its capability to allow some constituents to pass through it while holding back others. The osmosis phenomenon in nature is one where a dilute solution is transported across a semipermeable membrane toward a concentrated solution on the other side. The process of RO is just the opposite of osmosis and is illustrated in Figure 4. In osmosis, the solvent water passes through the membrane until the pressure difference across the membrane is equal to the osmotic pressure. In the RO desalination process, a pressure greater than the osmotic pressure applied to the saline water will cause fresh water to flow through the membrane while holding back the solutes (salts). The higher the applied pressure above the osmotic pressure, the higher the rate of fresh water transports across the membranes. In seawater RO desalination field, energy saving and water quality improvement have always been two major subjects. Today, the energy consumption of RO membrane treatment process is one fifth and the operation cost is less than one tenth, compared to those of 1970's [7].

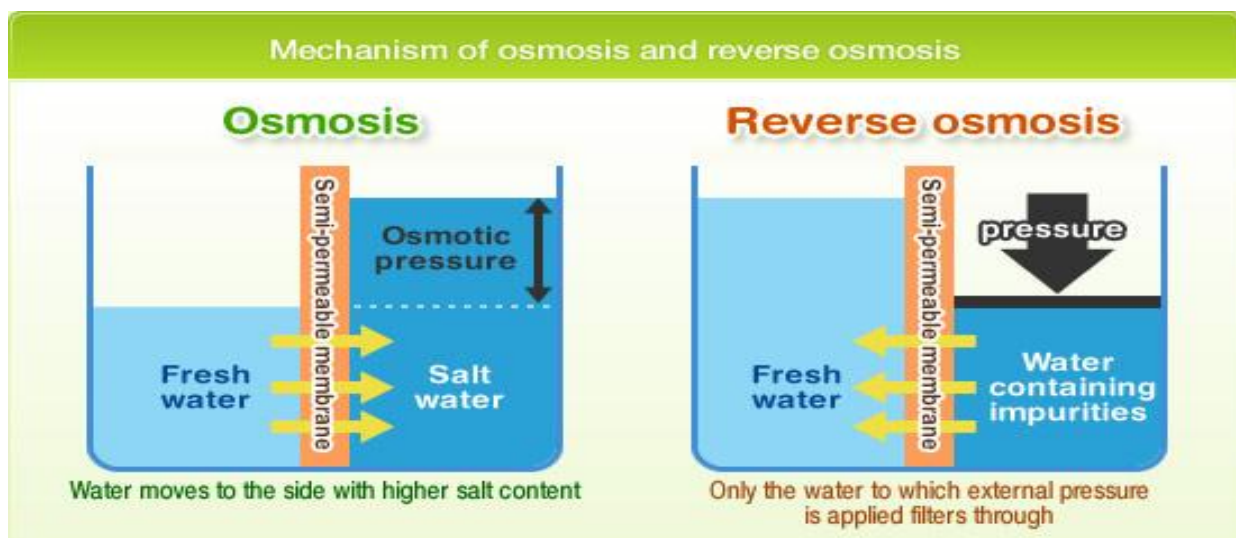


Figure 4 Mechanism of Osmosis and Reverse Osmosis [8]

Two main technologies are currently used in the Kingdom for water desalination, these are the Multistage Flash method (MSF) which constitutes about 90% of Saudi Arabia desalination plants and the Reverse Osmosis membrane (RO) process [5]. Indeed, MSF plants are suffering mainly from scale and corrosion problems, whereas the RO membrane processes are actually suffering from fouling, biofouling and biocorrosion. Hence, attention in the present work is given to the development of Inorganic membrane, especially for the water desalination because of its significant importance to the water sector in Saudi Arabia. The most commonly used and commercially available membranes utilized for water desalination are made of polymeric materials. Due to their limitations and low performance in harsh environment such as high temperature and corrosive medium, ceramic-based membranes constitute a viable alternative. Ceramic membranes are made from inorganic materials such as aluminum oxide, titanium oxide, zirconium oxide and zeolites. Ceramic membranes display a number of performance advantages for water treatment applications such as their excellent resistance to chlorine, oxidants,

radiation and solvents. Furthermore, they exhibit high thermal and chemical stability allowing them to be quite suitable for processes involving high temperatures and harsh chemical environments.

1.3 Aim and objectives:

- To develop controlled thickness, continuous, crack-free and oriented thin MFI zeolite active layer on porous alpha-alumina substrate potentially for reverse osmosis (RO) water desalination process.

To achieve the above aim, it is proposed:

- To fabricate macro-porous alpha-alumina support using uniaxial compaction and sintering (powder metallurgy process).
- To enhance the surface of the substrate by several surface pretreatment steps.
- To use in-situ crystallization for synthesizing MFI zeolite layer on alpha-alumina substrate.
- To use secondary growth technique for synthesizing MFI zeolite layer on Alpha-alumina substrate, and this requires:
 - Synthesis of nano-sized MFI zeolite crystals using microwave to be used as seeds.
 - Deposition of the seeds by spin-coating technique.
 - Growth of zeolite layer using microwave synthesis technique.
 - Calcination of the zeolite layer to remove the TPA from the MFI zeolite channels/pores.
- To gain an understanding of the mechanism/kinetics of these processes by carrying out a thorough characterization of the surface morphology, phases, crystallinity, pore size, porosity thermal stability and continuity of the MFI zeolite membrane/layer using FE-SEM/EDS, XRD, PSA, TGA/DSC.

CHAPTER 2 LITERATURE REVIEW

2.1 Zeolite membrane

Zeolites, crystalline aluminosilicate materials, possess 3-dimensionally connected framework structures constructed from corner-sharing TO₄ tetrahedra, where T is any tetrahedrally coordinated cation such as Si and Al. These framework structures are composed of n-rings, where n is the number of T-atoms in the ring (e.g. 4-, 5-, and 6-rings), and large pore openings of 8-, 10-, and 12-rings are framed by these small rings. Figure 5 shows the pore sizes and framework structures of typical zeolites. The sizes of the intracrystalline pores and nanospaces, depending on the type of zeolite providing the framework, are close to the molecular diameters of lighter hydrocarbons. Moreover, strong acid sites exist on the nanopore surfaces, enabling the zeolites to be used as shape-selective catalysts in industrial applications such as fluid catalytic cracking of heavy oil, isomerization of xylene and synthesis of ethyl-benzene[9].

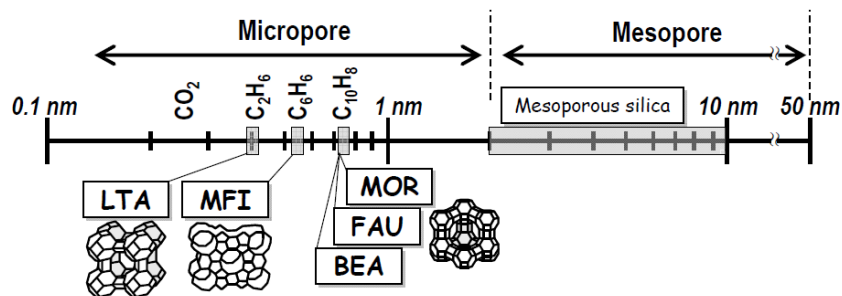


Figure 5 Zeolite structure, pore size and molecular diameter of hydrocarbons [9].

Recently, zeolite membranes have attracted considerable interests in both industrial and academic sectors. Zeolite membranes can be applied to high-temperature and high-pressure conditions. They offer high permeance and excellent separation properties because of the molecular sieving pore size with uniform distribution, and excellent adsorption properties of zeolites. Zeolite membranes can be used in membrane reactors by taking advantage of both separation and catalytic properties.

2.1.1 MFI zeolite membrane

Zeolite with MFI framework topology has an orthorhombic crystal symmetry with nearly cylindrical, 10-member ring channels (diameter~ 5.6 Å). Silicate-1 (PSZ) has a crystal structure like zeolite ZSM-5. It can be crystallized from a relatively simple mixture of tetrapropylammonium hydroxide (TPAOH) acting as template, a silicon source, and water. Moreover, it is considered as AL-free analogues of ZSM-5. The characteristic crystal shape of TPA-silicate-1 is a hexagonal prismatic shape, more commonly referred to as a coffin shape.

With the order of crystal dimensions $L_c \geq L_a > L_b$ (where L_i indicates crystal size along i -axis), the channels in the b -direction are straight with a pore diameter of 0.51x0.55 nm and they are connected to zig-zag channels in the a -direction [10]. The pore diameter of zig-zag channels is 0.51x0.57 nm. No channels are present in c -direction as shown in Figure 1.

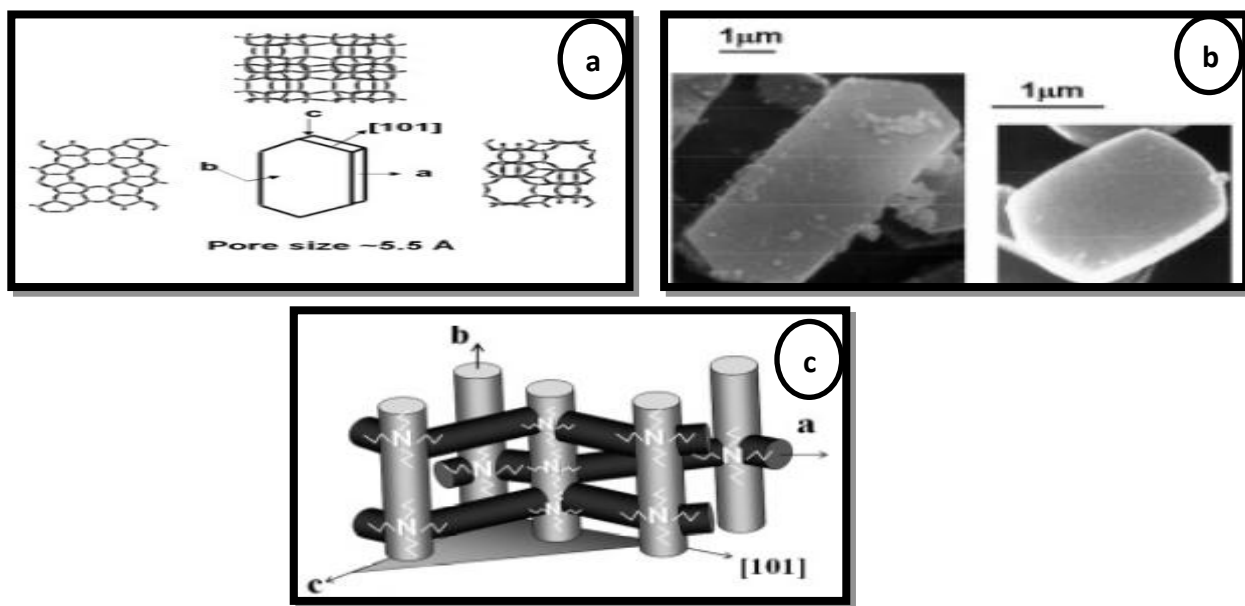


Figure 6 (a) A schematic identifying the crystal faces and directions along with corresponding framework projections. (b) Typical SEM images of coffin-shaped crystals. (c) Schematic of the pore structure of PSZ with the TPA located at channel intersections [10].

However, mass transport is still possible in this direction, since molecules can jump from the straight channels to the sinusoidal channels at their intersections and thus diffuse in a tortuous path in the c-direction [8]. Because the MFI Zeolite membrane is easy in preparation and show high separation performances, the number of papers and patents are increasing on this specific topic.

To this aim, MFI is a particularly interesting Zeolite structure topology due to the pores with a size close to the kinetic diameter of many industrially important molecules. Due to their excellent chemical, thermal, mechanical stabilities and microstructure, PSZ membranes are potentially useful for treating saline wastewater by reverse osmosis RO technique [9]. Until now, most of the zeolite membranes are still in laboratory study, and there exist some challenges in both synthetic and application aspects [10].

2.1.2 Synthesis of Zeolite membrane

The traditional synthesis procedure for zeolite powders has been adapted and improved upon for the preparation of zeolite films and membranes. Moreover, in the synthesis of high-quality zeolite films, the accurate manipulation and optimization of their microstructures, such as crystallographic preferred orientation (CPO), thickness, intergrowth and grain boundary structures, is critical. These microstructures may dramatically influence the performance of devices incorporating zeolite films. Mainly the synthesis of MFI Zeolite membrane can be through two deferent techniques:

- 1- In-Situ Crystallization Technique.
- 2- Secondary Growth Technique.

2.2 MFI film formation by in-situ technique:

The in-situ synthesis method has been widely used for preparation of zeolite films and membranes. By using this technique, the substrate is placed in a synthesis mixture containing the zeolite precursors and growth-directing agents. The zeolite is then crystallized by the hydrothermal action generated either by conventional or microwave heating of the mixture. During the synthesis, nuclei formed on the support grew into crystal that inter-locked to create a continuous layer free of nonzeolitic transmembrane pathways. The benefit of direct in-situ method is its simplicity. Generally, it is a one-step process where the need is eliminated for specially designed substrates (e.g., organic-functionalized or microstructured) and for preparation of a seed crystal layer by dip- or

spin-coating[11]. In-situ crystallization also has the advantages that it produces excellent adhesion to a wide variety of substrates and can easily coat surfaces of complex shape and in confined spaces. The orientation of the zeolite microcrystals can influence the membrane performance in most of these applications because the zeolite pore structure varies through different crystal axes. Hence, many researchers investigated the influence of synthesis parameters to control the orientation of the MFI crystals on the top of different supports. G. Xomeritakis et al. observed that the film obtained by in situ growth exhibits $[0k0]$ or $[h00]$ -out of-plane preferred orientation [18].

Crystal orientation control in a continuous MFI thin film can be achieved by simple adjustment of synthesis compositions using direct in-situ crystallization. Yushan and co-workers showed that within the synthesis system of TPAOH:NaOH:TEOS:H₂O:NaCl, OH-/Si and Na⁺/TPA⁺ ratios play a critical role in controlling crystal orientation by direct in-situ crystallization in stainless steel as shown in figure 6. It should be noted that this map is generated by using TEOS as the silica source and may not be directly applicable to composition in which other silica source (e.g., colloidal silica) is used.[11]

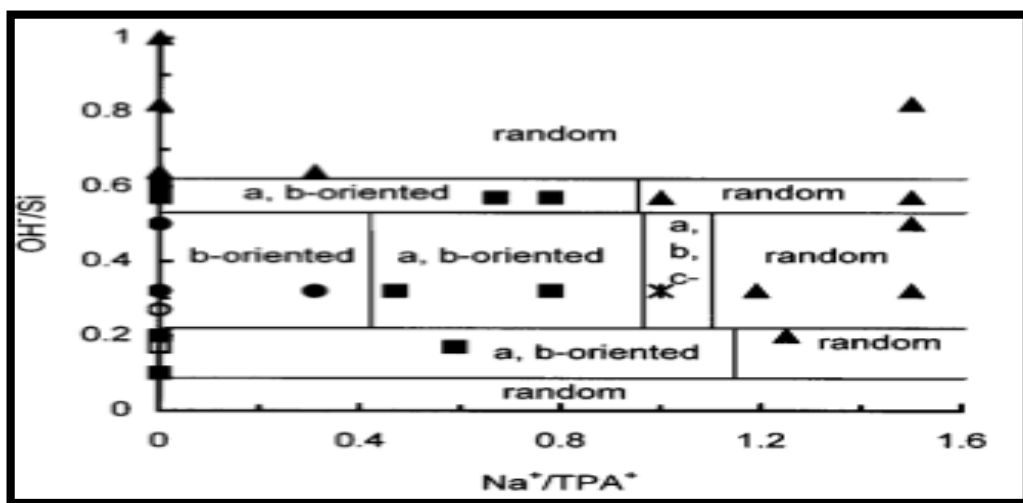


Figure 7 Crystal orientation-synthesis composition map. [11]

A heterogeneous nucleation model has been proposed to explain formation of b-oriented MFI films. Koegler et al. [24] proposed a model for the growth mechanism in which a thin gel layer with low template content is formed on the silicon wafers substrate by the agglomeration of primary gel particles present in solution, which are transported to the support by Brownian motion. This gel layer formation is relatively independent of the type of support and of its positioning in the autoclave. Both Nucleation and growth occur at the interface of gel and liquid, Where only the region both silicon source and template are present in abundance. Crystal growths proceeds into the gel phase until the crystals bond with the support and finally align with their (010) faces parallel to the substrate. At a stage where the gel layer formation is reduced, nucleation will occur at the interface of the gel and the (clear) synthesis solution. Further gel settlement is probably still proceeding, either burying or otherwise disturbing some of the nuclei. The nuclei themselves already have a preferred orientation, as described above, but a second orienting mechanism provided by the fact that the nuclei at first can grow only in the

plane of the gel and liquid interface as shown in stage 2 of Figure 7. Therefore, only the nuclei with their preferred growth directions i.e. the a- and c-axes in the plane of the interface can give rise to crystals. The crystals will consume the gel, thereby sinking to the substrate surface. Here they will be subject to even stronger orientation by the flat surface shown in stage 3 from Figure 7. When conditions are chosen properly, the crystal coverage at that point is as high as possible.

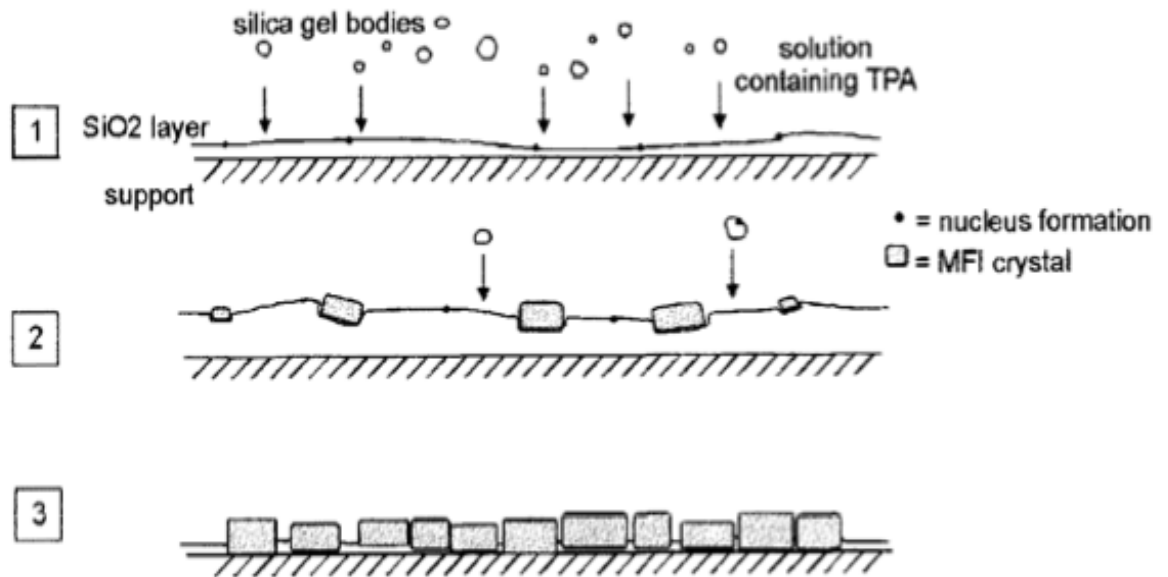


Figure 8 Growth mechanism model [24].

When synthesis proceeds beyond this point, a secondary crystal layer will be formed on top of the first, which is undesirable. This secondary layer, surprisingly, also has a preferred orientation, with the a-axis perpendicular to the surface. The secondary nuclei probably start from the b-planes of the first crystal layer and have a strong tendency to

form 90° intergrowths. Although, this model can explain well the fact that *b*-oriented crystals are formed on both horizontally and vertically placed substrate, it will be difficult to use this model to explain why *a*-oriented crystal appear in the film sometimes. This model also has difficulty in the explaining why second layers are present under certain conditions.

Zhengbao Wanget al. [12] proposed and discussed an alternative film formation model(Figur8) to explain all of their observations. From Figure 8 the film formation process can be separated into five stages. The first stage is the formation of colloidal sub-micron crystals which is less than 0.5 μm possibly via aggregation of nanoslabs in bulk solution. In the second stage, the colloidal crystals in the vicinity of the substrate are attracted onto the substrate surface to form a nearly continuous first layer due to favorable electrostatic and van der Waals interactions. Since these sub-micron MFI crystals are disk shapes with *a-c* plane is the largest flat surface, they are most stable when they are *b*-oriented.

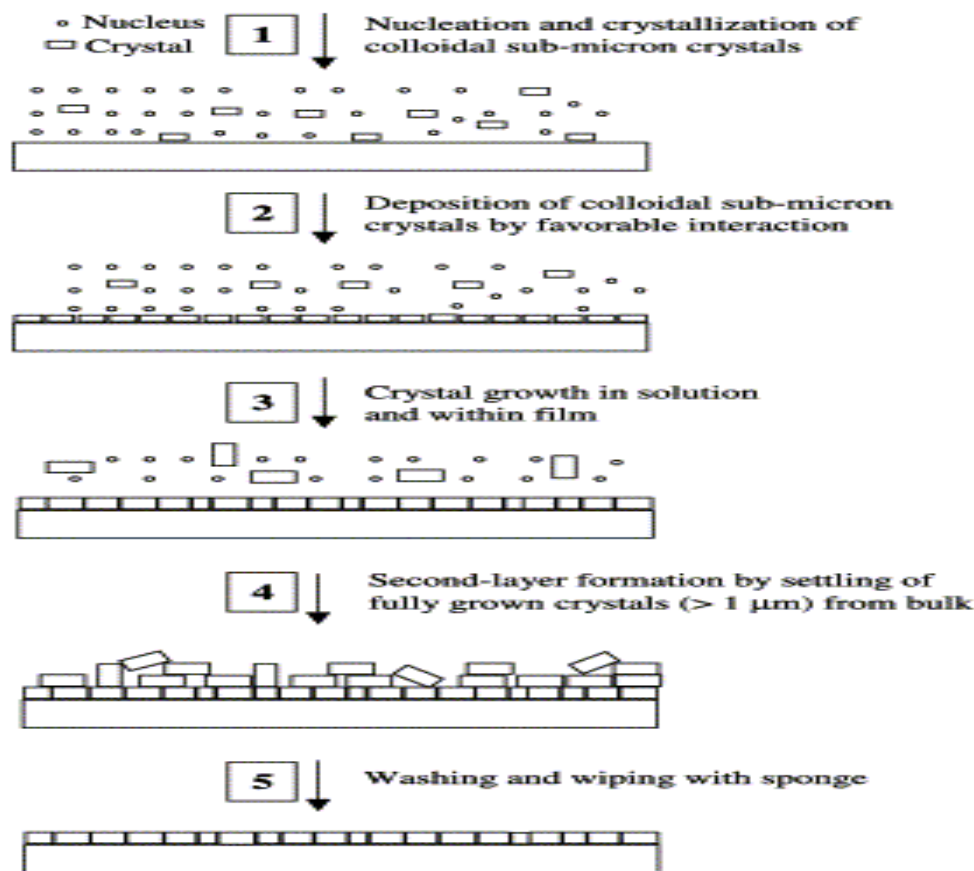


Figure 9 A schematic drawing of a possible formation mechanism for b-oriented MFI zeolite membrane on Stainless steel [12]

This deposition process is a self-assembly process and *b*-orientation helps maximize the favorable interaction between the crystal and the substrate surface. In the third stage, both the sub-micron crystals inside the first layer film and in the bulk grow larger. Because of the limited space available on the surface, a continuous film soon forms on the substrate. By contrast, the crystals in the bulk continue to grow until they reach certain size (e.g., $>1 \mu\text{m}$) and then they start to settle primarily by gravity, as it is clear from the fourth stage of figure 8. Unlike the sub-micron crystals, these relatively large crystals (e.g., $>1 \mu\text{m}$) have well-developed faucets (coffin shaped). Under normal synthesis conditions described [12]

horizontally fixed substrate with 4 g solution loading, these settling large crystals form a continuous loosely packed second layer on top of the first-layer film. To form a continuous b-oriented MFI film, sufficient high concentration of disk-shaped colloidal crystals is required within relatively short crystallization time. If the number of these disk-shape colloidal crystals is too low, the substrate will not receive sufficient coverage for the first layer in stage 2. And then in stage 3, large coffin-shaped crystals with well-developed faucets will settle into the open surfaces. These large crystals can sit on their b-c plane with reasonable stability leading to a-oriented crystals. Although b-oriented may still be favored thermodynamically, these crystals may not be able to achieve this configuration because they are relatively large and there is insufficient driving force within the system. MFI crystals with their *b-axis* perpendicular to the substrate surface prepared by In-situ crystallization were usually deposited on nonporous substrates such as stainless steel, aluminum alloy. However, in 2005, Takahashi et al. studied the growth of MFI crystals on alpha-alumina substrates and they showed the effect of coated the substrate with mesoporous silica sublayer (Fig.9, 10). While *b-oriented* membranes with a thickness between 2-3 micrometer at 453 K and sufficient coverage of the substrate surface with preliminary crystals can be grown by in situ crystallization on porous alpha-alumina precoated with a mesoporous silica sublayer due to some reasons such as; Si-OH groups may provide a strong interaction between the silica sublayer surface and the silicate species, Smoothness of the silica sublayer and the elimination of intrinsic defects on the porous substrate, a membrane with a randomly oriented top layer with long period of hydrothermal heating was obtained on the uncoated alpha-alumina substrate using the same preparation conditions[13].

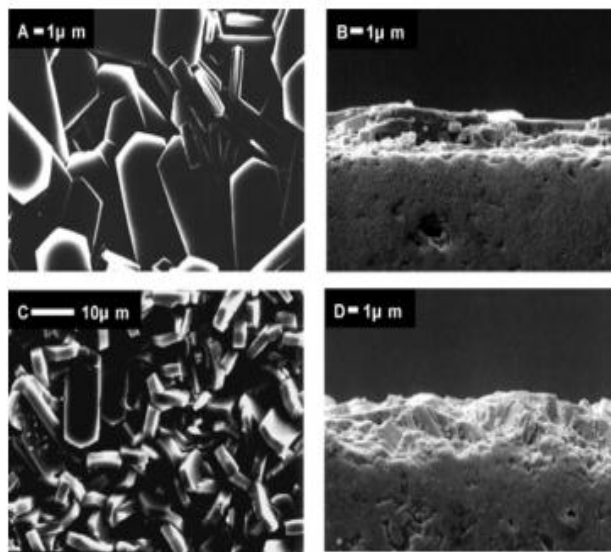


Figure 10 SEM of the surface and cross section on silica sublayer coated (A,B) and uncoated alpha-alumina substrate (C,D) with 10 h crystallization. [13]

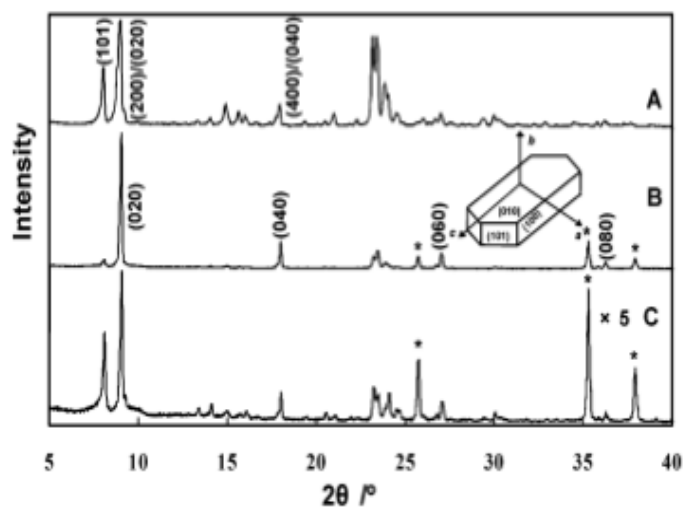


Figure 11 XRD patterns of MFI powder at the bottom of the autoclave when using silica sublayer-coated substrate (A), MFI membrane on silica sublayer-coated substrate (B), and uncoated alpha-alumina substrate (C) with a crystallization of 10 h. "*" is for the substrate.

The low nucleation site density often observed in membranes crystallized in situ can be improved by using synthesis conditions that favor a high nucleation site density, e.g. a highly alkaline synthesis mixture for MFI synthesis [14] and [15]. When applying in situ crystallization methods, multiple crystallization steps are usually required to close all defects [15] and [16]. To avoid these multiple immersions, it is also possible to increase the synthesis temperature in a stepwise manner to induce further zeolite deposition [17].

However, this method has a number of disadvantages. Because of a relatively low nucleation site density, a considerable film thickness of several micrometers is necessary to close all defects or complex treatment technique used to repair the defects (e.g. Chemical vapor deposition CVD). The synthesis mixture can also penetrate the pores of the support, which has several consequences. Firstly, the synthesis mixture may leach components from the support, which may contaminate the growing zeolite film. Secondly, zeolite crystals or amorphous material may deposit inside the pores of the support. This may reduce the support pore size, increase the effective zeolite film thickness, and also reduce the effective membrane area, since the porosity in the top layer of supports is typically 30–50%. All of these factors will limit the flux significantly. In addition, the combination of leaching and zeolite crystallization within the support may change the mechanical properties of the support, leading to cracks in the film and the support.

2.3 The secondary Growth

The secondary Growth of the supported zeolite seed layers, which brought in improved flexibility for crystal growth and greater control of film microstructure, is now recognized as one of the most attractive methods for orienting the formation of consolidated thin membrane, including good quality ZSM-5 and silicate1 [23]. Several MFI zeolite membranes have been successfully made into a membrane using this synthesis method[18-25,34&35]. The technique provides a better control over the zeolite membrane growth and morphology. Lovallo and coworkers [35] have reported the preparation of well-orientated membranes using this procedure. In the typical synthesis, the zeolite crystals grow outward from the seed layer towards the synthesis solution. Chau and coworkers [38] have demonstrated that the zeolite growth direction is not fixed, but can be manipulated by the surface structure of the support. Most of the porous supports used in the preparation of zeolite membranes are made of sintered crystalline particles and are inherently heterogeneous. Some supports like the stainless steel, are alloys and contain several structural phases. The heterogeneous nature of the support material contributes to the poor reproducibility of the zeolite membranes prepared by in situ method. G. Xomeritakis et al. [8] and Chu et al. [34] have demonstrated that pre-seeding the support with colloidal zeolites can significantly reduce the influence of the support that lead to better reproducibility in both the deposited microstructure and separation properties of the membrane.

The synthesis of membrane by this technique can be divided into four steps:

1. Seed preparation.
2. Seed deposition.
3. Secondary growth.
4. Template elimination.

2.3.1 Seed preparation

The secondary growth method allows a free selection of crystal seeds with different sizes and shapes. The size of zeolite seeds is important parameters. If the size is too small, it can enter into the pores of the support, which will reduce the permeation flux. Moreover, the small size will grow to tiny crystallites and those crystallites formed gaps in between, leading to a reduction in separation performance. On the other hand, if the size of seeds is too large, the cross-linkage of the membrane will be decreased. As a result, the thickness of the membrane would be increased. The crystal size of the zeolites seeds varies with synthesis conditions. However, conditions that favor the synthesis of smaller crystals are typically accompanied by a lower zeolite yield and/or a longer crystallization time.

2.3.1.1 Influence of synthesis parameters on seeds size

Table.1 shows different recipes for preparing MFI zeolite seeds with result of different sizes. The crystal size of these zeolites seeds vary with synthesis conditions. However, conditions that favor the synthesis of smaller crystals are typically accompanied by a lower zeolite yield and/or a longer crystallization time. Many researchers investigated the influence of synthetic conditions and parameters such as the concentration of water, template temperature etc.

Table 1 Synthesis conditions and recipes of MFI-type zeolite seeds. [27]

Recipes	Temperature	Duration	Size
25SiO₂:9TPAOH:360H₂O	60 C	2 weeks	60 nm
25SiO₂:9TPAOH:0.1Na₂O:480H₂O	98 C	24 h	95 nm
25SiO₂:9TPAOH:0.1Na₂O:480H₂O	Reflux	48 h	100 nm
10SiO₂:2.5TPAOH:0.8NaOH:110H₂O	125 C	8 h	120-15 nm
10SiO₂:2.4TPAOH:1NaOH:110H₂O	125 C	8 h	100 nm
5SiO₂:1TPAOH:500H₂O:20EtOH	130C	12 h	500 nm X 200 nm X 100 nm
SiO₂:0.12TPAOH:0.08NaOH:60H₂O	95 C	50 h	400 nm
SiO₂:0.12TPAOH:0.008NaOH:60H₂O	95 C	1 week	2000 nm

2.3.1.2 Influence of temperature

Temperature is an effective synthesis parameter for controlling the final average crystal size of the product. A lower synthesis temperature favors the formation of a larger number of nuclei resulting in a product with a smaller final crystal size. However to produce a product with a smaller final crystal size, the lower linear growth rates at low temperatures greatly extend the total crystallization time and also the final zeolite yield is

reduced. Q. Li et al.[26] studied the effect of varying temperatures on the size of MFI zeolite seeds. From Table.2, it is apparent that at 100°C a product with an average final crystal size of 96 nm could be produced after 34 h with a yield of 62%, whereas at 45°C the final crystal size could be reduced to 50 nm as shown in figure.6but this required an excessively long crystallization time of 2040 h and gave a product yield of only 51%. Independent of temperature, the crystal size distributions are rather narrow with coefficients of variation ranging from about 10 to 11%.

Table 2 Effect of MFI zeolite seeds synthesis temperature on the final crystal size. [26]

Temperature (°C)	Synthesis time (h)	Final crystal size (nm)	Zeolite yield (%)	Linear growth rate (nm h ⁻¹)	Crystal concentration (#(g sol) ⁻¹ × 10 ¹⁴)	C.V. (%)
100	34	96	62	3.5	0.85	10.34
80	67	77	57	1.1	1.54	10.76
60	360	57	53	0.22	3.43	10.97
45	2040 (85d)	50	51	0.027	5.03	10.88

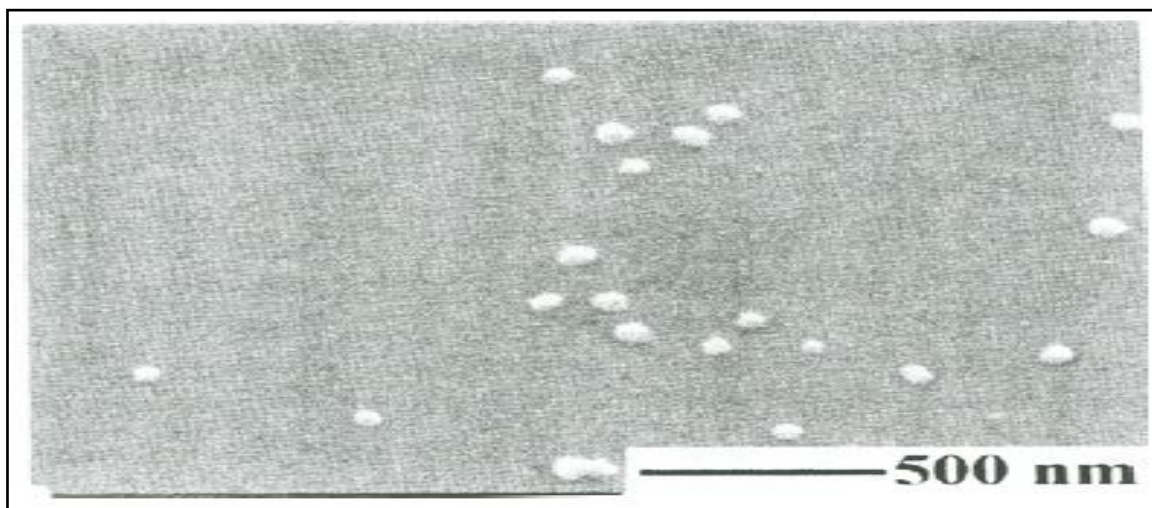


Figure 12 SEM image of zeolite seeds synthesized at 45°C. [26]

D. Creaser et al. [27] proposed a relation between the crystal size and the duration of crystallization. As it is shown in figure 12, single particle population with an average hydrodynamic diameter of 4 nm existed for the hydrolyzed suspension prior to hydrothermal treatment (time zero). Upon heating, the sub-colloidal particles existed for the first 15 h of crystallization, during which their size is nearly constant at 4 nm. After 10 h of hydrothermal treatment, a second particle size population with an average size of 26 nm appeared. This second larger particle population represents the growing MFI Zeolite particles. They increased in size almost linearly during the crystallization, until about 31 h, when they reached an ultimate average crystal size of 96 nm and this confirms the SEM image of the product of the one-stage synthesis at 100°C in Fig.13.

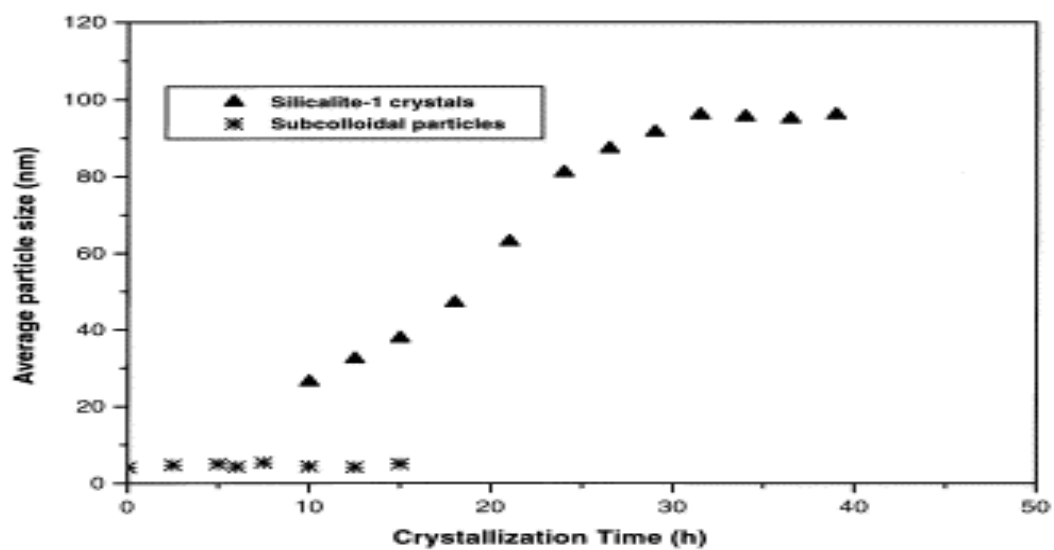


Figure 13 Effect of crystallization time on the average particle size at 100 °C. [27]

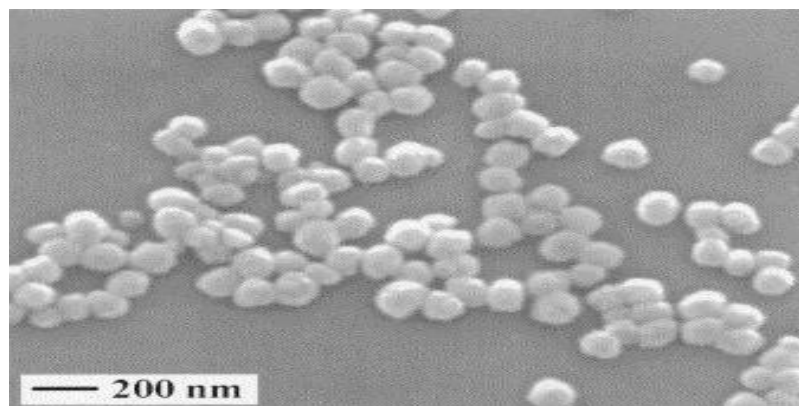


Figure 14 SEM image of the ultimate product of MFI zeolite Nano-crystals at 100°C. [13]

Such a two-stages varying temperature synthesis procedure was first proposed by Li et al. [26] and was shown to produce 60 nm nanocrystals within 7 days (aging 6 days at 60 °C and then raising to 100 °C for 1 day). Following the same logic, Mintova et al. [29] synthesized 30 nm silicalite nanocrystals by aging at room temperature for 30 days before heating to 90 °C for a few hours. Moreover, figure 14 represents a comparison between the two stages heating and one-stage showed by the study of Q. Li et al. [26]. The average crystal sizes for two-stage syntheses shown in Figure 12 are those measured only after the temperature increase to 100°C. They found that the rate of crystal growth greatly increases after the temperature increases and is about the same as that for the one-stage synthesis at 100°C, 3.5 nm h⁻¹.

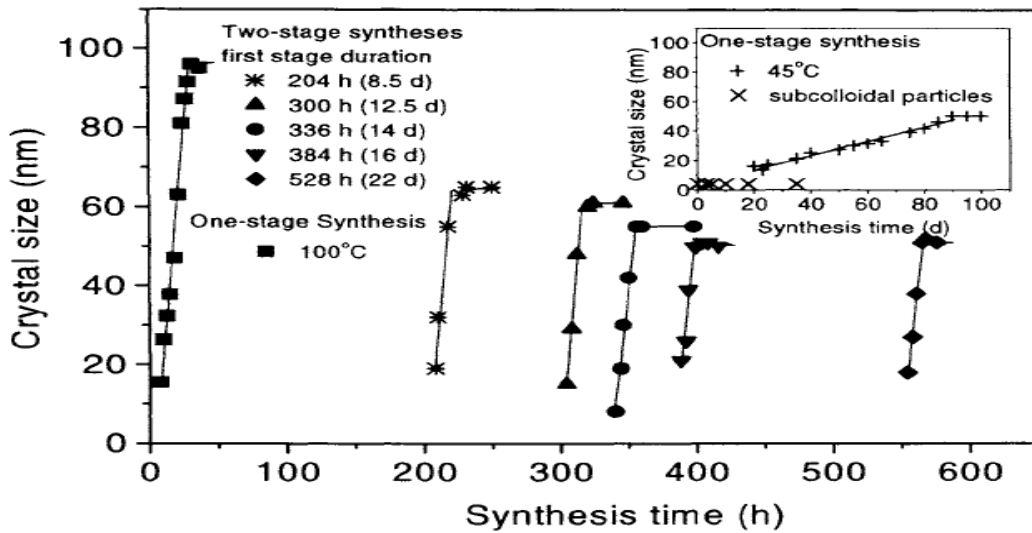


Figure 15 Comparison of average crystal size for one and two-stage crystallizations starting at 45°C and ending at 100°C. [26]

The inset diagram in Figure 12 shows the average crystal size during a one-stage synthesis at 45°C and there is a long induction period during which only subcolloidal particles with a constant size of about 4 nm are detected and it is not until 17.5 days that the growing crystal population was first detected. Linear growth at 45°C occurred slowly, at a rate of 0.027 nm h⁻¹. When the duration of the first stage is extended, the series of two-stage syntheses in Figure 2 indicate that the final crystal size decreases gradually until it is approximately equal to that obtained for a complete synthesis at the first stage temperature, 45°C.

Table 3 lists the result of Persson et al. [28], the synthesis times, yield, linear growth rates and coefficient of variation for all two-stage syntheses started at 45°C and ending at 100°C. In all cases the zeolite yield ranged from 60.7 to 61.5% and was closer to that for a one-stage synthesis at 100°C 62%, than that for a one-stage synthesis at 45°C 51%. It is apparent that the zeolite yield for a two-stage synthesis is determined by the thermodynamic equilibrium at the final synthesis temperature, irrespective of the duration of the first stage. Van Grieken et al. [33] who used the same template/ silica ratio (0.36) as that of Persson et al. [28], but at a water/silica ratio of 10.8 instead of 19.2, was able to produce smaller colloidal zeolite than that of Persson et al. [28] at a higher reaction temperature 170 °C [26]. Also, as indicated in Figure 2, the linear growth rate at 100°C for all of the two-stage syntheses is close to that for a one-stage synthesis at 100°C. The crystal size distributions of the products of two-stage syntheses are constant with coefficients of variations ranging from 10 to 11%, similar to those for one-stage syntheses (Table 3).

Table 3 Effect of first stage duration on product of two-stage synthesis starting at 45°C and ending at 100°C [26].

Duration of first stage (d)	Total two-stage synthesis time (d)	Zeolite yield (%)	Growth rate (nm h ⁻¹)	C.V. (%)
4	5	61.03	3.26	10.66
8.5	9.5	60.75	3.67	10.70
12.5	13.5	61.96	3.45	9.95
14	14.8	61.47	3.51	10.81
16	16.5	60.69	3.69	10.35
18	18.5	61.01	3.48	10.12
22.5	23	60.84	3.72	10.72
29	29.5	60.96	3.91	10.39

It is possible to use the effects of temperature on nucleation, growth rate and yield in a two-stage crystallization to synthesize particularly small crystals of silicalite-1 with shorter total crystallization times and higher yields. Knowing the duration of the nucleation stage, crystallization can be started at a lower temperature that favors the formation of a larger number of nuclei. After nucleation is completed, the temperature can be increased to accelerate the growth of crystals and obtain a higher yield of silicalite-1.

2.3.1.3 Influence of the Structure Directing Agent SDA

Many researchers studied the influence of the TPAOH content in the synthesis mixtures on the size and the yield of MFI zeolite crystals and they found a clear dependence of the average particle size and the particle number on the TPAOH content. From Table 4, the particle size decreases while the particle concentration increases with increasing TPAOH contents, thus indicating that the TPAOH concentration influences the events occurring during nucleation. A greater number of particles per unit volume are the result of a large number of nuclei produced during the nucleation event.

Table 4 The influence of alkalinity on the average particle size, the particle concentration, and the conversion of SiO₂ to TPA-silicate-1 in synthesis mixtures with the molar ratio: X TPABR:Y TPAOH:0.1 N₂O:25SiO₂:480 H₂O:100 EtOH [28].

Run	x	y	Average particle size (nm)	Particle concentration (#/g sol) · 10 ⁻¹³	Conversion (%)
S1	0.0	9.0	95	7.2	64
S2	3.0	6.0	110	5.7	81
S3	0.0	5.0	155	2.2	82
S4	4.5	4.5	188	1.2	86
S5	0.0	3.0	307	0.3	88

In order to investigate more the influence of the TPAOH, the contribution of the TPA⁺ and the OH⁻ ions need to be separated by adding TPABr in addition to TPAOH, so that the total TPA⁺ content is constant.

Persson et al. [28] emphasized that in spite of the fact that the total TPA content (as TPA⁺) is constant; the ultimate particle sizes obtained do not follow the general trend of decreasing particle size with increasing TPA content. The particle-size curve shown in Figure 15 confirms this fact. This indicates that it is not the TPA⁺ content that affects nucleation but, rather, the alkalinity expressed as the TPAOH + NaOH concentration.

Also in their work they gave a proper explanation for why the linear growth rate is independent of alkalinity. By using a synthesis mixture composition: X TPAOH: 0.1 Na₂O: 25 SiO₂:480 H₂O: 100 EtOH and varying X in which both TPA⁺ and OH⁻ are present in amounts that are sufficient to sustain growth, They found that the integration of reacting species onto the surface is rate-determining and the linear growth rate is constant

for synthesis mixtures in which the silica concentration is constant but the alkali content varies.

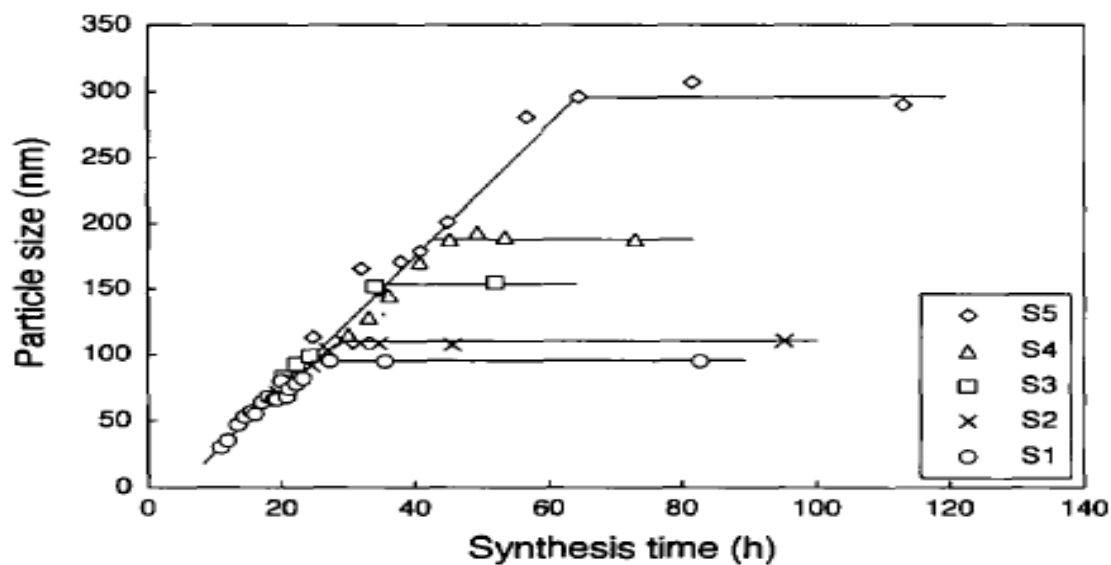


Figure 16 The increase in the average particle size as a function of synthesis time for synthesis mixtures molar ratio shown in Table 4 [28].

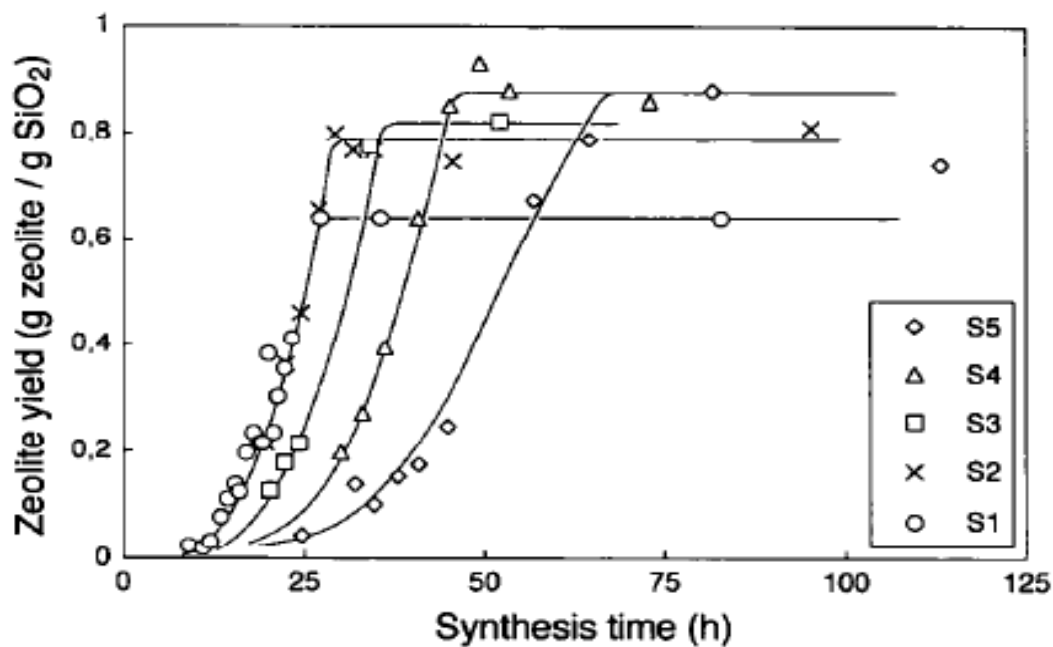


Figure 17 The calculated mass growth curves for synthesis molar ratio shown in Table 4. [28]

2.3.1.4 The influence of varying the water content

When the level of dilution of the standard synthesis composition is reduced the following will be decreased: alkalinity, the final crystal size [26-32] and the linear growth rate [28&29], but the reduction of the final crystal size at the expense of a slightly longer crystallization time and lower yield of silicalite-1. On the other hand, Using the combined effects of reduced temperature and dilution the final crystal size will be further reduced with an even longer crystallization time and lower yield [27]. Q. Li, D et al. [26] investigated the effects of dilution and temperature on one-stage syntheses as it is shown in table 5. and they found that the synthesis at 60 °C and reduced dilution is a more optimal one-stage synthesis for producing small colloidal crystals compared to the higher dilution synthesis at low temperature (e.g. 45 °C)[26].

Temperature (°C)	y* (H ₂ O molar ratio)	Crystallization time (d)	Average crystal size (nm)	Crystal Concentration (g sol) ⁻¹ × 10 ¹⁴	Zeolite yield (%)
100	480	1.4	96	0.85	62
100	200	2	66	2.22	52
60	200	18	46	5.29	42

Figure 18 Effect of dilution of the solution with molar ratio: 9 TPAOH: 25 SiO₂: Y H₂O: 100 EtOH [16]

Persson et al. [18] studied the effect of dilution of synthesis mixtures with the same molar composition, which will as consequence reduce the silica and by varying the silica content from 1.705 M silica to 0.926 M silica. They found there would be an increase in the linear growth rate from 3.79 nm/h to 7.78 and 10.1 nm/h, respectively h as it is shown in Table 5. On the other hand, more concentrated solutions result in a reduction in the linear growth rate to 2.61 and 1.30 nm/h. Moreover, the linear growth rate is constant irrespective of the alkali content for given water content.

Table 5 Effect of the dilution on the ultimate particle size. [28]

Run	Molar composition					Linear growth rate (nm/h)	Particle concentration (#/g sol) · 10 ⁻¹³	Average particle size (nm)
	TPAOH	Na ₂ O	SiO ₂	H ₂ O	EtOH			
S12	5	0.1	25	229	100	1.75	–	89
S13	3	0.1	25	229	100	1.75	0.9	245
S1	9	0.1	25	480	100	3.79	7.2	95
S3	5	0.1	25	480	100	3.79	2.2	155
S5	3	0.1	25	480	100	3.79	0.3	307
S7	9	0.1	25	1500	100	10.1	0.5	183
S10	5	0.1	25	1500	100	10.1	0.1	350
S11	3	0.1	25	1500	100	10.1	0.006	830

In addition, they stated that for a given $\text{SiO}_2/\text{TPAOH}$ molar ratio, the degree of conversion is constant and the rate of mass growth is constant. The alkalinity differs (due to dilution effects), thus resulting in a differing number of particles, which results in differing linear growth rates. A logical consequence of the constant mass growth behavior with different particle concentrations is that the linear growth rate in each run must vary with the synthesis mixture, with the highest particle concentration must exhibit the slowest linear growth rate, while the opposite must be true for the synthesis mixture with the lowest particle concentration whereas the linear growth rate is essentially unaffected by varying alkalinity. This conflicting behavior needs to be explained.

Additional evidence for the effect of the water/silica ratio can be found in the works of Kirschhock et al. [30-32] in which they proposed a 33-mer and the so-called “nanoslab” as the precursor units obtained from 1 $\text{SiO}_2/4$ EtOH/0.37 TPAOH/4 H_2O system at room temperature. Since the precursors were prepared by the direct hydrolysis of TEOS in a 40% aqueous solution of TPAOH, the water/silica ratio was determined by the TPAOH/silica ratio. Strangely, however, this low water recipe was never employed again in other works at least by the same group. A possible reason may be the difficulty in hydrolyzing TEOS in such a low water recipe. In fact, Kirschhock et al. [30-32] had to add the required TEOS to the 40% TPAOH solution in steps, with a few to 40 min of stirring each time to hydrolyze the TEOS.

Hsu et al. [29] were able to produce silicalite-1 nanocrystals smaller than 50 nm via the two-stage varying-temperature procedure within a day, this is far shorter than that required by the “rapid synthesis” claimed in the literature, on the order of several days. They were able to increase the concentration of the synthesis sol by using rotary

evaporation; as a result, this will accelerate the formation of aggregates. The generation and growth of more aggregates quickly consumed most of the primary units in the system and set a limit to the size it can grow. Therefore, although the aggregates generated were initially larger than that observed previously in more dilute systems, the ultimate crystal size was slightly smaller.

In contrast with the classical heating which required several days or even months for preparation of zeolite nano-seeds[26 - 32], the Microwave heating is fast, simple and energy efficient method, which reduces significantly the synthesis time of MFI zeolite seeds especially the synthesis of nano-sized seeds (45-1000) nm into several minutes [20 - 25].

2.3.2 Deposition of the seeds

In order to obtain a good quality MFI zeolite layer, seeding deposition is very important and critical step. Moreover, the seeds need to be uniform and with dense distribution. Dip-coating, rubbing, pulsed layer ablation and vacuum seeding are some the seeding methods employed for coating the support surface with seed crystals.

One of the most frequently used methods is dip-coating. In this method, a colloidal seed suspension is prepared with nanosize zeolite crystals. Then the support material is dipped into the colloidal seed suspension to attach seed crystals to the support surface. In order to prevent the loss of seed crystals from the support surface, dipping and withdrawal rates of the support are kept so slow like 1-2 cm/h. For complete coverage, coating process is repeated several times. The multi-seeding method is very promising since it gives a very dense deposition of seeds with good reproducibility. The drawback is that the deposition

is slightly too thick. Thin and uniform seed layers are obtained with this method but it is limited to nanosize seed crystals as larger crystals settle down quickly. In dip-coating sometimes cationic polymers are used to reverse the charge of the support to enhance the attachment of seed crystals to the support surface by electrostatic forces. But this method also requires an additional pretreatment step, which is impractical.

In rubbing, slurry of seed crystals is rubbed on the support surface with a brush. It is very simple method to obtain seed coated supports and applicable with either micron or submicron size seed crystals. However it is difficult to control the uniformity and thickness of seed layer.

Seeded layers can also be prepared by pulsed ablation method. Although uniform seed layers are obtained through pulsed laser ablation technique, it caused decomposition of seed crystals. Special equipment needed for this method also limits its usage.

Vacuum seeding method is also used for seeding the support surfaces. In this method a seed suspension is prepared and suspension is poured on the support surface. Seed crystals are deposited on the support surface by means of vacuum. The main advantage of this method over the others is that the amount of seed crystals deposited on the support can be controlled by changing the concentration and amount of the suspension.

Electrophoretic deposition (EPD) could be used for seeding the support. With EPD, colloidal particles suspended in a liquid medium migrate under the influence of an electric field and are deposited on an electrode. It can be used for a wide variety of particles as long as they are charged and in suspension. This process is already widely used in the industry for coating. Its main advantages are fine uniformity of the deposition,

easy manipulation and convenient control process. It should be noted that the process yields only results in a powder compact and therefore should be followed by a densification step if a fully dense material is needed.

2.3.3 Secondary Growth

The secondary growth on seeded support technique was studied under different synthesis conditions in order to guide for an excellent synthesis procedure for having a high quality MFI zeolite membranes. However, modeling the seeds growth mechanism play a role on understanding and controlling the effect of synthesis parameters.

2.3.3.1 Seeds Growth Mechanism

The formation mechanism of zeolite under hydrothermal condition is complex and not fully understood. It involves several reaction steps, molecular level self-organization, nucleation, aggregation, crystallization and growth. Pre-seeding the support with zeolite nanocrystals is a convenient way of circumventing the complex processes involved in the early formative stage of MFI zeolite and allows the direct measurement of zeolite crystal growth.

Tsapatsis et al. [18] proposed that in the presence of precursor gel layer the nucleation stage is bypassed and growth of the seed particles starts directly once they come in touch with the synthesis solution. In the presence this indicate that growth of the existing crystals , once initiated, is self-preserved by preventing the nucleation or incorporation of new crystals in the vicinity of the growing film. The steady consumption of nutrients, precursors and extended structures able to contribute to crystal growth is proposed as a possible explanation for the absence of new grain formation during secondary growth,

even under conditions which can lead to nucleation and growth in solution. In this respect, the role of the precursor layer is dual. It is not only leads to growth without the need for nucleation but also may prohibit or limit the incorporation of newly formed crystals. Based on the above, the final film quality will depend on the quality of the precursor layer. The absence of close-packed precursor seeds throughout the area of the substrate can contribute to the development of the defects. In fact, whether seeds directly grow or provide nucleation sites strongly depends on seed properties, such as sizes and calcinations, and synthesis conditions.

2.3.3.2 Influence of varying silica precursor on the MFI zeolite growth

Wan et al. [25] found that the growth rate was slow at low TEOS concentration, but the growth rate increases monotonically with addition of more silica source. However, this increasing will reach to a certain limit in which more addition of TEOS will result in slower growth. And this optimum value for TEOS concentration was 0.05 M according to their synthesis condition figure 17(a). Moreover, X-ray diffraction characterization technique was used to study the impact of varying the amount of TEOS on the MFI zeolite membrane. Figure 17(b) plots the intensities of the two main diffraction peaks detected from the analysis of the samples. The figure shows that the intensity of the (2 0 0)/(0 2 0) diffraction peak remained unchanged with increasing TEOS concentrations. This indicates that the zeolite film grew preferentially along the (1 0 1) direction. From the results, the growth rates at 0.027 and 0.22M TEOS were identical, but the film deposited from the more concentrated TEOS solution has a better crystallinity.

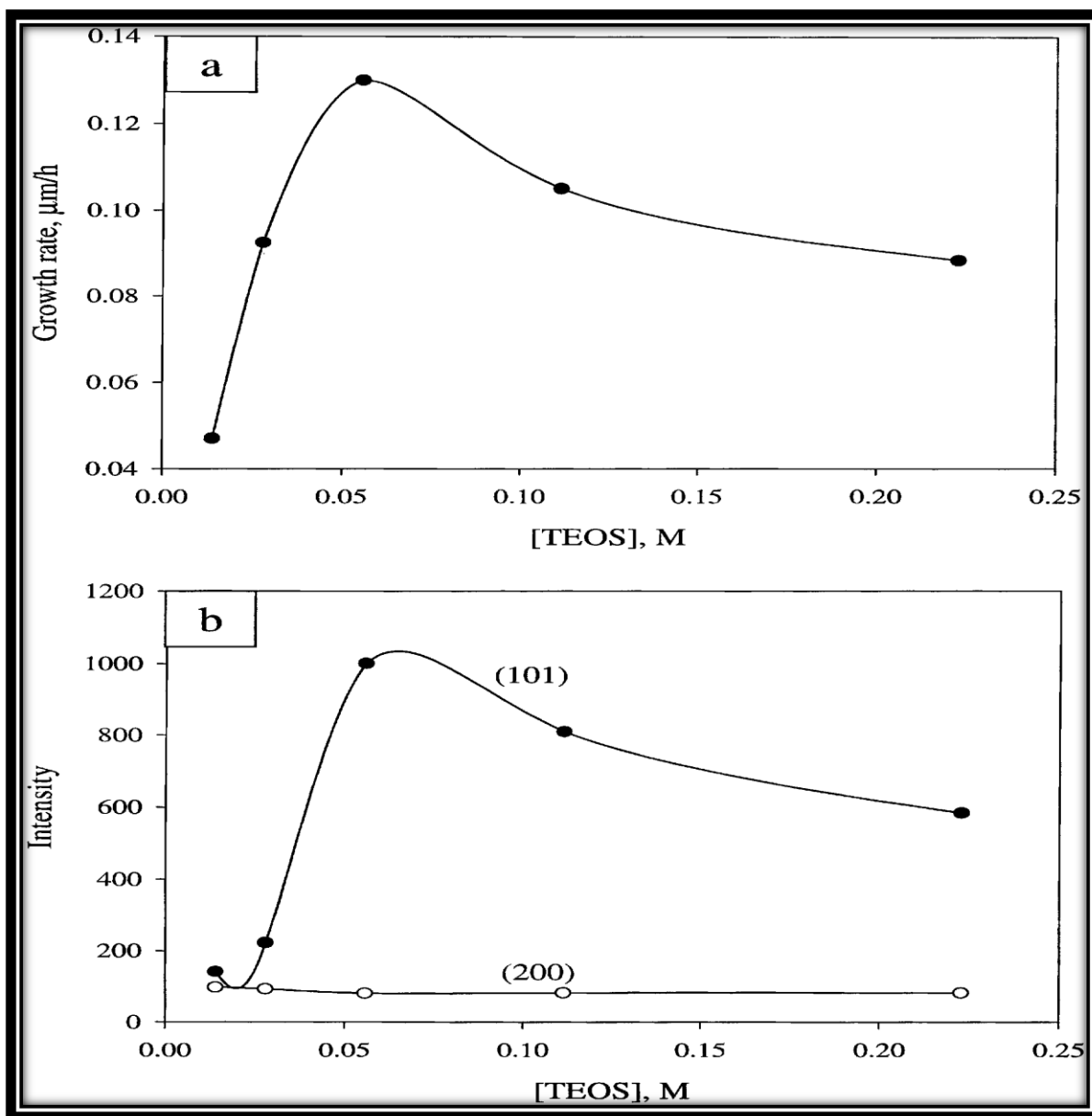


Figure 17(a) Growth rate of Sil-1 membrane and (b) XRD intensities of (101) and (200)/(020) zeolite crystallographic plane as a function of TEOS concentration ([TPA⁺] = 0.027 M, [OH⁻] = 0.027 M, $T = 403$ K, $t = 24$ h).

2.3.3.3 Influence of Varying Structure Directing Agent (SDA) on the MFI zeolite growth

The organic template, TPAOH had a dual role in this synthesis study. It served as structure-directing agent in the assembly of the zeolite framework and also maintained the alkalinity of the synthesis solution. Moreover, investigating the effects of alkalinity of zeolite growth using synthesis solutions containing a mixture of tetrapropylammonium bromide (TPABr) and TPAOH was reported [18,25]. Wan et al. [25] showed that the film growth rate increases with the addition of TPAOH reaching a constant value for TPAOH concentrations greater than 0.01 M. In addition, they investigated the impact of varying the TPAOH on The orientation and they noticed that the zeolite film had a pre-dominant (1 0 1) orientation and the zeolite film prepared at TPAOH of 0.04M exhibited poorer crystallinity compared to films of comparable thickness prepared at lower concentrations (i.e. [TPAOH] = 0.014 M). In addition, they found that the effects of alkalinity of zeolite growth after keeping TPA^+ ion content in the solution constant at 0.04 M, while the concentration of OH^- was systematically varied. The highest growth rate and best crystallinity was obtained for synthesis solution containing 0.03M hydroxide ions. Higher alkalinity gave slower deposition and poorer crystallinity. Furthermore, zeolite dissolution is known to occur at high alkalinity. The result suggests that alkalinity has a stronger influence on film growth and crystallinity than $[\text{TPA}^+]$ at the range of concentrations used in the experiments.

2.3.3.4 Influence of varying water content on the MFI zeolite growth

In the dilution experiments, the concentrations of the reactants were varied at a constant [TEOS]/[TPAOH] ratio. In very dilute synthesis solution, the zeolite growth was negligible and some etching of the seed layer was observed. The dilution has a different effect on the growth behavior of zeolite layer prepared from synthesis solution with [TEOS]/[TPAOH] ratio of 4. The growth rate displays an optimum with water concentration. The zeolite deposition was slow for the concentrated solutions due to their high alkalinity. In extreme cases, etching and dissolution of the porous glass support were observed. The growth rate was also slow for very dilute concentrations of reactants. Water concentrations between 52 and 55M gave a constant growth rate of 0.1 $\mu\text{m/h}$. Fig. 10d indicates that the crystallinity and orientation of the deposited film are sensitive to dilution. The intensity of the (1 0 1) diffraction peak reaches a maximum at water concentration of 54.5 M [28].

2.3.3.5 Influence of varying synthesis temperature and duration on the MFI zeolite growth

Xiao Lin et al. [28] silicate membranes prepared on silicate crystal seeded mullite tubes at 175 °C for 4 and 8 h of hydrothermal treatment with two different seeded size. They found with larger seed that After 4 h of hydrothermal treatment the seed crystals hardly grew at this stage, After 8 h of hydro- thermal treatment, a well-intergrown silicate.

Recently, in the hydrothermal pretreatment-induced synthesis of highly c-oriented $\text{AlPO}_4\text{-5}$ film by Tsapatsis et al. [73], the microstructure transition from random orientation to c-preferred orientation was also ascribed to the nutrient dilution effect induced by pre-crystallization. Moreover, they deduced that the in-plane secondary

growth proceeded through the oriented intergrowth of the original AlPO_4 -5 seeds [22]. These results confirmed the rationality [29]

JIANG et al. [29] introduced in their work a systematic investigation about the effect of hydrothermal pretreatment on the growth dynamics of b-oriented MFI seed. The study was carried out to investigate the influence of the secondary growth ($5\text{SiO}_2:1\text{TPAOH}:1000\text{H}_2\text{O}:20\text{EtOH}$, glass) temperature (at 130, 150, and 170°C) and duration (for 1.5, 3, and 5 h) after hydrothermal pretreatment on the morphologies of prepared MFI films. Moreover, the higher the synthetic temperature, the shorter the synthetic time required to completely seal the gaps in the seed layer without inducing undesired a-oriented growth: 5 h at 130°C , 3 h at 150°C , and less than 3 h at 170°C . Hence, they concluded that high-quality MFI films could be synthesized by combining appropriate secondary growth temperature and duration.

Another systematic investigation was also conducted to elucidate the influence of the synthetic parameters on the final microstructures of the zeolite films by preventing the twin growth. Twin growth which also known as the epitaxial growth along a-direct or (k 0 0) crystal faces would arise before the complete sealing of the growing MFI seed layers, potentially leading to significantly decreased performance of the prepared films [28]. They found that at a fixed synthetic temperature with the extension of the duration of secondary growth, or by fixing growth duration and synthesis temperature was increased these MFI seeds gradually grew larger and began to merged with each other and the more severe the a-oriented.

In addition, the influence of hydrothermal pretreatment parameters on the microstructures of the prepared zeolite films were investigated. The hydrothermal pretreatment temperature was changed from 110 to 185 °C, and the preheating duration was fixed at 2 h. As shown in Fig. 18, twin growth of the b-oriented seed layer could be effectively inhibited at hydrothermal pretreatment temperatures between 130 and 170 °C. However, if the pretreatment temperature was 110 °C (Fig. 18a), extensive twin growth arose during secondary growth; in contrast, increasing the synthetic temperature to 185 °C led to incomplete intergrowth among the MFI seeds (Fig. 18d), probably due to the overconsumption of the nutrient during the hydrothermal pretreatment. The effect of the duration of hydrothermal pretreatment was also investigated. The preheating temperature was fixed at 150 °C, while the hydrothermal pretreatment duration was changed from 0.5 to 12 h. As shown in Fig. 19, high-quality b-oriented MFI films were obtained at pretreatment durations from 1 to 5 h. If the preheat time was 0.5 h (Fig. 19a), twin growth was not effectively suppressed during secondary growth. At longer durations of hydrothermal pretreatment of the precursor solution (e.g., 12 h, see Fig. 19d), some bare space would remain uncovered by the MFI films after secondary growth, possibly due to insufficient nutrient supply.

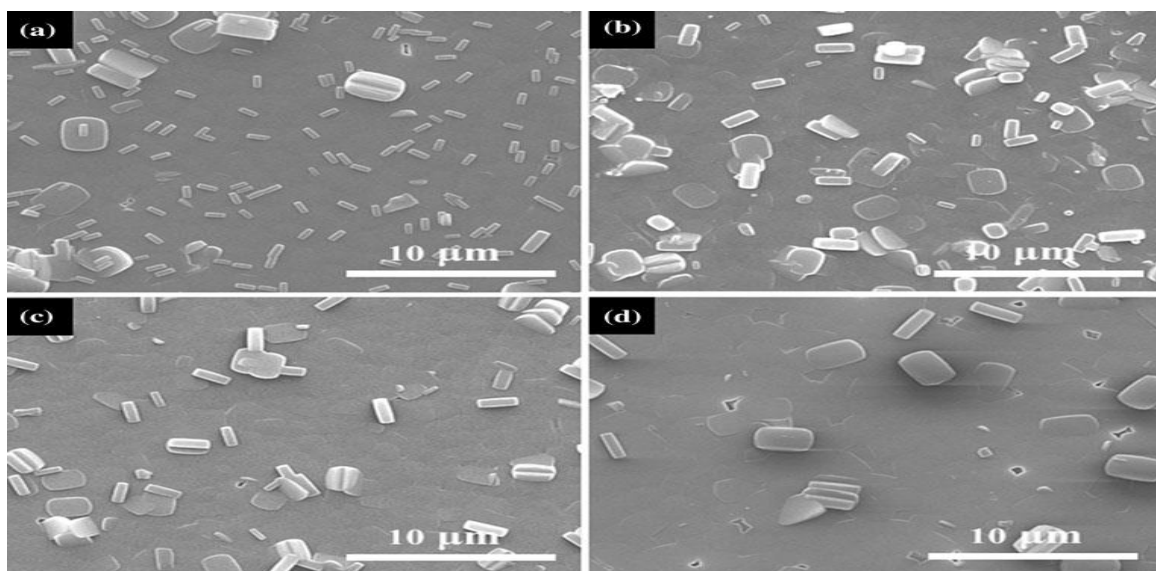


Figure 19 SEM images of MFI films synthesized in secondary growth solutions subjected to hydrothermal pretreatment at (a) 110 °C, (b) 130 °C, (c) 170 °C, and (d) 185 °C with the duration of 2 h. The secondary growth was initiated at 150 °C for 3 h

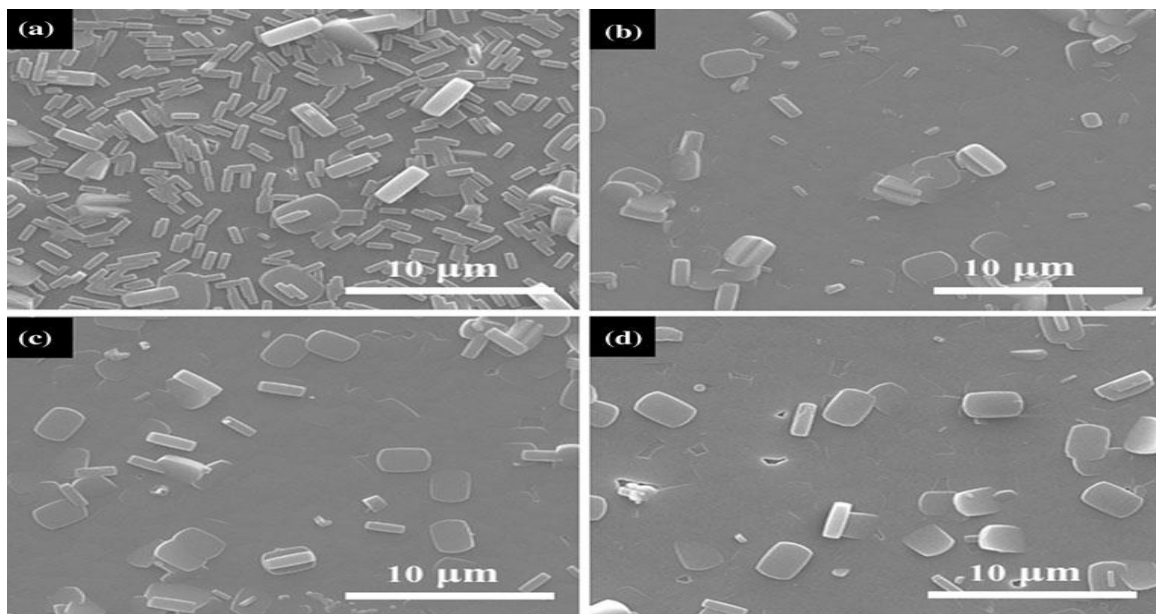


Figure 20 SEM images of MFI films synthesized in secondary growth solutions subjected to hydrothermal pretreatment at 150°C with durations of (a) 0.5 h, (b) 1 h, (c) 5 h, and (d) 12 h. The secondary growth was initiated at 150°C for 3 h

As shown above, hydrothermal pretreatment exerted great influence on the final microstructures of prepared MFI films. To elucidate the growth mechanism of MFI seed layers during secondary growth, the synthesis process was investigated in detail at 130⁰C. As shown in Fig. 20, if the precursor solution was not preheated before hydrothermal synthesis, the original seed layer served as an intermediate layer to facilitate nucleation and subsequent growth of the newly formed zeolite crystals on the substrate. Then new MFI nuclei formed and grew on the b-oriented MFI seed layer at the initial stage of secondary growth (Fig. 20a). Subsequently, with the extension of the synthesis duration, these newly formed seeds gradually grew larger and larger, and began to merge with each other (Fig. 20b). Finally, the original b-oriented MFI seed layer was fully covered by the secondary growth portion simultaneously, undesirable twin growth arose and became more and more severe (Fig. 20c), probably due to the high nutrient concentration in the solution.

In contrast, when the precursor solution was hydrothermally pretreated before the secondary growth, only a continuous and uniform epitaxial layer gradually formed on the surface of the b-oriented MFI seed layer (Fig. 20d, e) because MFI nuclei formed in the precursor solution during secondary growth and no new heterogeneous nucleation, which is one cause of twin growth nucleation, on the b-oriented seed layer was observed. Another reason, as the nutrient was largely over-consumed during the hydrothermal pretreatment. At the prolonged synthesis durations, these original MFI seeds gradually grew larger and began to merge with each other (Fig. 20f). As a result, the gaps among these MFI seeds were fully filled.

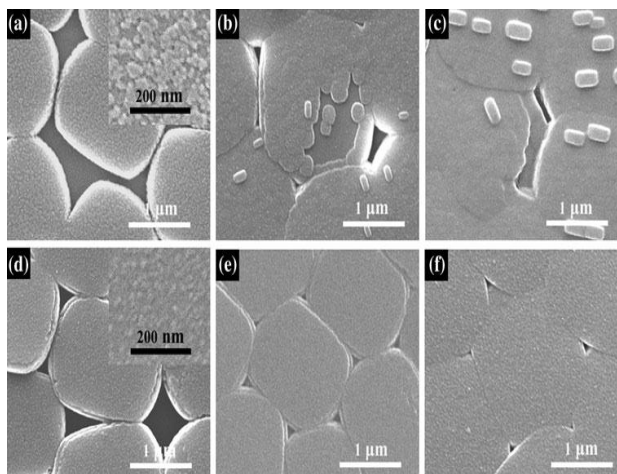


Figure 21 SEM images of MFI films synthesized in secondary growth solutions not subjected to hydrothermal pretreatment. The secondary growth was initiated at 130°C for (a) 1 h, (b) 2 h, and (c) 3 h, respectively; the MFI films were synthesized in secondary growth

2.3.4 Template Removal

In synthesis of MFI Zeolite membranes by the methods mentioned above, an organic agent, normally tetrapropylammonium is employed as a template. This template is required for formation of MFI Zeolite crystal structure. When the MFI membrane is formed, the SDA blocks the channels and needs to be eliminated either thermally or chemically in order to “activate” the zeolite pores. In most cases, the template is removed by thermal treatment with controlled conditions (atmosphere, heating rate, temperature and duration). A very low-heating rate (typically 0.1–0.5 °C/min) up to 400 °C is generally recommended in order to limit the formation of defects in the supported membranes. There numbers of attempts to prepare MFI Zeolite without the effect of template removing have been reported in order to avoid crack formation.

Motusaz J et al. [23] demonstrated that higher heating rates (5°C/min) can be applied to ultra-thin membranes without altering their performance. Assuming that the thermal behavior of MFI crystallites in a supported film is the same as for MFI crystallites in powder also it is stated that the residual stress in the film at a certain temperature during calcination is independent on heating rate and the template degradation treatment could even be shortened for thinner membranes.

In the work of M. Pan et al. [72], high quality MFI type zeolite membranes were prepared by the secondary growth process using a silica sol without organic template. Aluminum can transfer via solid state diffusion from the alumina support into the zeolite layer during the calcination step. At 650°C aluminum from the support can penetrate into the zeolite layer in the range from 2 to 5 μm from the interface within 8 h. Aluminum from the support can also get into the framework of the zeolite layer via dissolution into the synthesis sol. The amount of aluminum transferred to the zeolite layer by the first mechanism depends respectively on calcination temperature and time, and that by the second mechanism depends on the alumina solubility in the synthesis solution and hydrothermal synthesis conditions.

2.4 Use of microwave for MFI zeolite synthesis

In the past few years, synthesis of zeolite membranes using microwave was achieved. In many cases, microwave synthesis has proven to remarkably reduce the synthesis time. Moreover, the positive impact and the ability of controlling the orientation, thickness and morphology have been reported [21-25]. By considering the advantages of microwave dielectric over the conventional heating, the microwave can show a higher heating rate

compared with conventional one also it is volumetric and instantaneous heating with no wall or heat diffusion. Moreover, hot spot yielded on local boundaries by reflections and refractions may result in a super-heating effect, which can be described as local overheating and is comparable to the delayed boiling of overheated liquids under conventional condition [66].

2.4.1 Microwave

Microwave lie in the electromagnetic spectrum between infrared waves and radio waves. They have wavelengths between 0.01 and 1 m, and operate in a frequency range between 0.3 and 30GHz. For industrial applications the typical bands are 915 ± 15 and 2450 ± 50 MHz. There are many distinct frequency bands, which have been allocated for industrial, scientific, and medical (ISM) use, as shown in Table 6, with the principal frequencies centered at 896 MHz (915 MHz in the USA) and 2450 MHz for which equipment can be readily purchased [51]. All the reported microwave chemistry experiments are conducted at 2450MHz with a corresponding wavelength is 12.24 cm and this may occur because near to this frequency the microwave energy absorption by liquid water is maximal also there is another reason which is that 2450MHz magnetrons are mostly often used in the available commercial microwaves chemistry equipment[50]. In the microwave 2450 MHz, the dominant mechanism for dielectric heating is dipolar loss, also known as the re-orientation loss mechanism. When a material containing permanent dipoles is subject to a varying electromagnetic field, dipolar molecules try to orient themselves or be in phase with the field. However, the dipoles due to the motion restriction caused by inter-particle interaction and electric resistance they will be unable to follow the rapid reversals in the

field. This ensures that the resulting current density has a component in phase with the field, and therefore power is dissipated in the dielectric material.

Table 6 Frequency allocation for industrial, medical and scientific purposes [51]

Frequency MHz	Frequency Area permitted	Area permitted
	MHz tolerance + or -	
433.92	0-2%	Austria, The Netherlands, Portugal, West Germany, Switzerland
896	10 MHz	UK
915	13 MHz	North and South America
2375	50 MHz	Albania, Bulgaria, Hungary, Romania Czechoslovakia, USSR
2450	50 MHz	worldwide except where 2375 MHz is used
3390	0-6%	The Netherlands
5800	75 MHz	Worldwide
6780	0-6%	The Netherlands
24150	125 MHz	Worldwide

40680	---	UK
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2.4.2 Synthesis of MFI zeolite membrane by microwave

Mainly, there are two strategies developed for zeolite membranes synthesis using microwave. The most widely and the simplest technique used is the in-situ microwave synthesis [21-25&53-61] in which the surface of the substrate is exposed directly to the precursor solution. As a result, both of the nucleation and crystallization will occur in one stage. Whereas the microwave assisted secondary growth [21, 23, 44] consists of two stages. The first stage, the surface of the substrate is coated with seeds that have been synthesized by different techniques and different sizes. In the second stage, the coated substrate is placed in the Teflon reactor vessel in microwave oven for the secondary growth of the zeolite crystals on the substrate. Although the largest amount of work has been done on membranes with framework topology of MFI for both ZSM-5 and Silicate-1, the articles published on microwave synthesis of MFI zeolite membranes are limited. For a synthesis of MFI zeolite membrane, the conventional hydrothermal treatment lasts from 8h up to 3 days, depending on synthesis gel composition and temperature, which can cause chemical attack of the alumina support and aluminum incorporation into the zeolite layer [25]. Microwave synthesis of MFI zeolite membrane was reported by Koegrler et al. Films containing oriented 100nm Silicate-1 crystals have been in-situ synthesized on a silicon wafer using rapid cooling and heating. Table 7 below

summarizing most of the MFI zeolite membranes had been synthesized on Alumina substrate by using Microwave technique.

Table 7 MFI Zeolite membrane on Alumina substrate by Microwave

References	Substrate	Synthesis Strategy	Secondary growth solution molar ratio	Procedure / Conclusion/Application
J. Motuzas [10]	α -Al ₂ O ₃ asymmetric tubes	Seeded	25SiO ₂ : 3TPAOH: 1500 H ₂ O : 100 C ₂ H ₅ OH	• Duration: 30-150 min • Maximum temperature: 120-180 °C • Conclusion: 160°C and 2h for preferred orientation oblique (1 0 1) (1.2µm thick) • Application: Gas separation.
Reyes Mallada [11]	Capillary α - Al ₂ O ₃ Mean pore diameter: 200 or 800 nm	Seeded	25 SiO ₂ : 3 TPAOH: 1500 H ₂ O : 100 C ₂ H ₅ OH	• Duration: 2h • Temperatures: 155-160 °C • Conclusion: 155°C for preferred orientation oblique (101) (1.2-1.4µm thick) • Application: Pervaporation EtOH/H₂O: 5/95 wt.% mixture
Zhong Tang [12]	α -alumina discs Mean pore diameter: 0.1µm	Seeded	0.0095 NaOH + 0.0167 SiO ₂ + 2.31 H ₂ O + X Al ₂ (SO ₄) ₃ · 18H ₂ O. • X (0 to 0.069) • Without TPAOH	• Duration: 2 h, 3 h and 4 h. • Temperature: 180°C • Conclusion :>3h for well intergrown membranes Si/Al ratio of 111 (2-4µm thick) • Application: Gas separation
Jinqu Wang [13]	Alumina tubes Mean pore size 2-3µm	Double- Seeded	1SiO ₂ :0.3TPAOH:80H ₂ O:4C ₂ H ₅ OH	• Duration: 2 h • Temperature: 150°C • Conclusion :(4µm thick) dense and continuous • Application: Gas separation

Motuzas et al. [21][23][50] Their synthesis was by combining microwave heating with secondary growth strategy on alumina supports for MFI Zeolite with (101) and (001) preferred orientation. They have studied the influence of different parameters such as; ramping rate, temperature and the duration of heating in order to fully understand the effect of these parameters on the quality of the membranes. one of the most important factor, which will affect the use of these membranes especially on separation processes, is their thickness. Hence, the evolution of the silicalite-1 membrane thickness as a function of the synthesis temperature (403 K to 453 K) and with various synthesis durations (30-150 min) was reported (Fig.22).

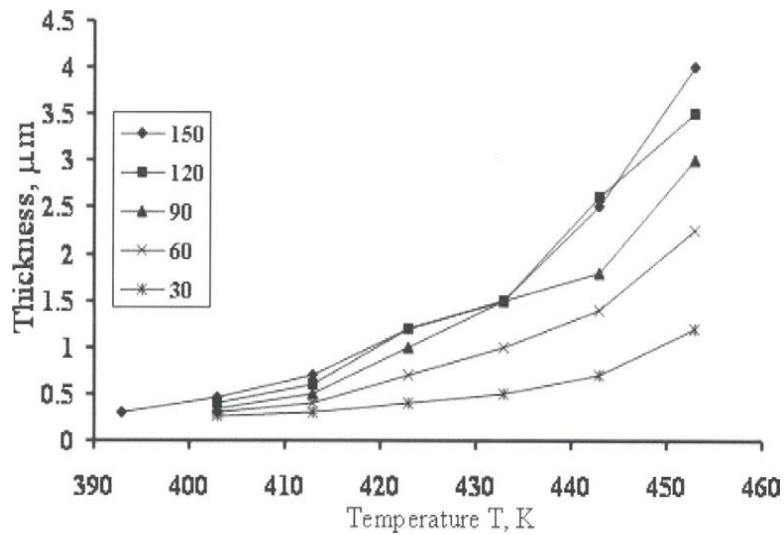


Figure 22 MFI zeolite membrane thickness at different heating temperature and time by microwave [24]

Very thin membranes can be obtained (below 500 nm) at low temperature (below 410 K) whatever the synthesis duration. The influence of the synthesis time on the membrane thickness is more effective at high temperature. A comparison of thickness of the silicalite-1 membranes with two different synthesis durations at either 453 K or 413 K is shown in Fig.1. At 453 K, the membrane thickness decreases from 4 micrometer to 1.2 micrometer, respectively when the synthesis is shorten from 150 to 30 min. The influence of synthesis duration on membrane thickness is lower at 423K. In addition, The influence of the synthesis time on the membrane thickness is more effective at high temperature i.e, from 420K and above. Figure 23 Shows the surface morphology and cross-section of a series of silicalite-1 membranes with different synthesis conditions. For a given synthesis duration of 150 minutes, the membranes typically have a columnar morphology and their thickness increases from 300 nm to about 4 μm when the temperature increases from 393 K to 453 K. Less oriented and angular morphologies can be obtained for shorter synthesis duration or at low temperature.

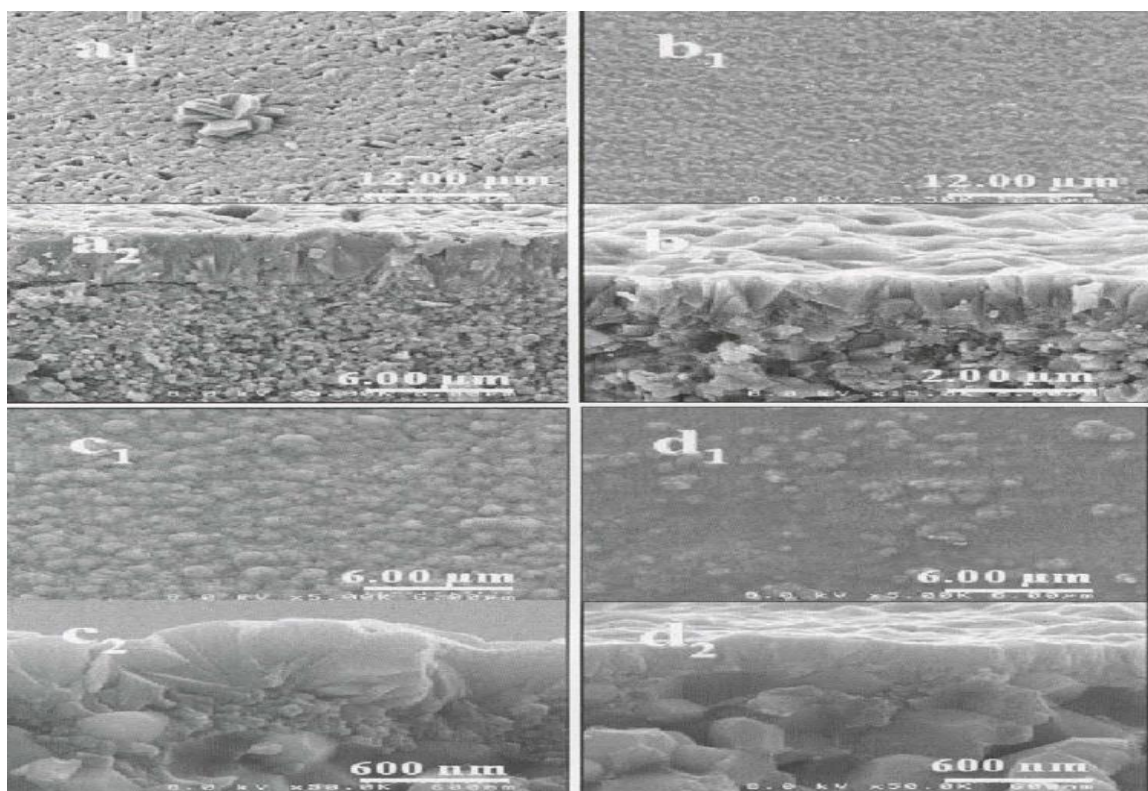


Figure 23 FESEM observations (surface in top a1,b1,c1,d1 and cross-sections in the bottom a2,b2,c2,d2) of MFI zeolite membranes made by microwave with different synthesis conditions: a) 2.5h,180C; b) 2.5h, 160C; c) 2.5h,140C; d) 2.5h,120C [24]

2.5 Defects

For good separation performance, no alternative pathways in the form of defects such as open grain boundaries, pinholes and cracks should exist in the film. Cracks are possibly the most troublesome type of defect and may form during calcination[43].

2.5.1 Types of defects

Typical defects that are observed by SEM are presented in the following Figures 24&25. As can be seen from these figures, some grains appear to grow larger and to an inclination compared to the rest of the columnar grains that form the dense polycrystalline film. These larger grains extend above the film surface, constituting a hemispherical dome. The formation of these defects is attributed to the absence of a close-packed precursor layer underneath the area of the defect, allowing for a less-competitive growth in this neighborhood and resulting in the inclined, less intergrown, and larger grains.

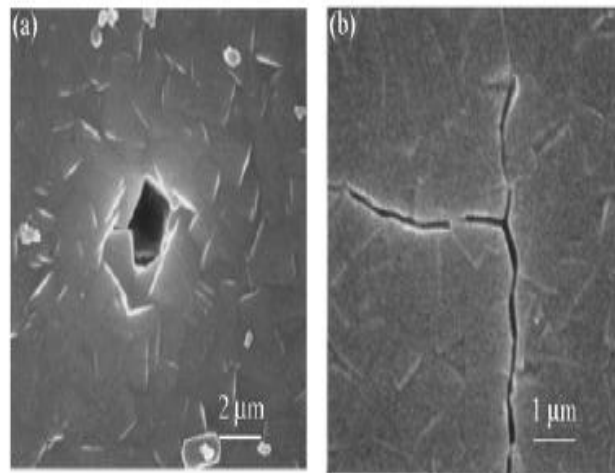


Figure 24 SEM photos of pinholes and cracks. (a) Pinholes.(b) cracks

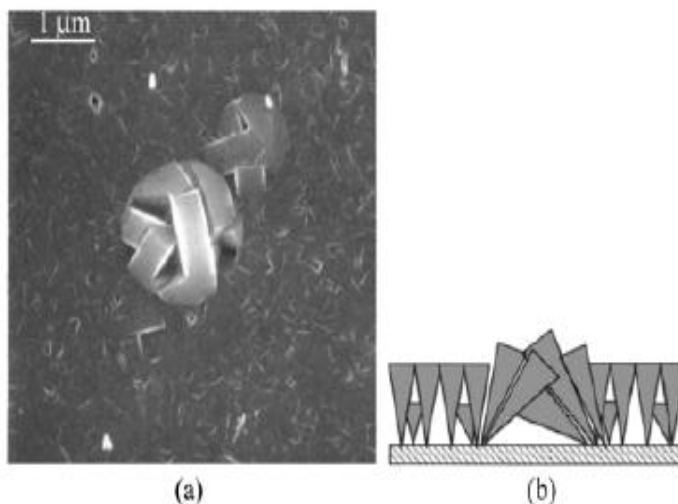


Figure 25 Dome-like defects and their formation model. (a) SEM photo of dome like defects.(b) model of defects formation

2.5.2 Defects Test

Uncalcined membrane allows the rapid assessment of the quality before the time-consuming calcination step. At this stage, a good quality membrane should be impermeable for SF₆. The SF₆ kinetic diameter of 5.5 Å is similar to the pore dimensions of the calcined ZSM-5 zeolite (diameter range 5.1 – 5.6 Å). Substantial SF₆ diffusion through the uncalcined membrane indicates the presence of detrimental membrane defects larger than the zeolite pores which will be opened during calcination[36].

2.5.3 Defects on MFI Zeolite membrane

Pachtová et al. [38] studied the TPA removal in large silicalite-1 crystals of three different sizes. No cracks were observed in the smallest crystal ($L_c = 130\mu\text{m}$) after calcinations in air. In larger crystals, cracks developed in both air and nitrogen

atmosphere. In the medium-sized crystals ($L_c = 190\mu\text{m}$), cracks were found after complete template removal, whereas in the largest crystals ($L_c = 230\mu\text{m}$) they already appeared after partial calcination. Hence, in concert with the results of Geus and van Bekkum[41], the formation of cracks was apparently dependent on the crystal size.

The MFI structure experiences a strong contraction during template removal, which occurs in the approximate temperature range 300–500 °C [40]. Den Exter et al. [42] studied *b*-oriented silicalite-1 films on dense silicon wafers. Derived from crystallographic data for as-synthesized and calcined silicalite-1, the authors reported that the change (%) in the unit cell dimensions after calcination was –0.71, +1.05 and –0.105 for the *a*-, *b*- and *c*-axis, respectively. Based on these results and a quantitative estimation of the *a*- and *b*-oriented crystallites in the film, the calcined crystal layer would show an expansion with respect to the as synthesized film. In fact, a buckling of the calcined crystal layer was evident. The cracks observed in the film were attributed to compressive stress in the calcined layer. Instead, the alpha-alumina supports used for MFI films expand during heating [40]. To better understand the crack formation process in MFI membranes, the thermal behavior of the porous support as well as that of the zeolite film must be investigated.

An appropriate technique is high temperature X-ray powder diffraction (HTXRPD) which allows to follow the *d*-spacings of the crystal planes as a function of temperature. Consequently, the strain in the sample can be followed as a function of temperature by comparing the *d*-spacings in the film with those in a non-stressed sample was used [36,40].

Dong et al. [40] performed a HT-XRPD study of silicalite-1 films on porous yttria-doped zirconia (YZ) supports as well as ZSM-5 films on porous alpha-alumina supports. In addition, the thermal expansion of the contraction ratio of the YZ-supported MFI zeolite film (0.65%) is larger than that for the alumina-supported MFI zeolite film (0.20%), it is expected that the former will have larger intercrystalline gaps than the latter. Assuming an isotropic shrinkage for the MFI zeolite film, changes in the size of the gap between the two crystallites due to template removal can be estimated from the contraction rate using the following equation(1):

$$Dd = L0[1 - (1 - KT)^{1/3}] \text{-----} (1)$$

Where $KT(\%)$ is the thermal expansion ratio of the substrate and $L0$ is the linear crystallite size of the as-synthesized MFI zeolite. These intercrystalline gaps clearly constitute the micro-porous non-zeolitic pores of the zeolite membranes [39].

2.5.4 Cracks Models

Models for crack formation or absence of cracks in MFI membranes were reported by researchers [36,40].

Margaret E. et al. [36] presented a modal for the crack formation based on that the crystals constituting the MFI film are strongly bonded to the support. During heating, the MFI crystals experience a weak contraction at about 175⁰C (dehydration) and a strong contraction in the temperature range 275–500⁰C (template removal). Instead, alpha-alumina support expands which results in a difference in the expansion coefficients of the

two phases inducing thermal stress in the composite. In the case of a relatively thick film it is expected for the cracks in the film after calcination does not only run between crystals but also within crystals, the thermal stress is released mainly via crack formation. In addition, part of the stress is also released via formation of structural defects in the alpha alumina support. Despite the formation of cracks, the thick zeolite film is not completely relaxed as a tensile stress is present in the film also at room temperature. However, In the case of a thin film in which it is assumed crystals are less intergrown, less or no stress develops and the grain boundaries are opened, as also suggested by Dong et al. [40]. In fact, defect distribution calculations for this type of membrane showed that defects with a width of a few nanometers are present. These nano-defects are probably open grain boundaries formed during calcination, according to Margaret E. et al. [36] The type of defects which can be cracks or open grain boundaries formed in MFI membranes during calcination should mainly be determined by the degree of intergrowth between adjacent crystals in the film. If the crystals are highly intergrown, the bonds between crystals and within crystals are equally strong and cracks may develop even within crystals. Less or no intergrown crystallites should result in the formation of open grain boundaries upon calcination. it is important to point out that the thickness of the film is not the only possible factor responsible for the crystal intergrowth and the associated defect formation.

Therefore, the synthesis conditions are probably important. Another factor which probably has a large influence on the quality of the membrane after calcination is the type of support and its properties such as; grain size, degree of sintering...etc. In fact, a large

difference in the quality of calcined membranes was observed for MFI films prepared on porous supports of α -alumina and yttria-doped zirconia [40].

Dong et al. [40] proposed the following model for the formation of defects in α -alumina supported MFI films (about 3 μ m thick): YZ material is inert to the synthesis solution and lacks hydroxyl (groups) on the surface. The as-synthesized MFI film will be devoid of strong chemical bonds to the YZ support, as shown in Fig. 26(a). During template removal at high temperature, the zeolite crystals may move on the support surface to maintain good contact between crystallites, as shown in Fig. 26(b). Therefore this zeolite film does not experience tensile stress, which is consistent with our findings that no cracks were formed during the heating process. After keeping the membranes at 450–500°C for 6 h, a chemical bond formed between the zeolite film and the YZ surface, and the zeolite crystals were no longer movable [Fig. 26(c)]. Severe compressive stresses develop in the zeolite film during the cooling process due to expansion of the zeolite crystals and shrinkage of the YZ support.

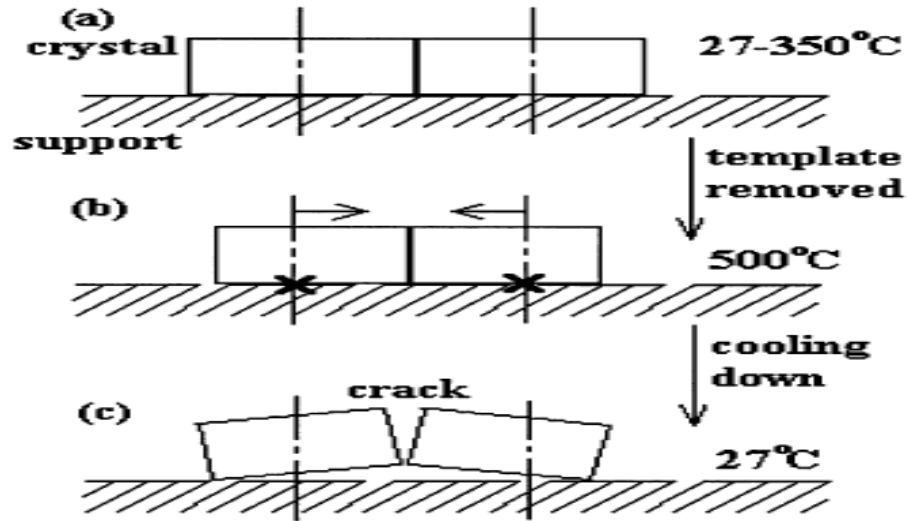


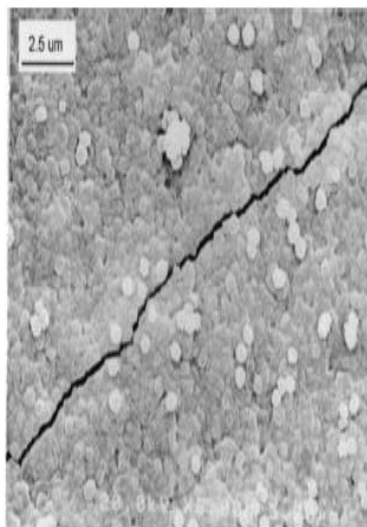
Figure 26 Schematic diagram showing template-removal associated microstructure development of a supported zeolite film with strong bonds between the crystallite and support formed after template removal. [40]

2.5.5 Defects Elimination

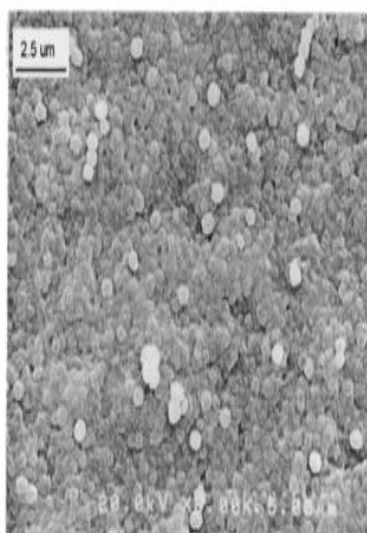
Although many researchers tried to solve the problem in order to eliminate the formation of defects on the layer, there is no a breakthrough solution until now for this problem. One of these solution is to repeat the hydrothermal synthesis with shorter time and more diluted solution to get rid of any existing large defects; partial coverage of the substrate and micro-cracks using a shorter reaction time and more diluted starting solution [37]. Dong et al. [8] proposed a solution for YSZ substrate which has a poor chemical bond with MFI zeolite crystals. They introducing an annealing step at Annealing at 350°C for 6 h prior to template removal. [Fig. 27]. The stress at the interface between the zeolitic layer and the alumina substrate due to thermal expansion mismatch can be minimized by using slow heating rates below 1°C/min. A typical successful temperature profile for the calcination is a heating and cooling rate of 0.5°C/min with a maximum temperature of

600°C maintained for 6 hours. This ensures the removal of water from the pores without creating detrimental defects within the membranes.

The situation is different from substrate to another depends on the substrate chemistry and condition. Dong et al. [40] proposed that for the alumina-supported MFI zeolite membranes. Due to good chemical reactivity of aluminum with silicate crystallites, the MFI zeolite crystallite can be chemically bonded to the support surface during the in situ synthesis and heating process of the calcination step [Fig. 28(a)].



(a) A typical crack on zeolite membrane calcined by program P1



(b) Crack-free membrane calcined by P2

Figure 27 SEM top view of the YZ-supported MFI membranes (a) calcination directly. (b) Hydrothermal pretreatment [40]

From 350 to 500°C, the template is removed and the MFI zeolite crystallites shrink. This may create tensile stress in the zeolite film if the bonding between the zeolite crystals is strong. With the strong chemical bonds already formed between the crystallites and support surface prior to template removal, shrinkage most likely results in opening up the gap between the two well-contacting crystallites [Fig. 28(b)] or enlarging gaps that existed prior to template removal. Cooling to room temperature is accompanied by expansion of the MFI zeolite crystallite and shrinkage of the alumina support. The intercrystalline gap becomes narrower but will not return its original gap size because the zeolite crystallite after template removal at room temperature is smaller than the as-synthesized zeolite

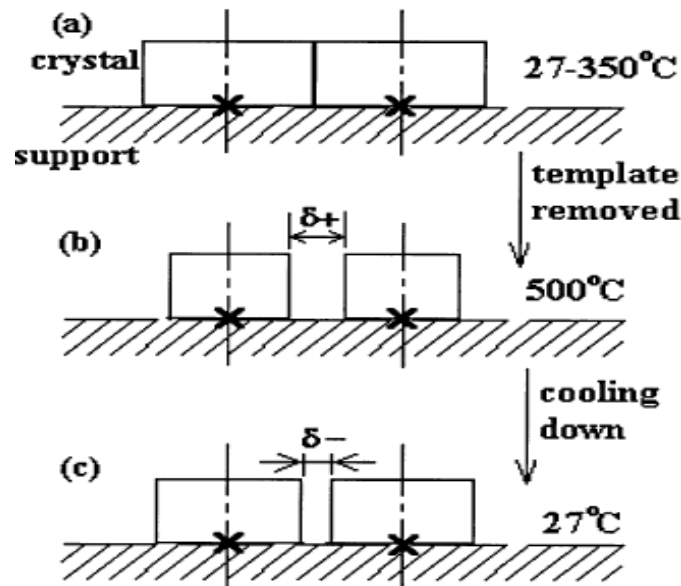


Figure 28 Schematic diagram showing template-removal associated microstructure development of a supported zeolite film with strong bonds between the crystallite and support formed prior template removal.[40]

CHAPTER 3 EXPERIMENTAL PROCEDURE

3.1 Materials

The list of materials, chemicals and their specifications are given in table 8. Moreover, all of these materials were used as they were received.

Table 8 Material information

Material	Specification
1-Propanol	High purity, FW:60.10, d:0.8, Riedel
Tetrapropylammonium hydroxide solution TPAOH	20% in water , MW:203.36, d: 1.012 , Sigma-Aldrich
Tetraethyl orthosilicate TEOS	99.99% MW:208,d: 0.933 , Sigma-Aldrich
Polyethylene glycol 400 PEG	Average M_n 400 , d: 1.466 , Sigma-Aldrich

3.2 Preparation and Characterization of ceramic substrate

The substrates were prepared by two main steps; I) preparation of supports which will provide the mechanical strength to protect the unity of the membrane under pressure and II) modification of supports to enhance the chemistry of the surface in order to get a selective membrane layer on the top of the support surface.

3.2.1 Preparation

The ceramic supports were prepared by cold-pressing of α - Al_2O_3 powders with uniform particle size distributions. The particle size distributions of ceramic powders were determined by using the particle size analyzer. Starch which is commonly used as a binder in ceramic processing was added to these powders (~2 wt. %) before uniaxial cold pressing at 40,000 lb (figure 29). After pressing, the starch was burnt out by heating the substrates at 450°C for 3 hours. Then the supports with their disk shape were placed into the high temperature furnace and heat-treated at 1400°C for 2 hours with heating rate 5°C/min (figure 30) which allow the formation of a porous structure with considerable mechanical strength. Porous α - Al_2O_3 disks (home-made: 25.3 mm in diameter, 2.5 mm in thickness, 0.15–0.2 μm pore radius, ~40% porosity) were used as supports. The surfaces of the support were grinded with 240, 400 and 800 grit-sand papers (figure 31), polishing with smooth cloth impregnated with alumina particles and cleaned with deionized water in a probe sonication (Sonics) for 10 minutes to remove the loosely particles created during Grinding and polishing. Before coating the seeds or hydrothermal synthesis, one of the surfaces of the supports were treated by washed with HNO_3 for 3 hours followed by washing with deionized water for 1 hour and dry them at 200°C for 2h. After the substrate surfaces pretreatment, they were coated with seeds layer by using spin-coating technique with 3000 RPM for 60 seconds.

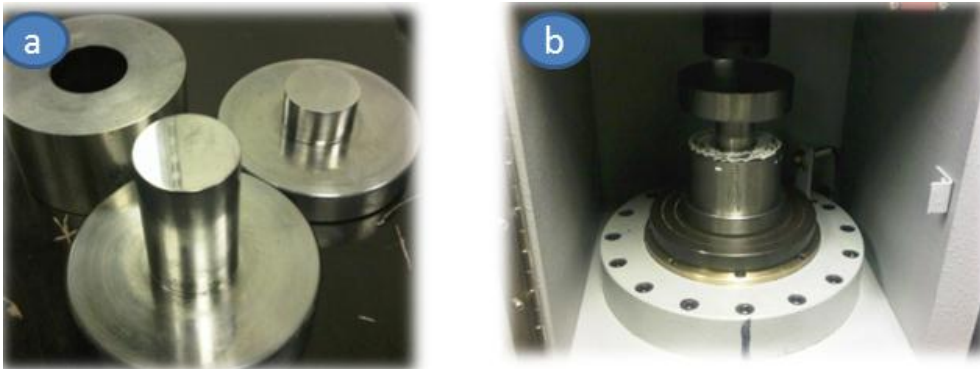


Figure 29 (a) The compaction die, (b) The compaction die inside the compaction machine



Figure 30 Conventional tube furnace for sintering



Figure 31 Handimet 2 Roll Grinder Buehler USA

3.2.2 Substrate pretreatment

The structure and chemistry of support materials play an important role in zeolite film formation and have a significant influence on the separation property of the membrane material. The most basic modification of a substrate is cleaning to remove organics that have accumulated on the surface and may prevent zeolite film formation. In many cases, the choice of the support affects the final film or membrane properties. For instance, Surface roughness and pore size define the optimum zeolite crystal size and membrane thickness. The chemical nature of the support surface influences zeolite nucleation, crystal growth and film adhesion.

Substrates may be modified to accommodate the needs of a specific zeolite composition or synthetic technique. Chemical and mechanical polishing techniques are used to modify the surface roughness of the substrate, as thin films are less likely to adhere to rough surfaces than smooth. Adhesion of the film to the substrate is generally a function of the hydrophilicity of the surface due to various van der Waals and hydrogen bonding interactions this enables, and can be improved by immersing the substrate in solutions of HNO_3 , which increase the number of surface oxygen groups and therefore the

hydrophilicity of the surface. It also increases the number of potential nucleation sites. Moreover the impact of using Ultraviolet (UV) for surface treatment was studied.

3.3 Seeding

3.3.1 Synthesis MFI zeolite seeds

The preparation of seeds started with preparing the seeds clear precursor sols. The precursor sols were prepared from TEOS (Tetraethyl orthosilicate and TPAOH (Tetrapropylammonium hydroxide solution). TEOS was added to a mixture of TPAOH and DI water. After stirring at room temperature in a sealed beaker for 50 min, the two phase mixture turned into a clear single-phase solution (pH=11.5-12) with the following molar ratio 1 TEOS: 0.25 TPAOH: 18 H₂O. For this molar ratio seeds synthesis solution there were different methods of preparation in order to understand the impacts of different parameters on the final size of MFI Zeolite seeds.

3.3.2 Aging

In order to see the effect of using Rotary evaporator for aging instead of aging with not sealed beaker at same temperature and duration (90°C, 80 min), two methods were used for comparison purpose. However, the aging with Rotary evaporator will be used for the rest of this work. Rotary evaporation was done for the prepared solution at 80°C in a 250 mL PFA round-bottom flask to remove ethanol and water. The concentrated precursor sol from the Rotary evaporator or the precursor sol which is aged in not sealed beaker was then aged at either Room temperature or 80°C for 24h. The aged solution at 80°C was aged for 24h or 48h in order to investigate the impact of the aging duration in a sealed beaker before hydrothermally treated.

3.3.3 Hydrothermal treatment

By considering the precursor solution which is aged by Rotary evaporator, there were two methods of hydrothermal treatments have been used for compering purpose; Microwave-assisted hydrothermal treatment and Conventional furnace hydrothermal treatment. After dilution the precursor solution 10 times in water, the solution was poured either into the vessel reactor and was placed on the microwave (Synthos 3000) for 120 min at 160°C or Teflon-lined stainless steel autoclave and was placed on Conventional furnace at 160°C for 120 min. Then the synthesized solution was centrifuged at 14000 rpm 5 times, after each time the solution were washed with DI water to bring the pH number to 7. Moreover, the solution was placed on the oven by using watching glass for drying overnight at 80°C. For comparison purpose the aged solution for 48 h was hydrothermally treated at different duration to investigate the effect of hydrothermal duration on the final MFI Zeolite Seeds size.

3.3.4 Seeding techniques

The surface of alumina substrate was seeded either by dip-coating or spin-coating technique.

3.3.4.1 Seeding by Dip-coating

The dip-coating technique was used in this research work in order to seed the surface of the substrate prior to the growth of MFI Zeolite crystals to form the active layer. The coating solution was prepared by dispersing 10 wt. % seeds in Deionized water. In addition, the solution was used for coating the substrate at Room temperature with varying both the dipping duration and the repeated number of dip-coating runs.

3.3.4.2 Seeding with spin-coating

One of the surfaces of each alumina substrate was coated with seeds layer by using spin-coating technique with 3000 RPM for 60 seconds and dried at 80°C for 3 hours. The concentration of the seed solution and the number of repeated spin-coating can play a vital role in the uniformity and coverage of the seeds on the top of Alumina substrates which at the end affect the formation and morphology of the final active layer. The concentration of the spin-coating solution was varied by dispersing different amount of MFI Zeolite seeds on Deionized water by using ultra-sonication probe for 20 min. There were 2 solution concentrations; 0.1%wt and 1%wt.

3.4 Secondary Growth of MFI Zeolite

The solution used for secondary growth was prepared by mixing TEOS, TPAOH and Deionized water with following molar ratio 25 TEOS: 3 TPAOH: 1500 H₂O. Sealed Sol were aged in air under stirring for 3 h at room temperature 24°C. After aging, the solution was poured in vessel reactor autoclaves and placed on the microwave for secondary growth at 160°C for 120 min.

3.5 Characterization

Using MFI Zeolite membrane for separation process required certain properties to be characterized and measured in order to enhance the quality of the fabricated membrane. Generally the characterization techniques for ceramic membranes can be classified according to the nature of obtained parameters: (1) morphology/structure related parameters and (2) permeation related parameters. Hence, characterization techniques such as scanning electron microscope (SEM) or field emission electron microscopy

(FESEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) was used for morphology/structure related parameters. Moreover, this membrane will be under pressure and fluctuation forces as consequence these membranes need to have enough mechanical strength in such application and this can be determined by conducting mechanical strength test such as three point test and diametrical compression test.

In this thesis work there are different characterizations methods have been used in order to build up a deep understanding of the results which lead to more accurate conclusions.

3.5.1 Scanning electron microscope (SEM)

Investigating the microstructure of any materials leads to a better control of the properties because of that scanning electron microscope (SEM) technique is widely used to generate high-resolution images of the shapes of objects, to show spatial variations in chemical compositions and to identify phases based on qualitative chemical analysis and/or crystalline structure. According to the powerful and capabilities of this type of technique, there is no doubt that SEM is one of the main characterization techniques on many science fields.

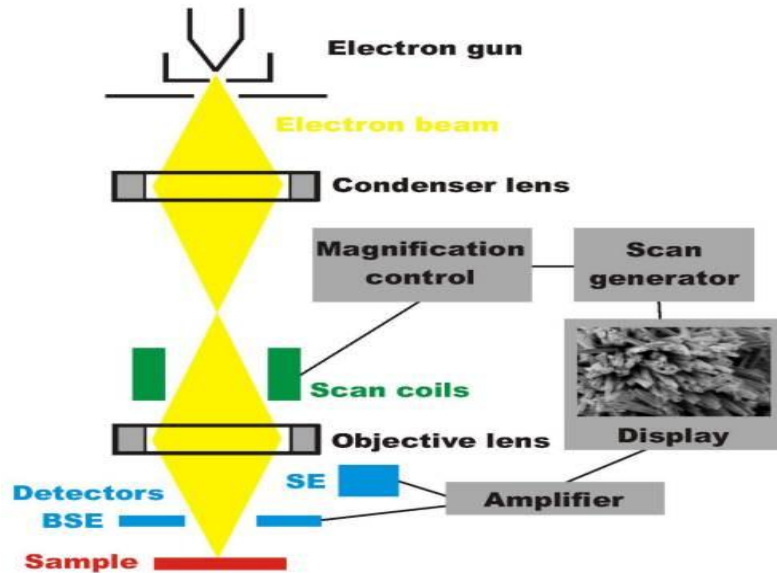


Figure 32 Schematic of Scanning Electron Microscope [74].

In scanning electron microscope, an electron beam is emitted from an electron gun fitted with a tungsten filament cathode. These accelerated electrons in SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by the interactions between the electron beam and the sample. Simultaneous to scanning the beam across a selected sample area, generated signals are being recorded and thereby an image is formed pixel by pixel (figure 32). These signals include secondary electrons which produce SEM images, backscattered electrons (BSE), diffracted electrons (EBSD) that are used to determine crystal structures and orientations of minerals, photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light and heat[75]. For imaging samples, both secondary electrons and backscattered electrons are common used. Secondary electrons are most valuable for showing morphology and topography on samples whereas backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples(i.e. for rapid phase discrimination).

3.5.1.1 SEM of MFI zeolite supported membrane

The final microstructure of the MFI zeolite layer, MFI zeolite seeds and alpha-alumina substrate can be investigated by using scanning electron microscope (SEM). Characteristic such as; crystals size, crystals orientation, defects, number of layers and others can be viewed clearly by using this technique. In this work, the morphology of the zeolite crystals, films and support was examined by scanning electron microscopy (SEM-JEOL, JSM-6460LV) (Fig.33). In order to inhibit "charging", reduce thermal damage, and enhance secondary electron emission, the samples were coated with a layer of gold using a sputter coating machine (Fine Coat Ion Sputter JFC-1100) (Fig.35) and imaged by SEM operated at 15 kV.



Figure 33 JEOL; Fine Coat Ion Sputter JFC-1100



Figure 34 SEM-JEOL, JSM-6460LV

3.5.2 X-ray diffraction techniques

In 1919 A.W.Hull gave a paper titled, "A new Method of chemical Analysis". Here he pointed out that "... every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others"[77]. Therefore, The X-ray diffraction pattern of a pure substance is can be considered as a fingerprint of the substance. Therefore the powder diffraction method is a powerful and rapid experimental tool used to study various aspects of crystalline materials. X-ray powder diffraction technique is most widely used for (1) chemical identification of unknown samples (2) crystal structure determination, (3) lattice size measurement, (4) quantitative analysis of powder mixture. Various kinds of crystalline materials can be characterized by XRD including metal, polymers and ceramics. Chemical composition identification of unknown samples crystalline materials is possibly by comparing the diffraction pattern of the unknown samples to a computer database of diffraction pattern of known materials. Files for hundreds of thousands of inorganic compounds are available from the International Centre for Diffraction Data (ICDD). ICDD's release 2011 of the Powder Diffraction File (PDF) contains 715,953 unique material data sets. Each data set contains diffraction, crystallographic and bibliographic data, as well as experimental, instrument and sampling conditions, and select physical properties in a common standardized format[76].

X-rays, which are considered to be the heart of the X-ray diffraction technique, are electromagnetic waves with wavelength allocated in the range 0.05 to 0.25 nm. When a beam of x-rays (in phase) having a wavelength on the order of the distances (d-spacing) between planes of atoms strikes a flat crystalline specimen, x-rays are scattered in all

directions. There are two types of waves interfaces; constructive interference (mutual reinforcement of the scattered x-rays) and destructive interference (scattered beams are out of phase and cancel each other). While Most of the scattered waves undergo destructive interface, constructive interference of waves only contribute to build the diffraction pattern. A typical diffraction spectrum consists of a plot of reflected intensities versus the detector angle 2θ or θ depending on the goniometer configuration (figure 36). The 2θ values for the peak depend on the wavelength of the anode material of the X-ray tube. It is therefore customary to reduce a peak position to the interplanar spacing d that corresponds to the h, k, l planes that caused the reflection. The value of the d -spacing depends only on the shape of the unit cell. In addition, the d -spacing as a function of 2θ can be calculated by using Bragg's law. Each reflection is fully defined when we know the d -spacing, the intensity (area under the peak) and the indices h, k, l . If we know the d -spacing and the corresponding indices h, k, l we can calculate the dimension of the unit cell.

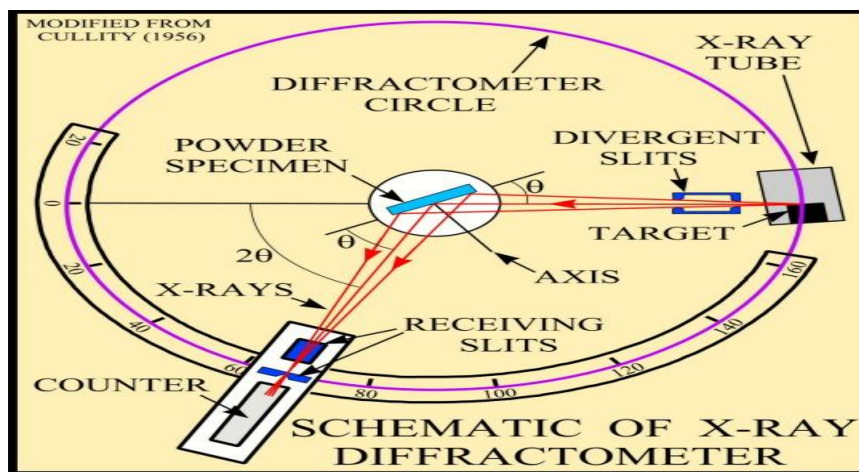


Figure 35 Schematic of X-Ray Diffractometer

3.5.2.1 XRD analysis of MFI zeolite

X-ray diffraction is used to ensure crystallinity of the MFI Zeolite crystals and Alumina support and to give a good view about the orientation of the crystals deposited on a substrate and this parameter is one of the most important parameter which play role on the permeation process. In order to use the XRD pattern for characterizing the structure of MFI zeolite it is important to know the diffraction angles of this type of material and their related planes. As shown in Table 1 which gives a clear picture about the diffraction angles and their related planes and it can be noticed that all MFI zeolite crystals orientation angles allocated on the range between (7-25degree) as shown in table 9. Knowing that can contribute on a better understanding of the effects of different parameters such as; temperature, time and chemicals on the final orientation of the MFI Zeolite crystals. Hence, the permeation process can be enhanced dramatically.

In this work, A BRUKER D8 Advance X-ray diffractometer (as shown in Figure 37) was employed for identifying the zeolite type, crystallinity and morphology of the zeolite crystals/layers. Using a $\text{CuK}\alpha$ radiation source ($\lambda=0.1508$), data were taken between $5^\circ \leq 2\theta \leq 80^\circ$ at a scanning rate of $0.02^\circ/\text{s}$.



Figure 36 BRUKER D8 Advance X-ray diffract meter

Table 9 Planes and related diffraction angles for MFI zeolite structure

Degree	Plane
7.5	(101) (011)
8.7	(200) (020)
13	(002)
13.5	(102)
14	(112)
20.2	(103)
23.1	(501)
23.7	(303)
24	(133)
24.5	(521)

3.5.3 Particle size analysis (PSA)

The particle size distribution of the excess product obtained during seeding and the size analyzing to the collected crystals from the bottom of the vessel reactor after hydrothermal treatment were determined by dynamic light scattering using Microtrac, Germany (figure 38).

3.5.4 Thermo-Gravimetric Analysis (TGA)

Powders were analyzed by Thermo-Gravimetric Analysis (TGA) to determine moisture and organics content. By using this technique it will be easy to know what required temperature is in order to completely remove the organic template from the channels of MFI zeolite.



Figure 37 Microtrac particle size analyzer machine

CHAPTER 4 RESULTS AND DISCUSSIONS

4.1 Alpha- Al_2O_3 ceramic substrate

A number of supports with the following specification were prepared by uniaxial cold pressing, from alumina powders which have fine submicron particle size distribution. The size distribution for the alumina powder given in figure 38 showing that almost over 95% of the particles are smaller than 1 micrometer. The heat treatment temperature was also effective on mechanical strength. Increasing the temperature increases the mechanical strength while decreasing the porosity. The porosity values of the supports were between 40-60 %. The supports have been characterized with SEM. The SEM image of the alumina support heat treated at 1400⁰C is given in figure39. As it is seen in Figure 40 the alumina support heat treated at 1400⁰C has a uniform pore structure. The porosity was to be approximately 45% by using the dry and soaked weight of the support. The SEM picture indicates that the pores are open.

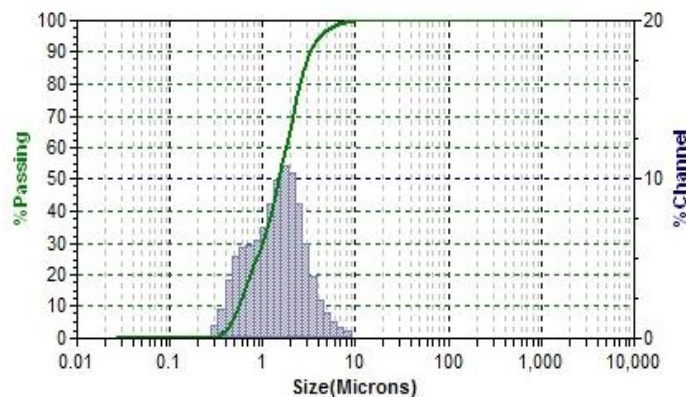


Figure 38 Particle size distribution of alumina powder

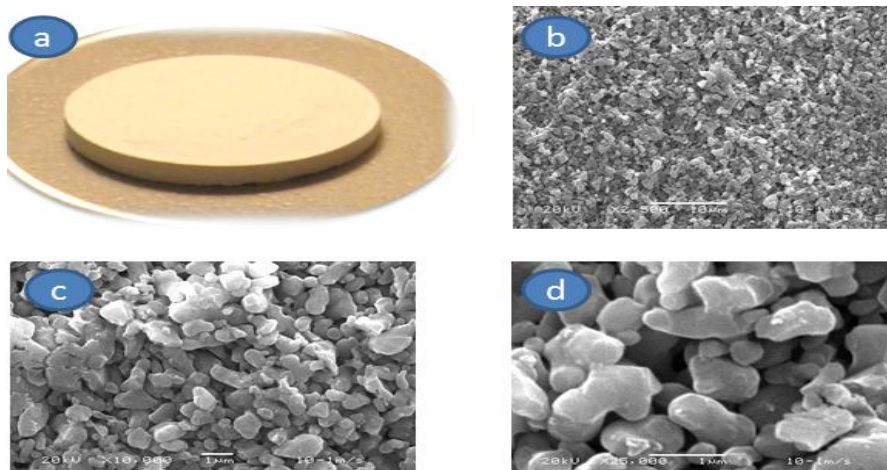


Figure 39 (a) Sintered alumina substrate. (b, c & d) SEM images of alumina substrate at different magnifications

4.2 In-situ crystallization technique

There were different approaches in order to fabricate the active layer by using this technique. While other techniques involve number of parameters and procedure steps, In-situ crystallization consider the easiest technique due to the simplicity of the experimental procedure. Figure 40 shows the SEM images of the MFI zeolite crystals synthesized after hydrothermally treated inside the oven for 2h at 160°C at the top of alpha-alumina substrate placed horizontally in the bottom of the Teflon cup. From this figure it is shown the coverage of the synthesized crystals for the whole surface area of the substrate in which there is no chance to see the surface of alpha-alumina substrate. However, do all of these crystals deposited on the alumina surface or these crystals shown here are representing the precipitate crystals that formed in the solution during the synthesis in other words, these crystals are not related to the substrate. In order to answer this

question the alumina substrate was placed horizontally under a stainless steel stirrer. Moreover, this type of stirrer will try to prevent the participated crystals from attaching the surface. The results which are shown by SEM images in figure 41 answer the question clearly. In figure 41 the synthesized MFI zeolite crystals are not fully covering the surface of alumina which means most of the crystals shown in figure 40 were not bonded strongly to the substrate because they were not deposited on alumina surface. In addition, still there is a doubt about the crystals shown by SEM images whether are these images reflecting only the deposited crystals or most of what are shown are a mixture of deposited and precipitate. Furthermore, introducing a stirring condition during the synthesis may prevent the deposition of the crystals. In order to avoid these problems the substrate was placed vertically in the synthesis solution. After hydrothermal treatment for 2h at 160°C the X-ray diffraction pattern shown in figure 42(a), present the existing of crystallized MFI zeolite and alumina. Although, the SEM images confirmed the existing of these crystals on top of alumina surface, the small number of crystals which are distributed over the alumina surface make the formation of a continuous zeolite layer somewhat difficult to achieve.

Furthermore, in order to enhance the results there were two approaches; one approach was by increasing the duration to 24 h the second one was by increasing the temperature to 275°C during the hydrothermal treatment. The results of both increasing the duration and temperature of Hydrothermal stage were analyzed by XRD and SEM. Figure 42(b&c) show the existing of crystallized MFI zeolite crystals beside to alumina. In addition, The SEM images shown in figure 44 confirm the existing of these crystals. However, these different conditions still resulting in very few crystals which cannot

contribute to form a continuous layer. In addition, investigating the SEM images it is easy to notice that all the images contain 3 parts; MFI zeolite crystals, alumina surface and gel layer. Moreover, the existing of this gel layer is due to the dissolution of aluminum ions from the substrate and these ions try to incorporate into the formation of the zeolite crystals as a result this will delay the formation of these crystals. Hence, one can conclude that increasing the temperature of heating or/and the duration by using this technique will not contribute towards increasing the coverage of the substrate. On the other hand, it will facilitate the dissolution of alumina particles from the substrate and these leaching components from the support will contaminate the growing zeolite film. As a result, that will affect the MFI zeolite layer by delaying the crystallization and deposition on the support. In addition, the combination of leaching and zeolite crystallization within the support may change the mechanical properties of the support, leading to cracks in the film and the support.

This technique are not practical in order to get a continuous layer in the top of alumina substrate due to low nucleation centers which required long period in which the alumina substrate will effect negatively on the final results.

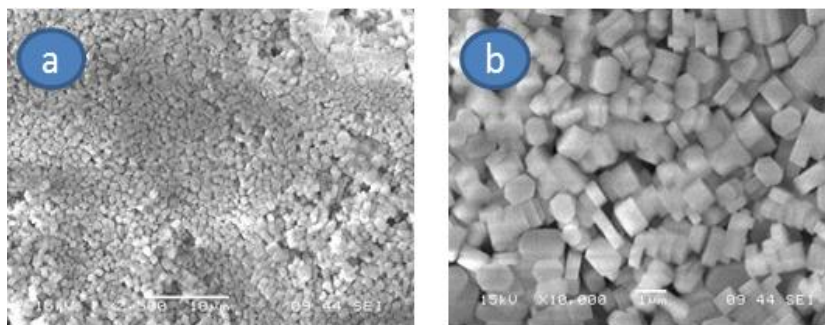


Figure 40 SEM images of MFI zeolite crystals hydrothermally treated inside the oven at 160°C for 2h on the surface of alumina substrate placed horizontally at the bottom of the stainless steel vessel

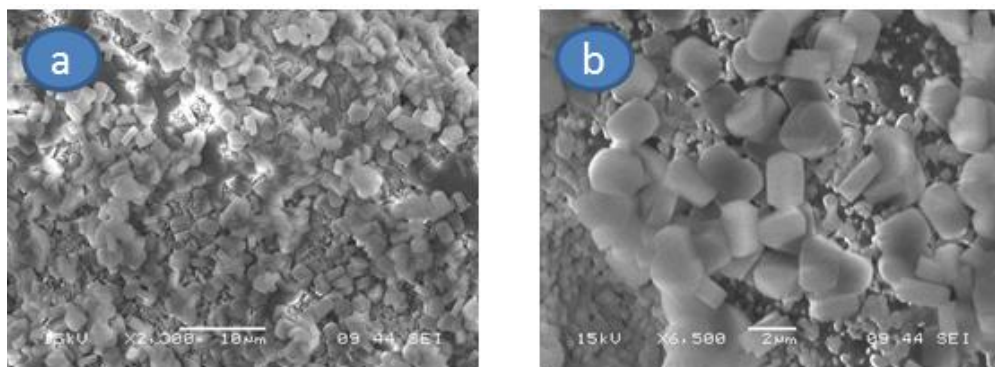


Figure 41 SEM images for MFI zeolite crystals hydrothermally treated inside the oven at 160°C for 2h on the surface of alumina substrate placed horizontally at the bottom of the stainless steel vessel under stirring at 200 rpm

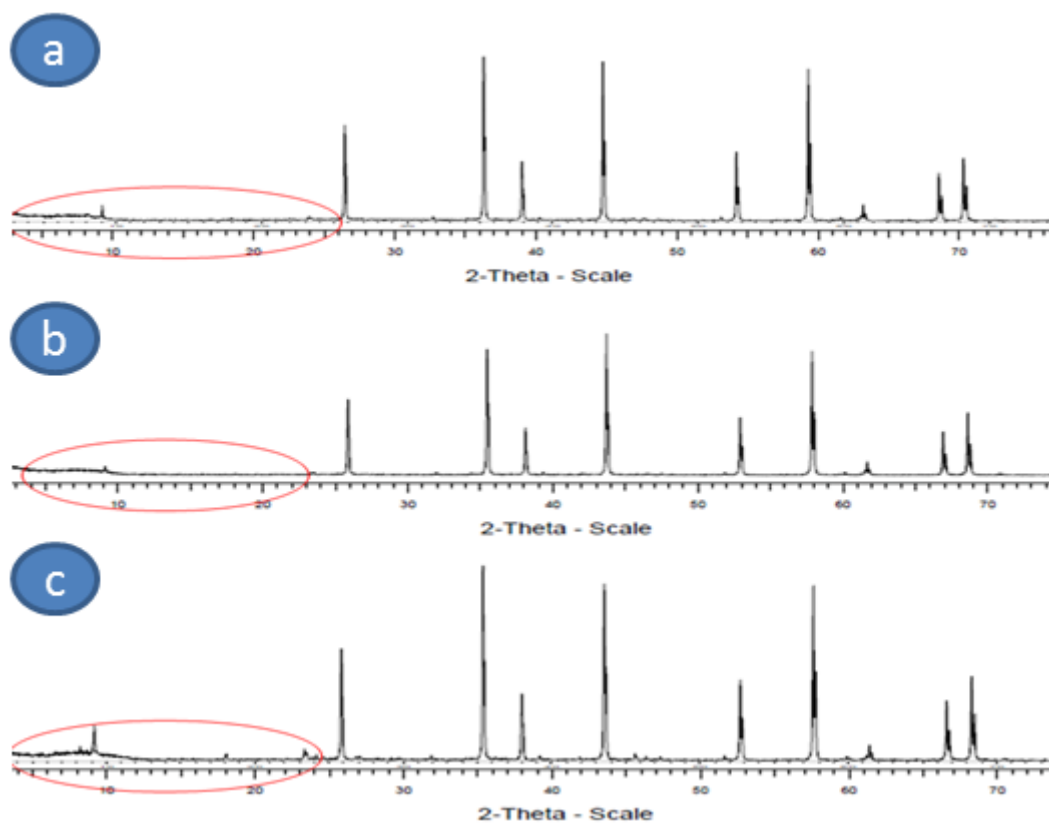


Figure 42 XRD patterns for MFI zeolite crystals synthesized in the top of alumina substrate by using in-situ crystallization at different conditions (a) 2h, 160°C, (b) 2h, 275°C & (c) 24h, 160°C

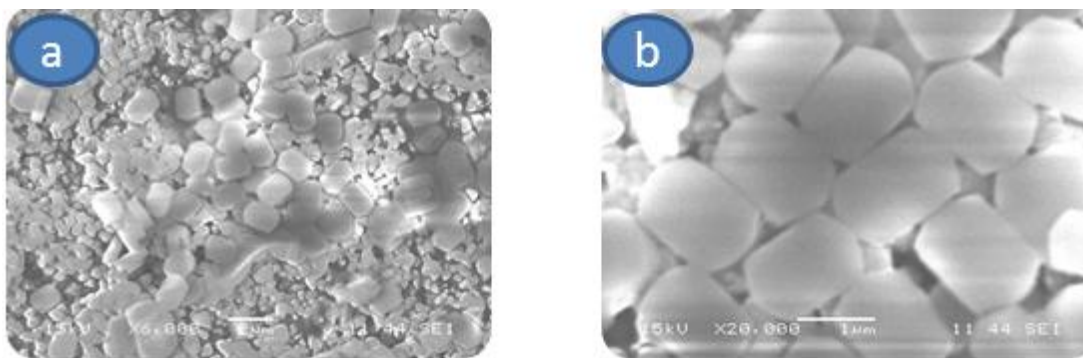


Figure 43 SEM images for MFI zeolite crystals synthesized in the top of alumina substrate by using in-situ crystallization at 160°C for 2h

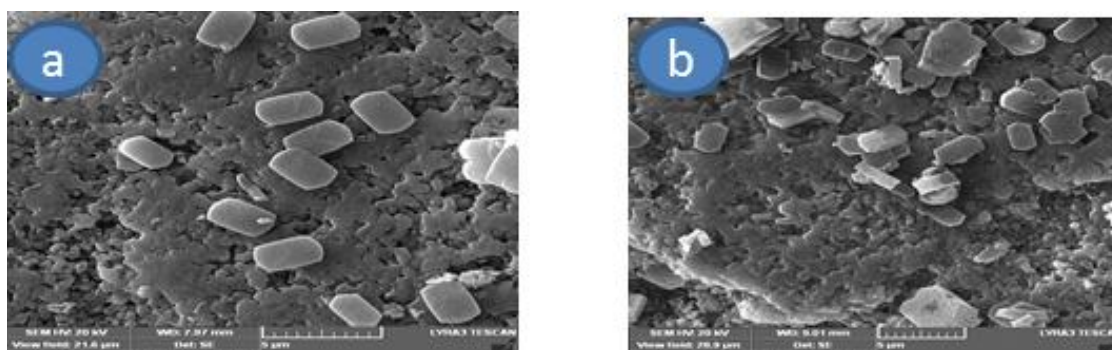


Figure 44 SEM images of MFI zeolite crystals synthesized on top of alumina substrate using In-situ crystallization at different conditions: (a) 24h, 160°C& (b) 2h, 275°C

4.3 Synthesis of MFI zeolite seeds

For seeds synthesis, different methods were followed but with the same molar composition solution in order to study the effect of using Rotary evaporator for aging, duration of aging, aging temperature, types of hydrothermal treatment and duration of hydrothermal treatment on the seeds size and distribution which as a consequence affect the growth and final morphology of MFI zeolite membrane/layer. Figure 45 shows the result of particle size distribution for the seeds synthesized by using Rotary evaporator

during aging and microwave for hydrothermal treatment. From this figure, the average particle size is around 89 nm which is also confirmed by the SEM image as it is shown in Figure 46.

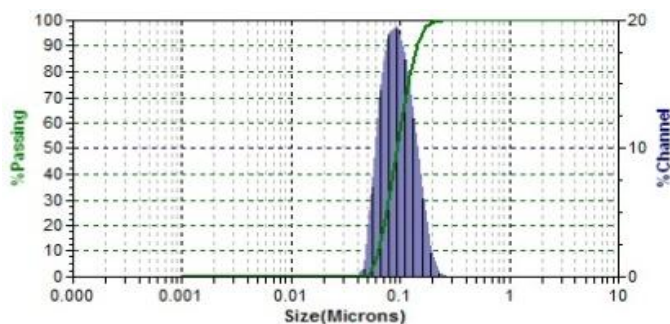


Figure 45 Average Particle size distribution of MFI zeolite in case of using Rotary evaporator during aging.

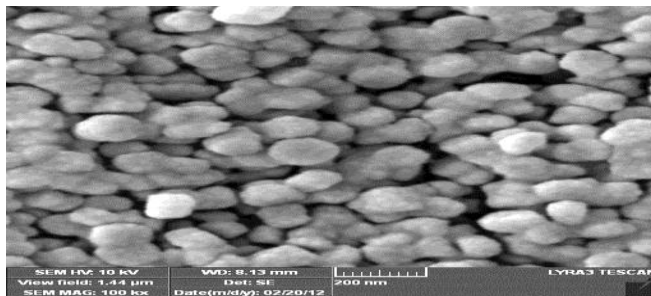


Figure 46 SEM images of MFI zeolite in case of using rotary evaporator during aging.

However, when the aging was done without the using of Rotary evaporator there was a clear difference on the average size of the synthesized MFI zeolite seeds. Figure 47 shows the particle size distribution of the Seeds synthesized by normal aging. The average particle size increased by almost 20% from the seeds size that synthesized by using Rotary evaporator to be 117 nm with same molar solution composition and heating temperature and duration as it is shown in figure 46. This result can be explained by

understanding the nucleation stage and how the aging with rotary evaporator affect the nucleation and finally affect the size of the synthesized seeds.

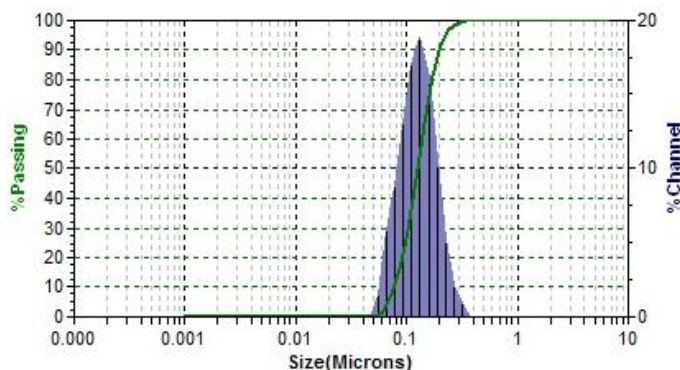
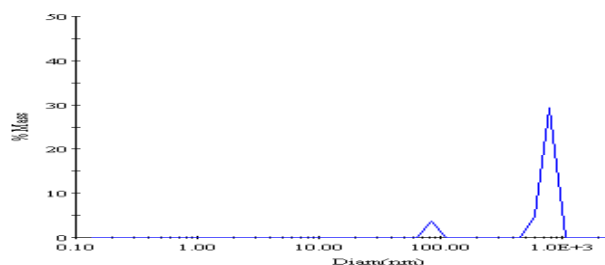


Figure 47 Particle size distribution of MFI zeolite seeds synthesized by microwave without the using of Rotary evaporator during aging.

To increase the nucleation rate, the conventional wisdom suggests the use of higher supersaturation conditions, that is, by using a lower water/silica ratio. Kirschhock [78] , 1 SiO_2 /4 EtOH/0.37 TPAOH/4 H_2O system at room temperature. Since the precursors were prepared by the direct hydrolysis of TEOS in a 40% aqueous solution of TPAOH, the water/silica ratio was determined by the TPAOH/ silica ratio. A possible reason may be the difficulty in hydrolyzing TEOS in such a low water recipe. In fact, Kirschhock et al [78] had to add the required TEOS to the 40% TPAOH solution in steps, with a few to 40 min of stirring each time to hydrolyze the TEOS. In their synthesis, the precursor sol was prepared with a recipe of 1 SiO_2 /0.36 TPAOH/19.2 H_2O /4 EtOH. The clear sol was aged. To highlight the difference of our approach, we have compared our results with that

of Cundy et al. [80].. In their synthesis, the precursor sol was prepared with a recipe of $1\text{SiO}_2 / 0.36 \text{ TPAOH} / 19.2 \text{ H}_2\text{O} / 4 \text{ EtOH}$. The clear sol was aged at 22°C for days and then subjected to a microwave synthesis at 175°C for 2 h. Nanocrystals about 50 nm could only be produced after 150 days of aging. A similar exponential decay curve had been reported by Li et al. [79]. on the same recipe using an aging temperature of 60°C . The required aging time for producing 50 nm nanocrystals was 150 h. In our case, 50 nm nanocrystals were produced with just 12 h of aging. The mechanism of forming silicalite-1 from a clear solution has been articulated by a number of reports as beginning with the aggregation of primary units followed by the zeolitization (restructuring and densification) and growth of these aggregates. It is believed that the higher silica concentration we employed led to a faster and more complete aggregation of the primary units and consequently eliminated crystal growth during the later hydrothermal process. All researchers agreed on the fact that the silicalite-1 precursor solution formed by hydrolysis of tetraethylorthosilicate in a TPAOH-containing solution under ambient conditions comprises discrete particles with a size of about 3 nm.

While the hydrothermal treatment under the irradiation of Microwave for the normal aging show average seeds size with 117 nm as shown in figure 46, the conventional oven for hydrothermal treatment with same heating temperature and duration showed bigger seeds size with average seeds size around 384 nm as shown in figure 48 and confirmed by the SEM images in figure 49.



Item	R (nm)	%Pd	MW-R (kDa)	%Int	%Mass
Peak 2	384.7	8.8	3765260	82.8	34.2
Peak 3	3396.2	16	615181000	15.3	62.1

Figure 48 Average particle size distribution of MFI zeolite seeds hydrothermally treated in the oven

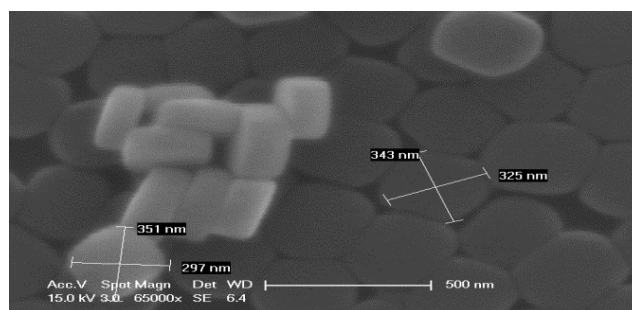


Figure 49 SEM images of MFI zeolite seeds hydrothermally treated in the oven

In addition, when the same molar composition ratio and aging with Rotary evaporator was used but with some of the parameters were changed such as the aging time, and hydrothermal duration, there were significant changes on the synthesized seeds sizes. For instance, when the synthesis aging period changed from 24 h to 48h at 80°C and with the same hydrothermal condition, the result of the average particle size distribution technique showed a wide range of Seeds size. The SEM images shown in figure 51 prove and confirm the PSA results. The proper understanding for having this kind of result was

generated after watching the condition of the solution during the aging period. It has been noticed that when the period of time exceed 32h at 80°C the liquid solution transformed to completely transparent solid. After 48 h the solid was crushed and diluted with deionized water prior to hydrothermal treatment. The proposed mechanism of the nucleation and growth for this condition is due to the temperature gradient throughout the solution with the height of the beaker during the aging as a consequence when the most of the water and organic material evaporated and the synthesis solution transformed to solid, this temperature gradient will vary the nucleation and growth stages from one point to another. After this 48 h of aging there were three different hydrothermal durations for synthesis of MFI zeolite seeds. It is found that increasing decreasing the hydrothermal duration (0.5h, 2h and 3 h) have direct impacts on the size range of the seeds. In addition, by considering the result shown in figure 50, it is clear that increasing the duration of hydrothermal stages will broaden the range of the seeds sizes.

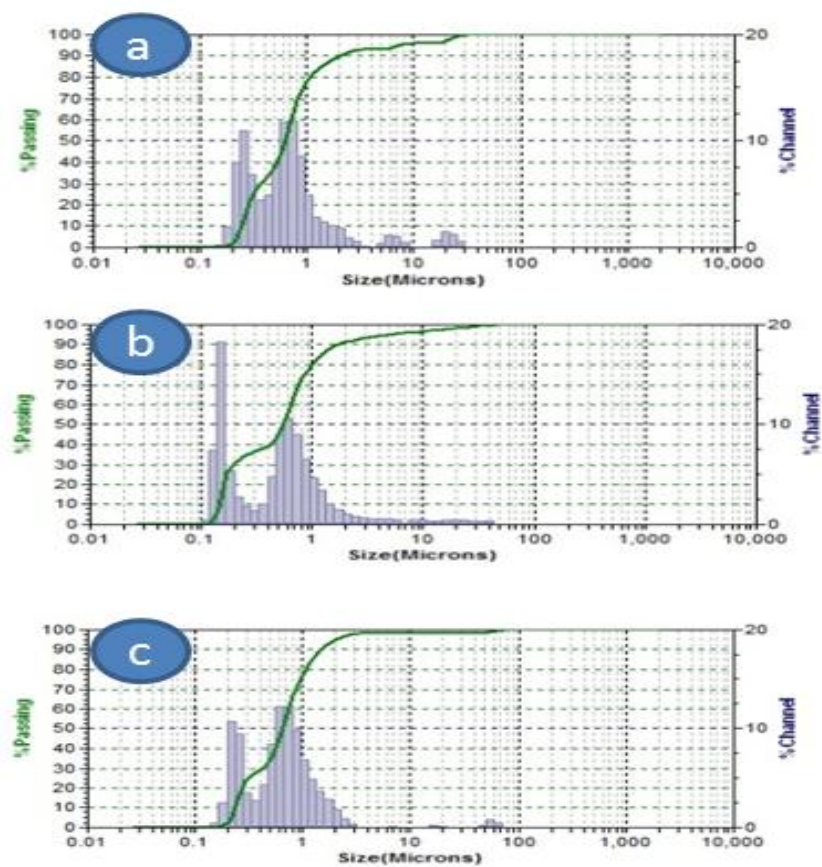


Figure 50 Average particle size distribution of MFI zeolite aged for 48h and hydrothermally treated by microwave for a) 3h, b) 2h and c) 0.5 h.

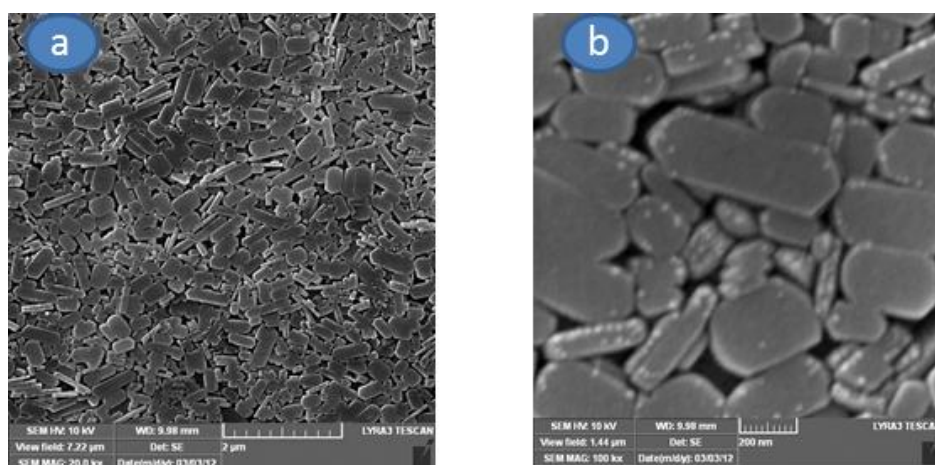


Figure 51 SEM images at different magnification (a&b) of MFI zeolite seeds aged for 48h and hydrothermally treated by microwave for 3h

4.4 Secondary growth after seeding with dip-coating

Figure 53 shows the XRD patterns of the coated substrate by using the dip-coating technique for different dipping durations (10s or 180s) and different number of dip-coating runs (1run or 3 runs). It was observed in all dipping durations and number of runs that the MFI Zeolite peaks are existed which obviously confirm the deposition of MFI Zeolite crystals on the surface of alpha-alumina substrate. However, the X-ray diffraction patterns cannot tell about whether there is intergrowth between crystals toward forming a layer or the crystals are only distributed on alumina surface without having intergrowth between them and in case if there is layer, is it continuous layer or it is involved different type of defects. In order to answer these questions the SEM images needs to be investigated. After Investigations of SEM images which are shown in figure 52, it was observed that although the MFI Zeolite crystals covered completely the surface of the substrate in all the cases, the morphology of these layers differ from one condition to another. For instance, in figure 52 (a) the SEM image can be divided into two areas; one is dark area in which there is a good intergrowth between the crystals and a light area in which there is scattered crystal that are not intergrown well. The proper explanation for this difference is the non-uniformity and low seeds density of the dip-coated layer before the growth as a consequence there will be location with low/no nucleation sites and other with high nucleation sites. This difference will lead to a good intergrowth on the location where there is good number of nucleation sites and not well intergrowth on different location where there are low/no nucleation sites.

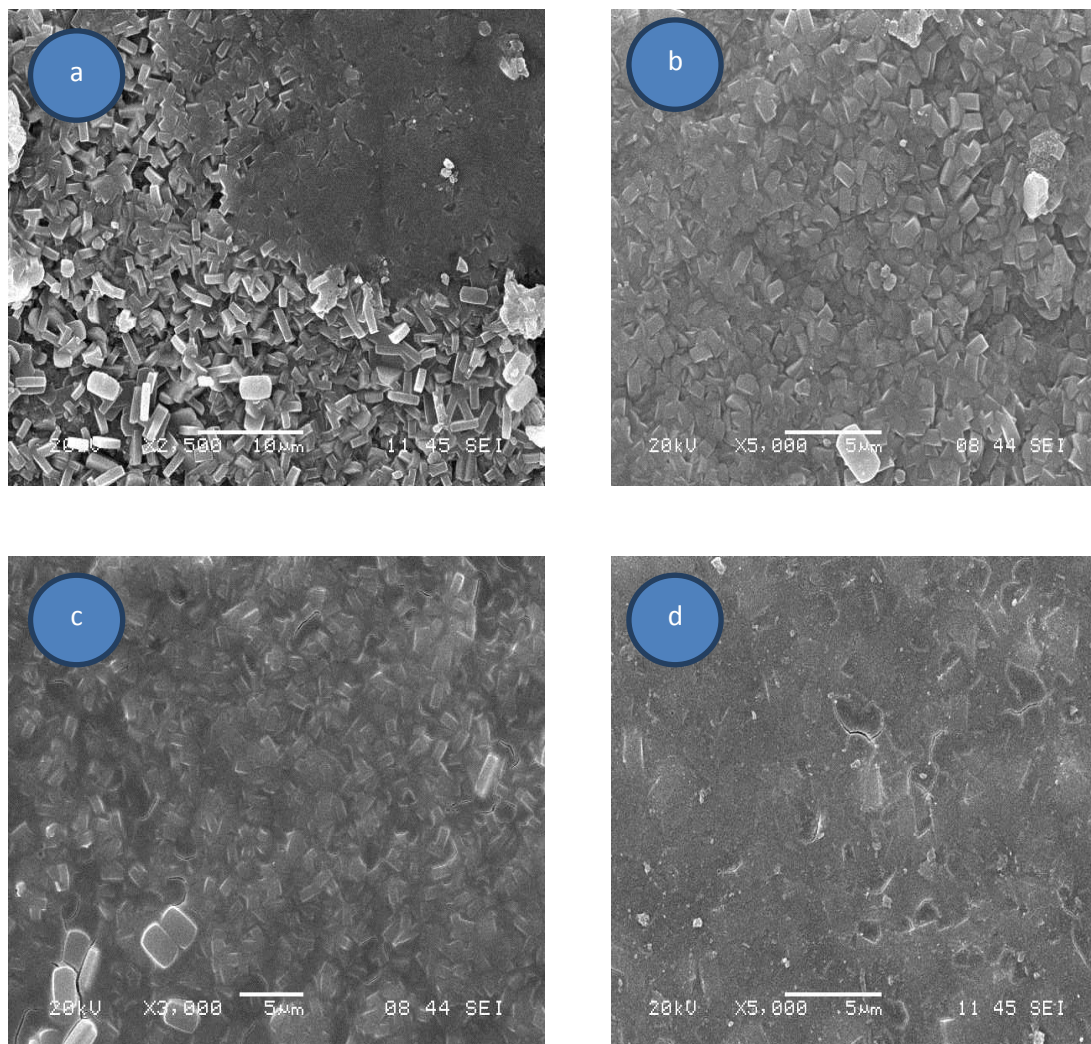


Figure 52 SEM images of MFI zeolite layer grown on alumina support at 160°C for 2h with different seed dip-coating parameters: (a) 10s, 1time. (b) 10s, 3times. (c) 180s, 1time. (d) 180s, 3times.

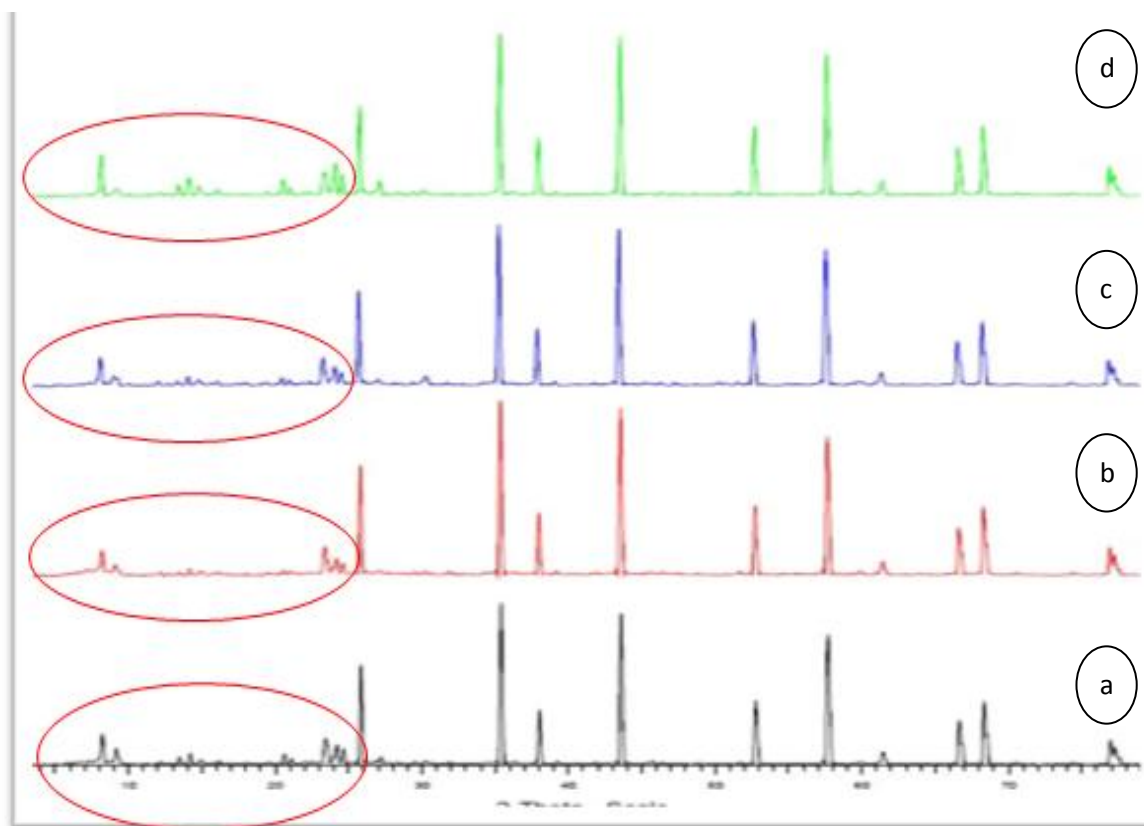


Figure 53 XRD patterns of MFI Zeolites growth on Alumina support at 160C for 2h with different seed dip-coating parameters: (a)10s, 1time. (b)10s, 3times. (c)180s, 1time. (d)180s, 3times.

As the dipping durations and number of dip-coating runs were further increased there is significant improvement in crystal intergrowth as the density of seeds increased underneath the grown MFI zeolite crystals. However, the bad quality of this type of membranes can be seen clearly by analyzing the SEM images (figure 52&54) which are taken over the surface of the membrane in which the cracks appeared in many locations (Fig.55) and the issue of non-uniformity of seeds distribution still exist even though if the repeated number of dip-coating runs increase.

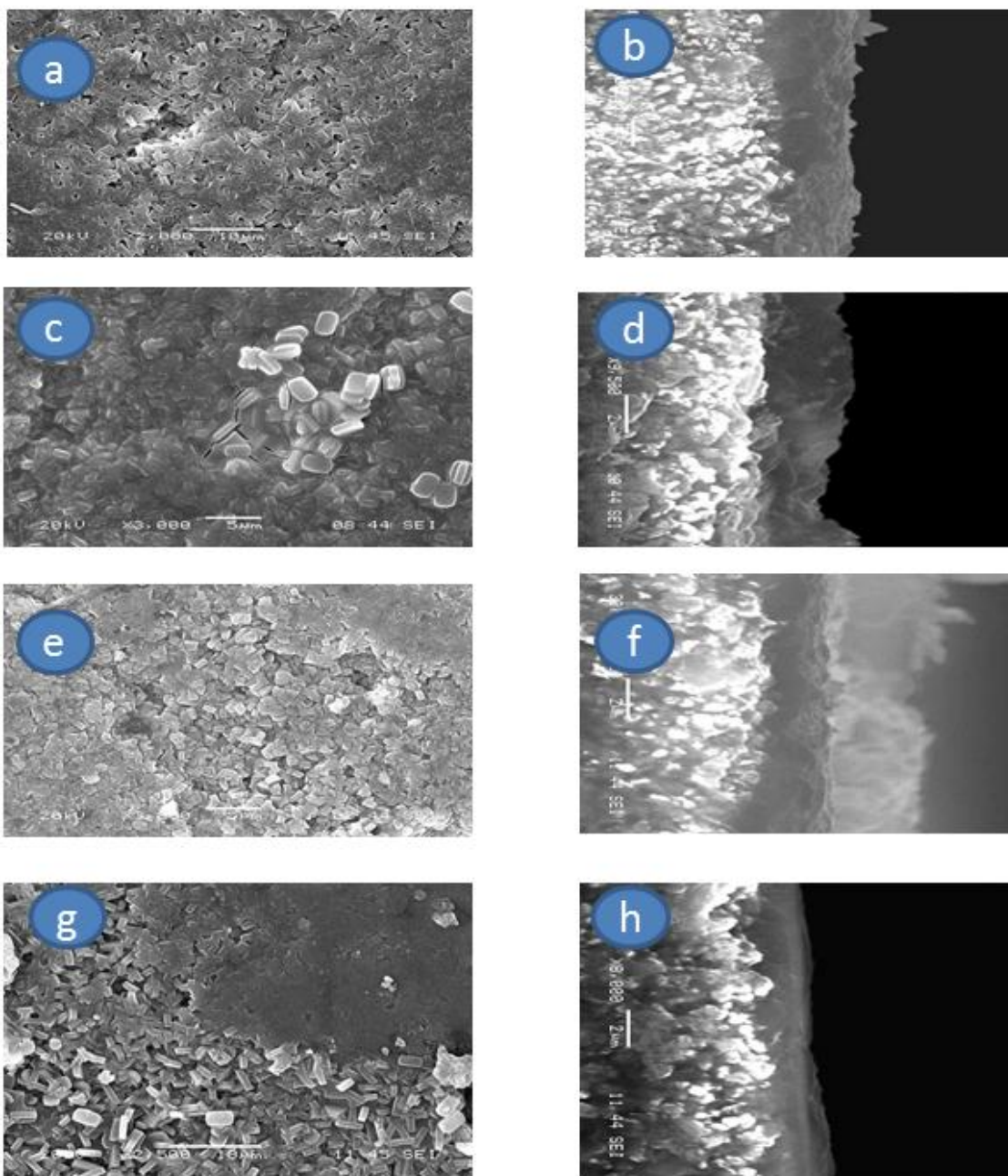


Figure 54 SEM images of top and cross sections for MFI zeolite crystals grown in the top of alumina substrate after seeding by dip-coating technique at different conditions; (a,b)180s,3times,(c,d)180s,1time,(e,f)10s,3times &(g,h)10s,1time

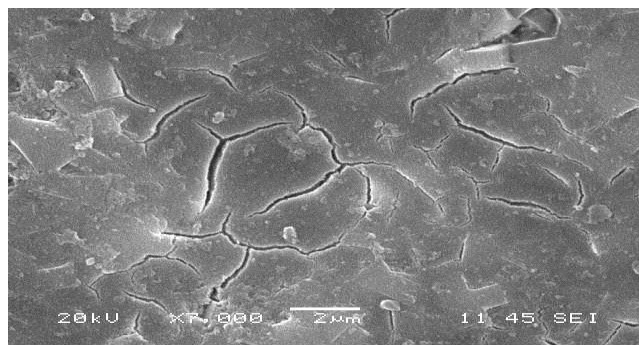


Figure 55 Top view of SEM image showed the existing of cracks for the Grown MFI zeolite crystals after seeded by dip coating with 180 s dipping ,3 times

Indeed, it is important to understand the reason for having cracks and the non-uniform distribution of seeds by using dip-coating technique. In the dip coating process, the capillary force drives the zeolite seeds in the colloidal suspensions move to the support surface slowly with water being sucked into the support pores. When the support pores are fully filled with water, the action of the capillary force disappears, and the zeolite seeds in the colloidal suspensions moving onto the support surface are stopped. Consequently, it is necessary to repeat the drying and dip coating in order to obtain high coverage seeding layer by the capillary force only, so lengthening the coating process. In addition, more zeolite seeds move to the bottom surface of the support owing to negative influence of the gravitation force, so it is difficult to obtain uniform seeding layer by dip coating method. In addition , by looking to which type of bonds are generated between the surface of alumina substrate and MFI zeolite crystals, it is known that both of them has negative charge on the surface as a result there will be no chemical bond between them but only physical bond. In order to remove the excess amount of water from the coated layer for coating a second layer or for hydrothermal treatment there will be two

choices; either to dry the coated layer in furnace at 80⁰C for several minutes which will generate cracks due to the internal stresses that are created within the coated layers after each dipping especially when this layer is coated porous and rough surface as the one used in this research work. In addition, drying at this temperature may break the hydrogen bonds which hold the seeds on the substrate and as a result the seeds will be easily disattach from the surface of alumina substrate. The second choice in which the coated layer is kept on air to be dried and according to this slow drying mechanism, this will take several hours which will not be practical especially this seeding mechanism needs several layers in order to fully cover the surface of the substrate.

This limitation of this seeding technique requires either a further investigating of different dip-coating techniques or using another technique which can overcome the above mentioned dip-coating disadvantages. Hence, in this research work the spin-coating technique is proposed as a promising technique for seeding the alumina surface.

4.5 Secondary growth after seeding with spin-coating:

4.5.1 Seeding by spin coating

The SEM images of the seeded substrate with the 0.1% concentration of MFI Zeolite seeds solution for different number of spin-coating are shown in figure 56&57. When the magnification was increased while investigating the coverage of the coated layer it was observed clearly how the MFI Zeolite seeds distributed on the top of the alumina surface after the spin-coating(see figure 56&57(b)).

In Figure 56 (a,b) the seeds can be seen deposited on the surface of the alumina substrate but with poor coverage of seeds. Furthermore, most of these seeds try to fill the pores

between the alumina grains with almost no contributing on covering the outer grains of the substrate. On the other hand, when the number of repeated spin-coting increased to ten times, beside of filling the pores the seeds seems to be able to cover some of the outer big alumina grains as it is shown in figure 57 (a,b). Although, the number of repeated spin-coating increased from one to ten times (Fig.56 (a,b) and Fig.57(a,b), respectively) the MFI Zeolite seeds are not fully covered the alumina substrate surface. As a result, the concentration of 0.1%wt MFI Zeolite seeds solution is not practical because it needs more than 10 times of repeated spin-coating in order to reach a fully coverage of this type of material.

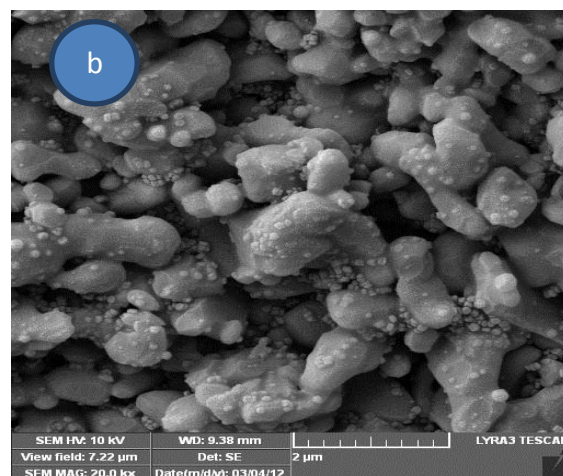
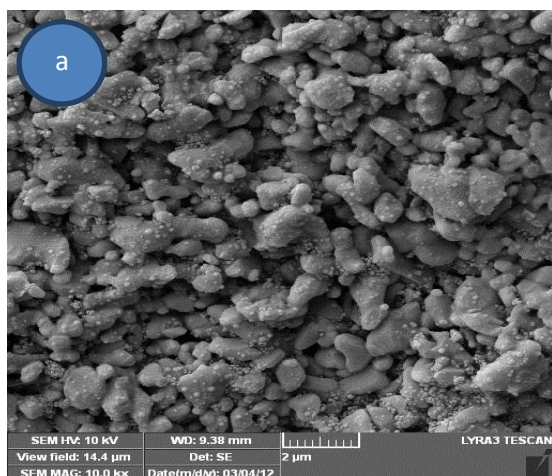


Figure 56 Top view of SEM images for seeded alumina substrate with spin-coating solution concentration of 0.1 wt. % seeds in water after 1 spin-coating run

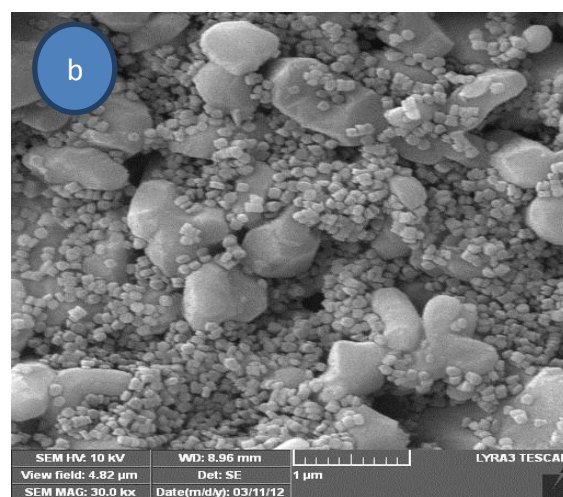
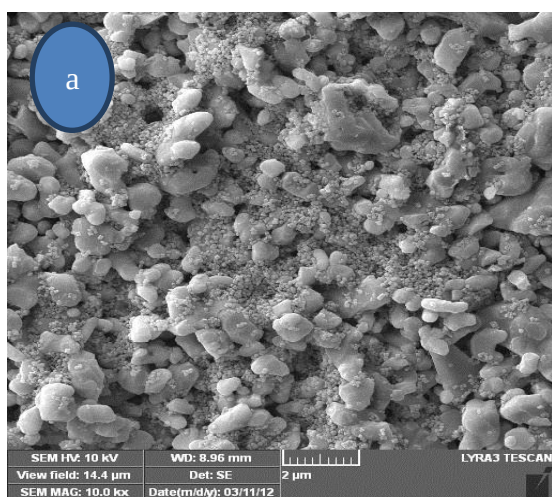


Figure 57 Top view of SEM images for seeded alumina substrate with spin-coating solution concentration of 0.1 wt % seeds in water after 10 spin-coating runs

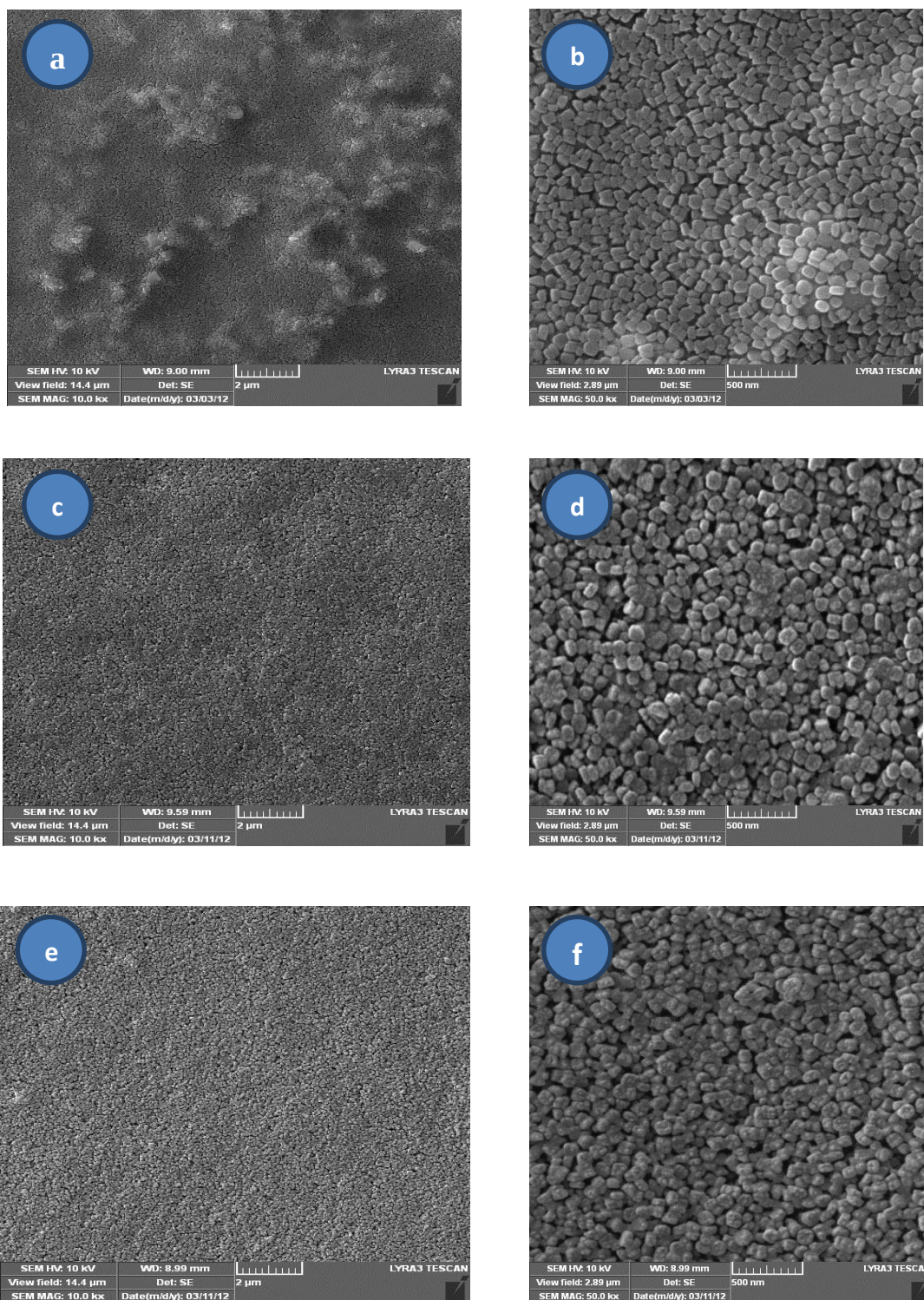


Figure 58 Top view at different magnifications of SEM images for the seeded substrate by spin-coating with 1 wt.% concentration of seeds in water at; (a,b) 1 seeds layer, (c,d) 2 seeds layer & (e,f) 3 seeds layers

As the concentration increased from 0.1%wt to 1%wt there was an obvious enhancement on the Coverage of MFI Zeolite seeds as it is shown in figure 58. In figure 58(a,b) it is parley to see the alumina surface after the spin-coating of 1wt% concentration of MFI seeds solution for one time of spinning as the seeds almost covered the surface except small areas of the surface. Moreover, increasing the number of the repeated spin-coating can completely cover the surface of the substrate with a continuous layer of seed which is able to eliminate the difference between different roughness and morphology of the substrates (see figure 58(c,d,e&f). As a consequence, this type of surface modification will have an important role on the formation of a continuous and defect free active layer. However, increasing number of repeated spin-coating mainly can have two negative impacts on the final active layer need to be considered; I). The concentration of the spin-coating suspensions has a proportional relation with the thickness of the MFI zeolite films. As a result, increasing the thickness will increase the resistance of the permeation through the membrane. II) Possibility of creating cracks on the seeds layer during the drying stage after each spin-coating run. Hence, it is important to state clearly what is objective of having the seeds layers.

The main goals for having these seeds layers are to provide nucleation sites which can ease the growth and deposition of MFI zeolite crystals on the top of alumina substrate, also to control the orientation and to neglect the morphology or the surface chemistry on the grown crystal. As a result, an optimum number of layers needs to be specified in order to achieve these goals without consuming more chemicals or/and increasing the permeation resistance by increasing the thickness of the active layer. Another approach toward approving the deposition of the seeds on the top of alumina substrate was

examined. This approach is to modify the surface of the alumina support by UV before the spin-coating step. The SEM image in figure 59 compares between the deposition of MFI Zeolite seeds by spin-coating for alpha-alumina substrate treated and non-treated with UV. Indeed, The result was opposite to what it can be expected from the impact of UV on the surface as it is usually used as a surface pretreatment before the deposition. It is found that the UV will remove the loosely bonded OH group from the surface which will affect the deposition of seeds on alumina surface.

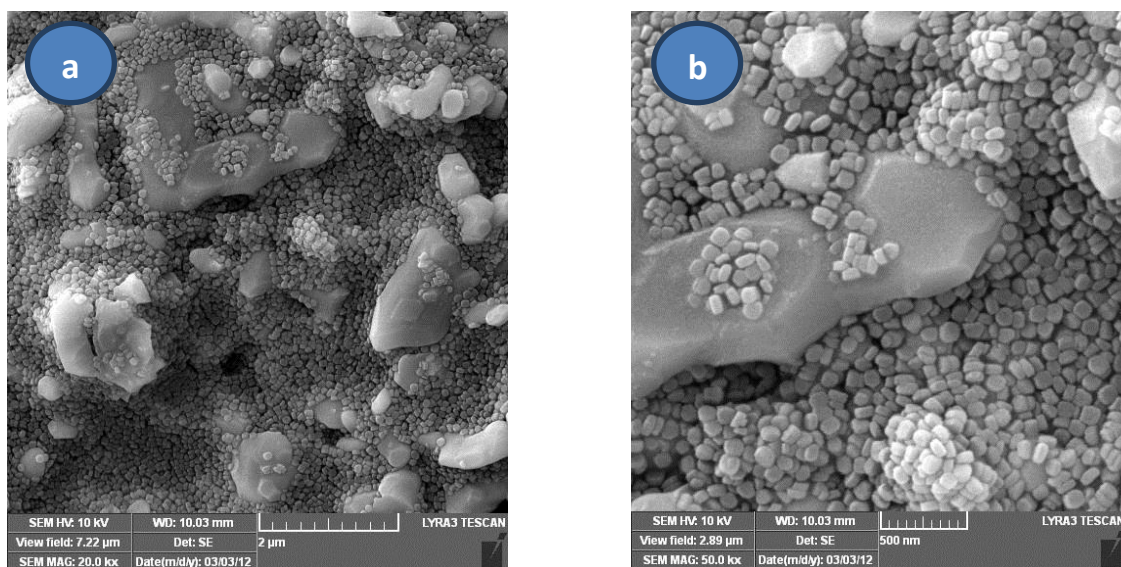


Figure 59 Top view of SEM images for the UV treated alumina substrate after seeding with spin-coating solution concentration of 1 wt. % , 3 runs.

In order to investigate the effects of these different seeding conditions on the final active layer, further investigations need to be done for these different seeded substrates. Hence, the seeded substrates were exposed to synthesis solution for the secondary growth in which the analysis of the characterization results can build a good understanding for the impact of seeding on fabrication of MFI zeolite layer.

Zeolite membranes can be reproducibly prepared by the secondary growth method with spin-coating seeding technique for seed particle size of 87nm, suspension concentration of 1wt.% in deionized water with 3000 RPM for 60 seconds and dried at 80⁰C for 3hours.

4.5.2 Secondary growth after seeding

Seeding the support introduces more growth centers resulting in greater competition for nutrient and space. This also causes perturbation in the local nutrient concentration that can have a large impact on the zeolite growth. Figure 60 shows top view of MFI Zeolite film grown into uniformly seeded α -alumina substrates by using the spin-coating technique with different number of seeds layers. It can be seen from these figures that all the MFI Zeolite crystals formed continuous, homogeneous well intergrown layers. In addition, figure 11, 12 & 13 show cross section SEM images of a MFI membrane fabricated by using the secondary growth technique with (1 wt.% seeds solution, one run). The MFI film appears to consist of three layers. The thick top layer consists of crystals with columnar character. The next layer with around 89-180 nm thick and is composed of small grains. Zeolite is also formed in the pores of the support. This penetrating on the support pores assures a strong anchoring of the film to the support and the crystals in the film appears to be well intergrown.

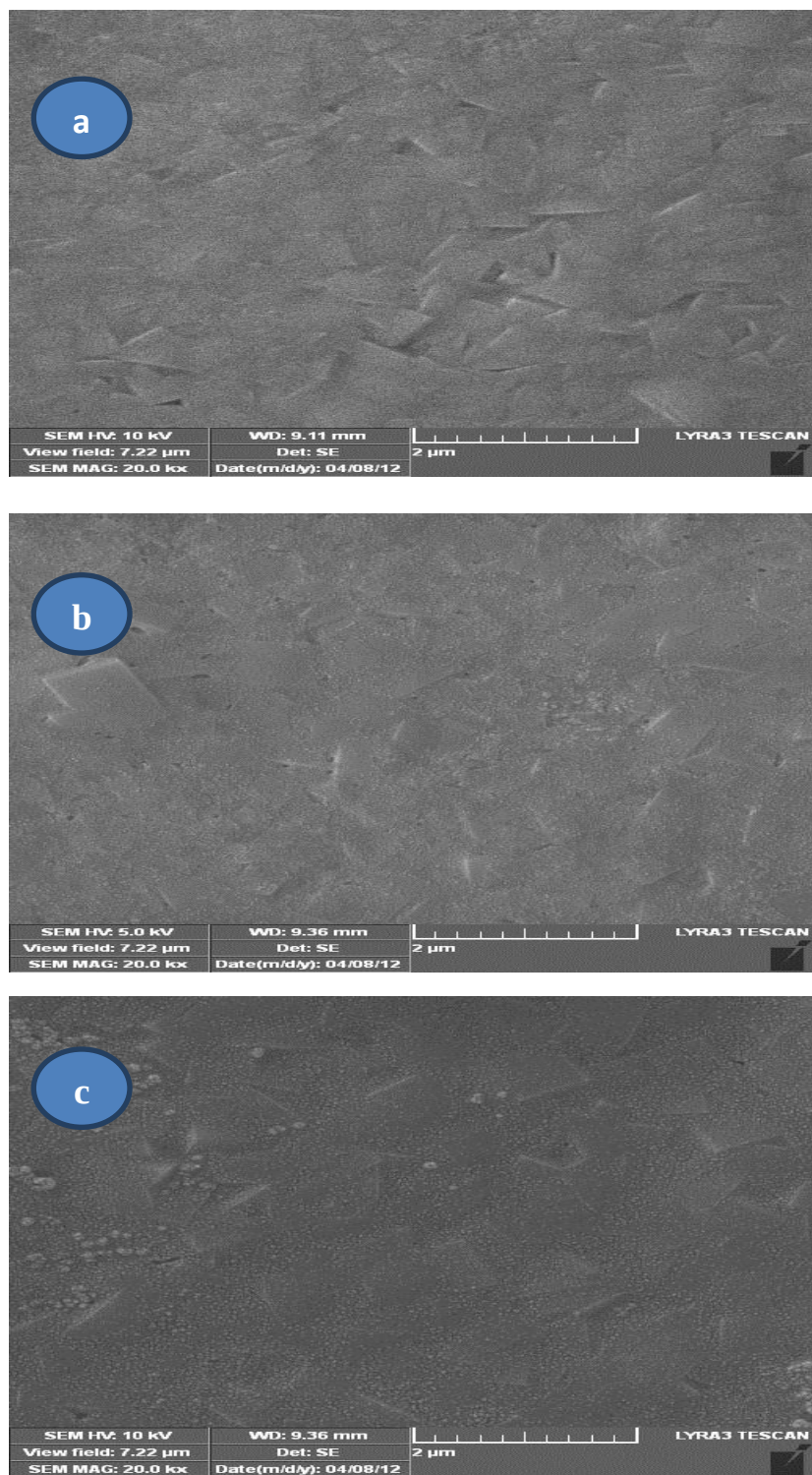


Figure 60 SEM images of MFI zeolite crystals grown after Secondary Growth for different seeding conditions; (a) 1 seed Layer, (b) 2 Seed Layers & (c) 3 Seed Layers

The cross sectional views indicate that there is only one layer of crystals grown on the seeded surface and most of the weakly bonded crystals from the solution were removed after the formed layer were washed with water. As a result, thickness of these formed layers (~1.3 μm) is similar to the particle size distribution results of MFI Zeolite crystals formed in the solution during the hydrothermal heat treatment in MW as shown in figure 61. As shown in figure 62, for one seeds layer the grown film was continuous but with some defects existed on the surface of MFI Zeolite layer which are referred to the seeding condition. Although one seeds layer can almost cover the rough alpha-alumina surface, this low concentration of seeds cannot eliminate the impact of the alpha-alumina surface morphology on the formation of MFI zeolite membrane.

Moreover, it is apparent from the cross-sectional views the crystals which formed the MFI zeolite layer show different orientation. This result was confirmed by X-ray diffraction which is shown in figure 61. The X-ray patterns for this membrane display diffraction peaks corresponding to MFI zeolite crystals in which they are randomly oriented in different directions including (1 0 1) peak intensity.

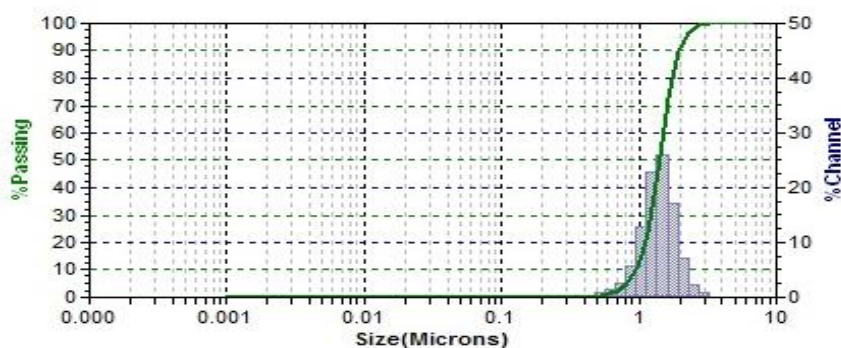


Figure 61 Particle size distribution of MFI zeolite hydrothermally treated by microwave at 1600C for 2h.

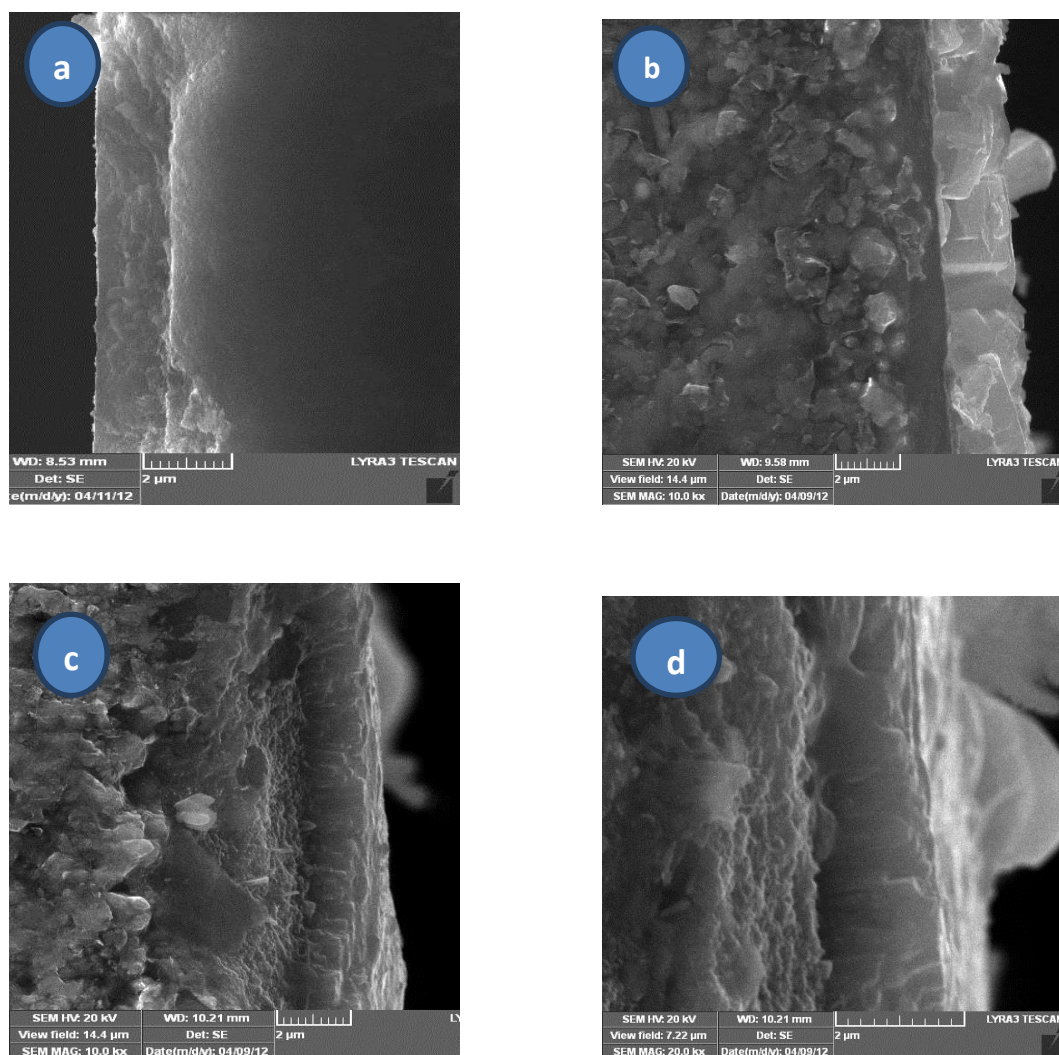


Figure 62 Cross Sectional SEM images of MFI zeolite crystals grown after Secondary Growth for different seeding conditions; (a) 1 seed Layer, (b) 2 Seed Layers, (c & d) at different magnifications for 3 Seed Layers

As the seed population was further increased there is a significant improvement in crystal intergrowth. From the cross-section it can be seen that the MFI Zeolite crystals start to deviate from random orientation to be aligned nearly vertically on the support with (1 0 1) direction. The XRD pattern shown in figure 63 indicates that the crystals in the film with (1 0 1) orientation can be deducted and the ratio between the peaks intensities (1 0 1)/ Highest Peak (h k l) is greater than the ratio of (1 0 1)/Highest Peak (h k l) for one layer seeds. Figure displays the zeolite film obtained after the growth of 3 seeds layers. The intergrowth between neighboring crystals is excellent as shown in figure. From both the cross-section and the X-ray data, it can be seen that a large fraction of the crystals in the film aligned with (1 0 1) crystallographically preferred orientation with the highest ratio (1 0 1)/ Highest Peak (h k l) compering to the pervious seeds conditions. Moreover, it is important to note that as the deviation from random orientation to an oblique (1 0 1) crystal preferred orientation (CPO) as the surface morphology change from being rough to be smooth. These results demonstrate that the growth environment also plays a determining role in MFI Zeolite film orientation and morphology. The local growth environment was manipulated through seeding of the support with MFI Zeolite nanoparticles. Hence, the seeds concentration can play a vital role on the growth and formation of MFI Zeolite layer and there will be no elimination for the effects of the substrate surface before having two seeds layers with seeds size, spin-coating conditions and substrates similar to what had been used in this work.

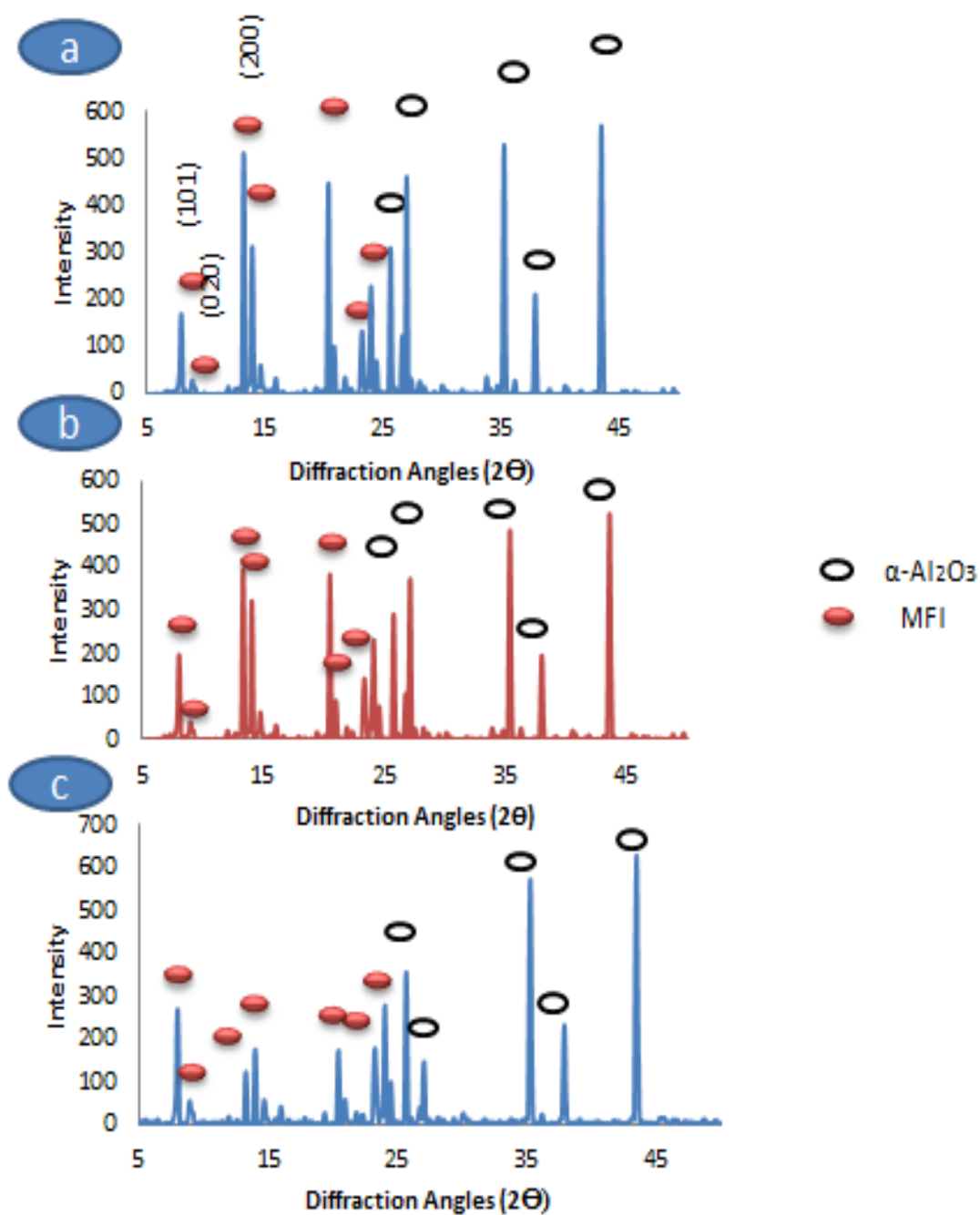


Figure 63 XRD Patterns for Grown MFI zeolite Crystals before calcination at different seeding conditions; (a) 1 seeds layer,(b) 2 seeds layer& (c) 3 seeds layers

Table 10 lists the Al and Si concentrations measured by XPS on the surface of the zeolite layers on alumina supports prepared in different conditions. Moreover, these result can tell how much of the aluminum ions can incorporate during the secondary growth due to the leaching from the substrate.

Table 10 Energy-dispersive X-ray spectroscopy (EDS) for the MFI zeolite crystals grown at different seeding conditions

Situation	Si (%)	Al (%)	Al/Si
One time spin-coating	46.34	2.02	0.043
Two times spin-coating	37.25	1.26	0.033
Three times spin-coating	37.31	0.0	0.0

The final Al/Si ratio of the zeolite membrane was determined by (EDS) technique after the secondary growth process. As shown in table 10, one seeds layer by spin-coating has Al/Si ratio of 0.043. Twice spin-coated seed layer has a smaller Al/Si ratio with 0.033. However, the ratio of Al/Si become zero in which no aluminum was found on the surface of the three spin-coated seed layers membrane. This indicates that this number of spin-coating is sufficient to prevent the incorporation of the aluminum into the formation and MFI zeolite framework.

Since silicate seeds suspension or silicate synthesis solution used for zeolite membrane synthesis contained no aluminum source, the aluminum in zeolite layer must have come from the alumina support. During the synthesis of MFI zeolite crystals a template was used as a structure directing agent. Furthermore, this template has to be removed from the zeolite pores to activate the membrane since the TPA^+ ions for MFI zeolite membrane is blocking the zeolite channels as shown in figure 64.

In order to determine the minimum calcination temperature required for eliminating the template from 1.2 μm membrane thickness, the different degradation steps of the template were studied by TGA on MFI Zeolite powders with average crystal size of 1.2 μm .

The TGA curve of MFI zeolite powders consists of two stages when heated at $5^\circ\text{C}/\text{min}$ up to 800°C in Argon atmosphere as given in figure 65. It has shown that heat treatment at 500°C was enough to get a stable zeolite layer, since the weight loss approach to negligible level after that temperature. The first stage is from room temperature to around 270°C where approximately 1% weight loss occurred which was probably due to water removal which was only absorbed on the surface of the MFI Zeolite as it is proved by Mass spectrometer (MS). The second stage is between 320 and 480°C during which 12% weight loss occurred. This amount of losses associated to stepwise thermal degradation of TPA entrapped within zeolitic pores. According to this result, this evacuation and totally template removed is completed at 490°C for MFI Zeolite crystals. However, removing this template from the channels from the MFI zeolite layer will introduce several issues which will affect the permeation properties of MFI zeolite membrane.

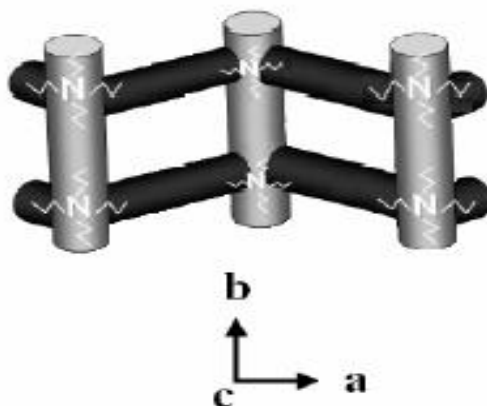


Figure 64 A sketch view of the MFI channel system showing the sinusoidal channels running along the a-direction, and the straight channels running along the b-direction. The TPA^+ template molecules are trapped in the channels/pores of the zeolite structure

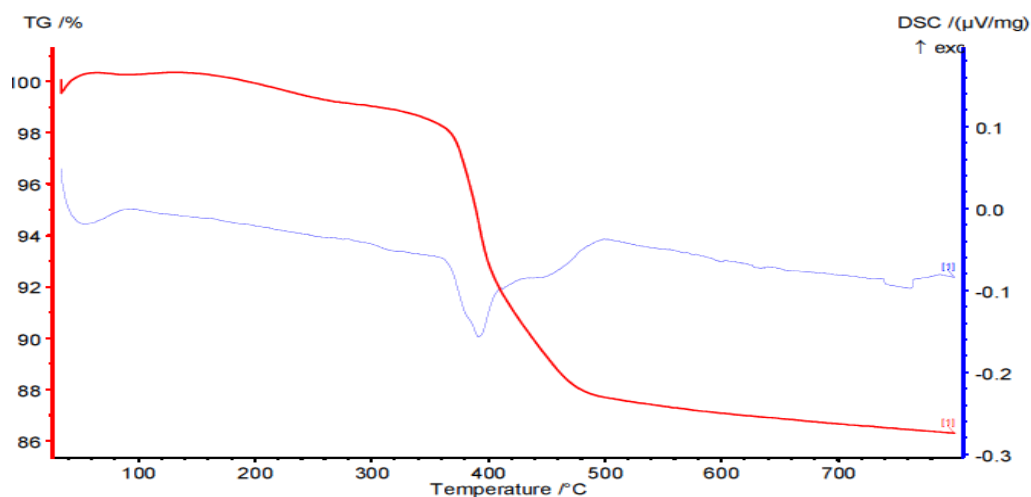


Figure 65 Thermo-gravimetric analysis (TGA) for MFI zeolite crystal heated at $5^{\circ}\text{C}/\text{min}$ up to 800°C in Argon atmosphere for 6 hours.

4.6 Effect of calcination step

The calcination step was carried on in order to remove the template from the MFI zeolite membrane channels. However, this step will affect the properties of the fabricated membrane which needs to be investigated on this study. Top view SEM images for the calcinated membrane are shown in figure 66-68. Indeed, the results of SEM images differ from one condition to another. For example, for the calcinated grown crystal after one seeds layer, the existing of large voids between the MFI crystals is higher than the other conditions as shown in figure 65. Furthermore, as the seeding layer is increased as the existing of these voids decrease more and more. The possible explanation behind these results is due the nature of bonds between the crystals and the bonds between the crystal and the substrate. Moreover, for this thin membrane the crystals are chemically bonded to the substrate which will be stronger than the bonds between the crystals. As a consequence, the zeolite crystal will be displaced and moved as response for the expansion behavior of the alumina substrate during heating stage. On the other hand, the MFI zeolite crystal will be displaced and moved as response to the contraction of alumina substrate. As a result, the resultant of this moving will be in term of grain opening between the crystals. In addition, increasing the seeds density underneath the zeolite layer help the crystals in the film appears to be well intergrown that's mean the bonds between the crystal will increase so the resultant of moving during the calcination will be less as shown in figure 67&68 for 2 and three seeds layers.

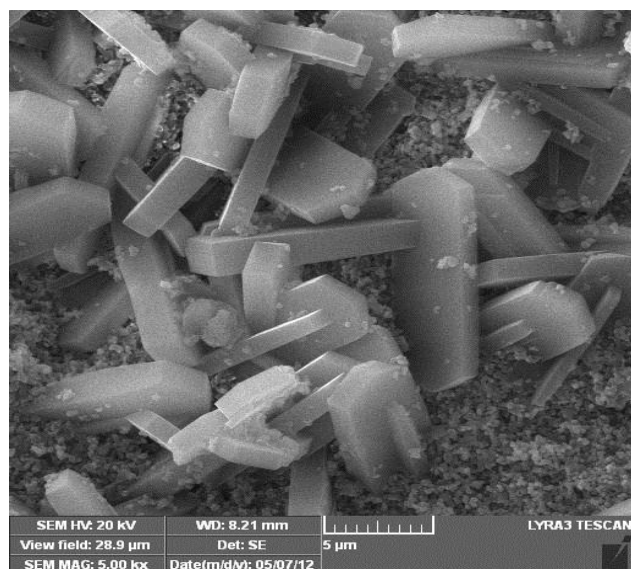


Figure 66 Calcinated MFI zeolite membrane grown from one seed layer

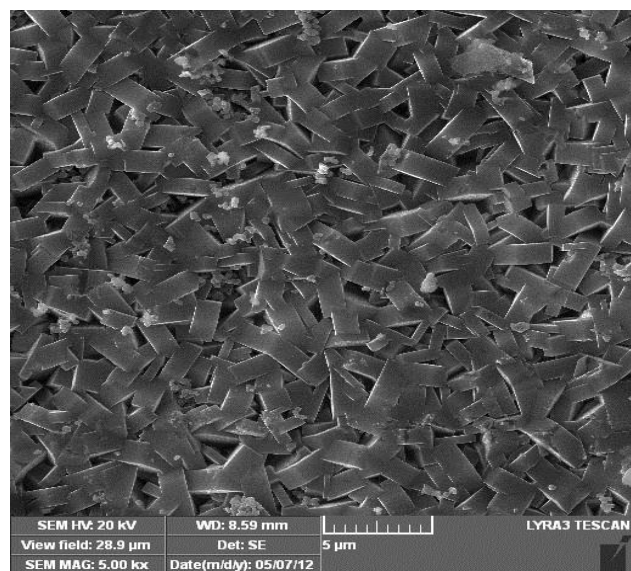


Figure 67 Calcinated MFI zeolite membrane grown after 2 seed layers

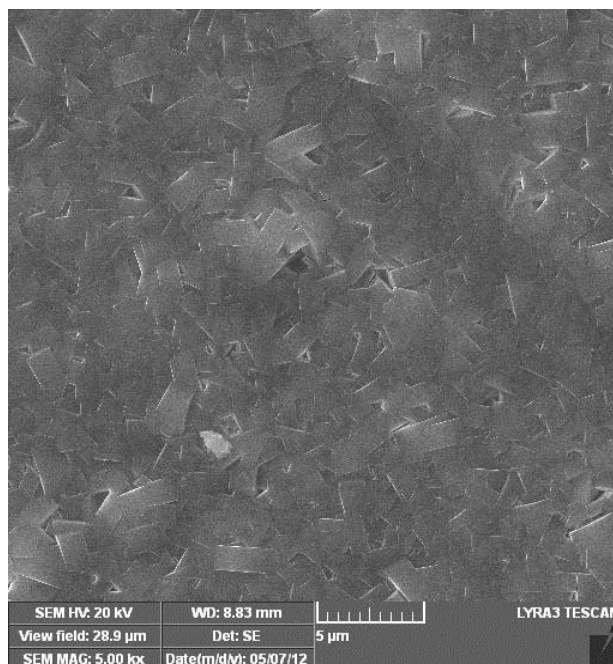


Figure 68 Calcinated MFI zeolite membrane grown after 3 seeds layers

The Energy-dispersive spectroscopy (EDS) results for the calcinated membranes in which the Al/Si ratio are presented. The (EDS) results for the calcinated MFI zeolite membrane grown from one seeds layer has Al/Si ratio of 0.1076 and this ratio is decreased to 0.0565 for 2 seeds layers. However, for 3 seeds layers the result showed a zero ratio. The proper explanation for these results can be generated by understanding what is happening during the calcination.

Beside the effect of calcination on the final morphology of MFI zeolite membrane there is another important issue which is the diffusivity of the Aluminum ions which can transfer to the MFI zeolite layer via two paths as shown in figure 69. This figure shows that the aluminum can transfer from the alumina support to the zeolite layer in a form of dissolved Al^{3+} via the synthesis solution during secondary growth process also the

aluminum ions can diffuse during the calcination and this hypothesis can be proven by comparing the Al/Si ratio before and after the calcination.

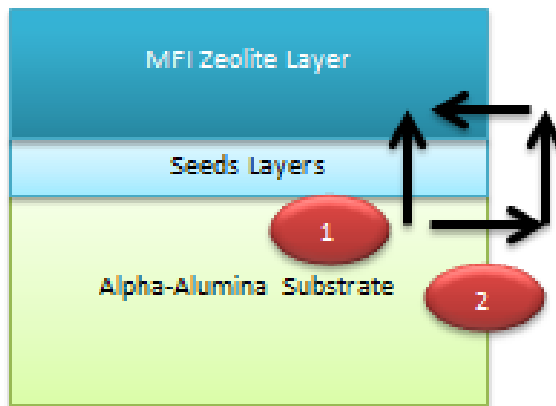


Figure 69 Influence of Al³⁺ from alumina substrate on seed layer and membrane

Figure 70 presents a comparison between the Al/Si ratio before and after calcination for different seeding layers. For the grown crystals after one spin-coating seeding the ratio after the secondary growth was 0.0435 however this ratio increased to 0.1076 after the calcination. Moreover, similar results are shown for crystals grown after two seeds layers in which the ratio increased from 0.033 to 0.0569. While three seeds layers were sufficient to prevent the incorporation of aluminum ions during the secondary growth, the aluminum ions can diffuse for this seeding condition during the calcination. Hence, the results shown in this figure prove the hypothesis which was expected regarding the diffusion of aluminum ions during the calcination.

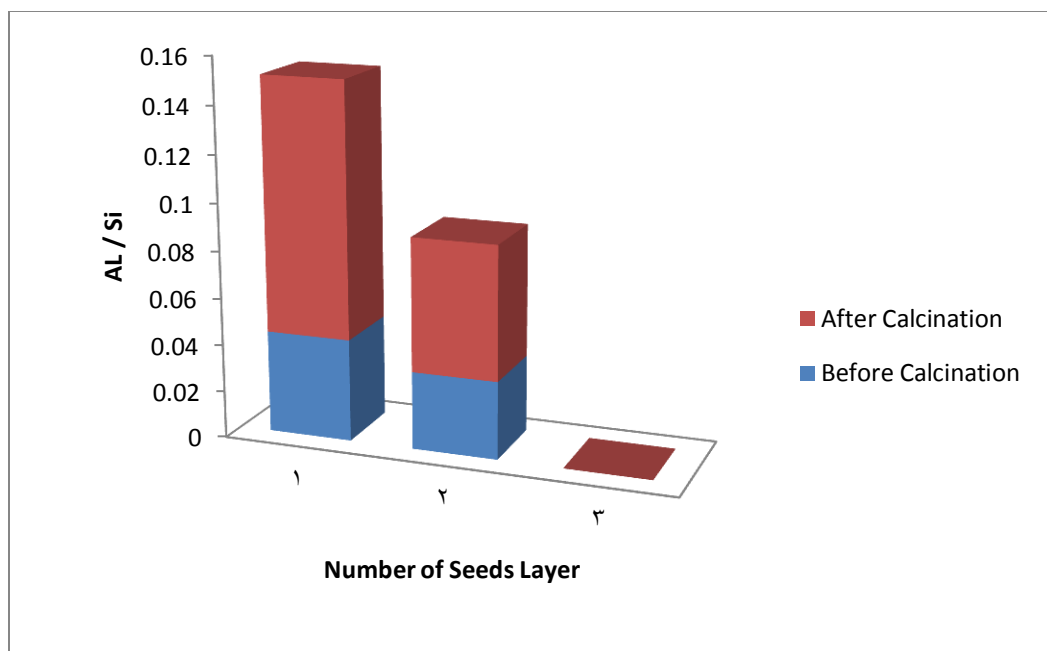


Figure 70 Comparison between the Al/Si ratio on the MFI zeolite crystals before and after the calcination for different seeding conditions

Another impact of calcination on the grown MFI zeolite membrane which is needed to be considered is the effect of calcination on the orientation of MFI zeolite membrane. The XRD results for the calcinated MFI zeolite membrane shown in figure 71-74. The results show peaks refer to MFI zeolite crystals with different orientation depending on the seeding conditions. For one seeds layer, the XRD results in figure 70 still show randomly oriented crystals with the highest peak refer to (0 0 2) followed by (1 0 1) for a- and oblique oriented crystals, respectively. Furthermore, the calcinated MFI zeolite membrane for two seeds layer in figure 71 also showed a randomly oriented crystals but with the increase on the intensity of (1 0 1) peak comparing with figure 70. Moreover, the intensity of (1 0 1) increased significantly comparing with previous results and become a predominant orientation on the layer as it is illustrated on figure 73 in which the ratio of

the Intensity of (1 0 1) peak to the highest intensity peak was used to compare between different conditions.

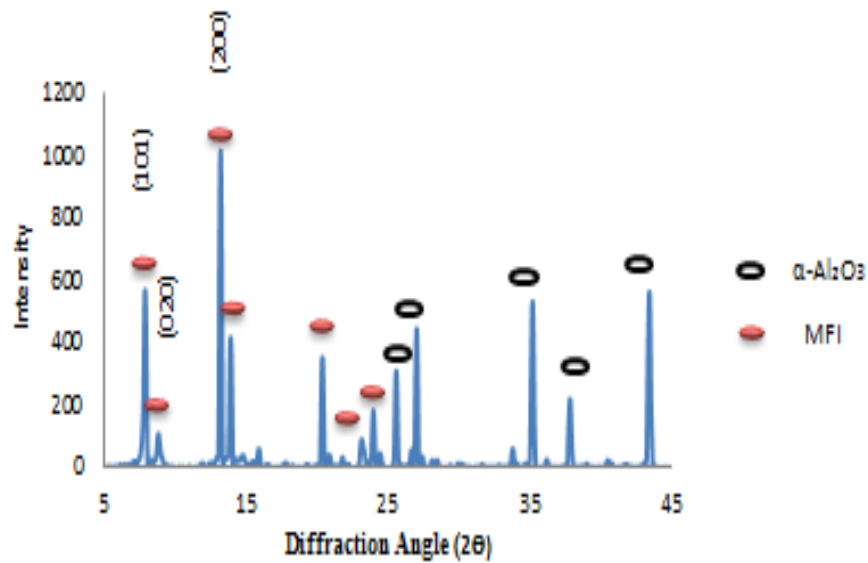


Figure 71 XRD results of calcinated MFI zeolite membrane after one seed layer

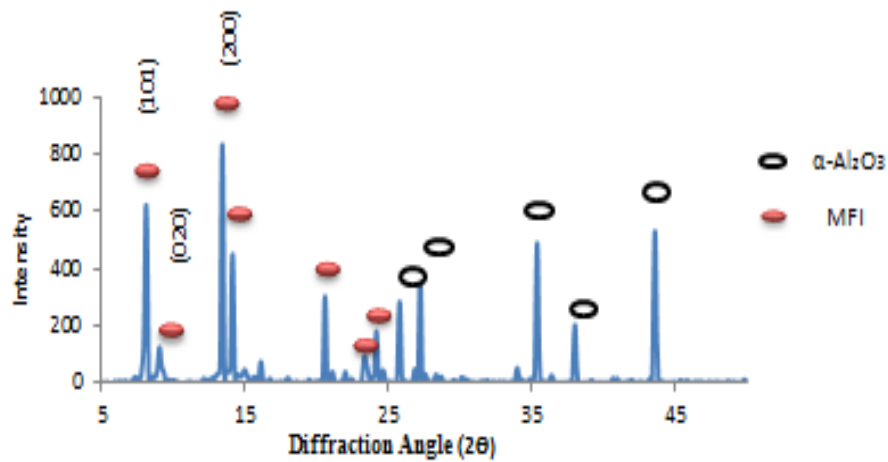


Figure 72 XRD results of calcinated MFI zeolite membrane after two seed layers

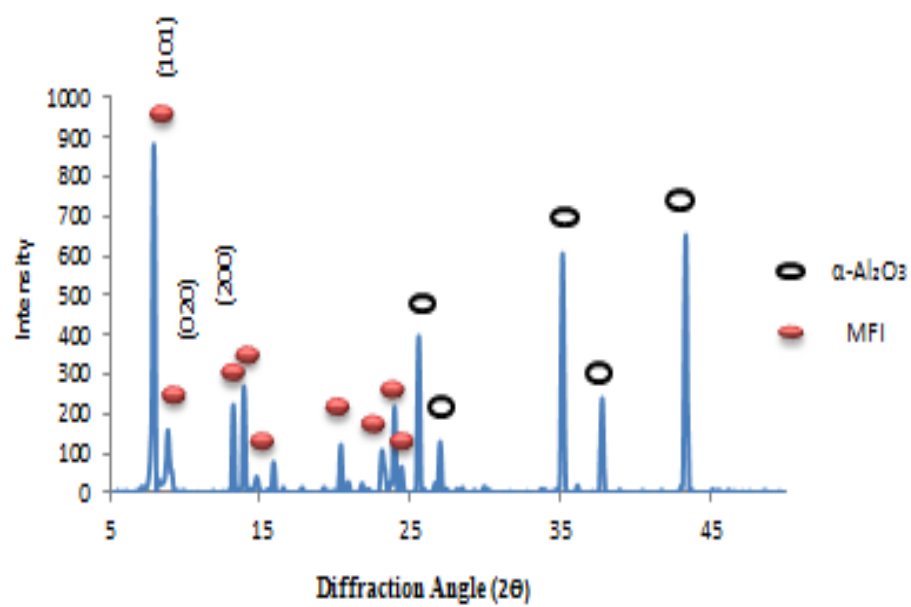


Figure 73 XRD results of calcinated MFI zeolite membrane after three seed layers

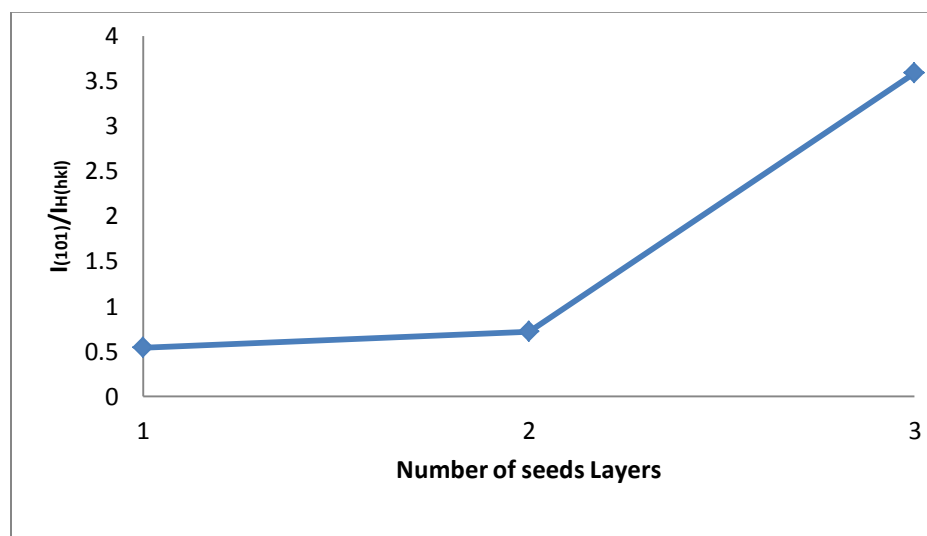


Figure 74 Effect of seeding layers on orientation of calcinated MFI zeolite crystals

The XRD result for the calcinated membrane after 3 seeds layers was confirmed by SEM images shown in figure 69. Furthermore, this SEM images shows how these crystals oriented with the crystallographic preferred orientation which is (1 0 1) direction or what is called oblique orientation with increasing on the thickness from 1.3 μm to 1.8 μm .

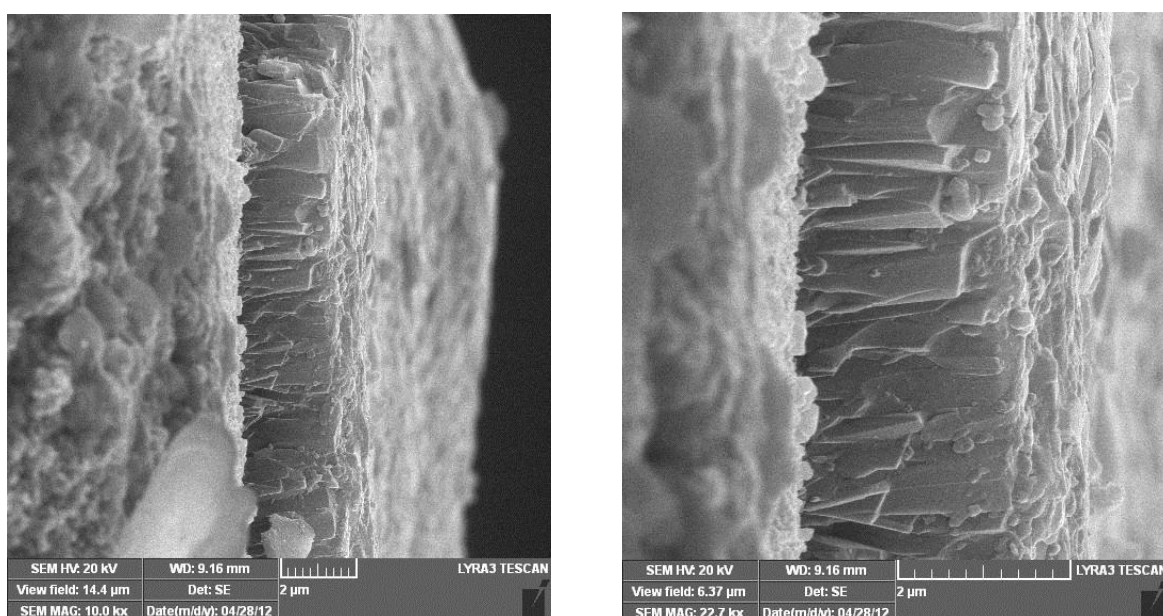


Figure 75 SEM cross-sectional images of MFI zeolite layer after calcinations, taken at different magnifications.

CHAPTER 5 CONCLUSIONS AND FUTURE SCOPE

Porous ceramic supports were prepared by cold-pressing α -Al₂O₃ powder with uniform particle size distribution. Starch powder, commonly used as a lubricant in ceramic processing, was added to alumina powder (~2 wt.%) before uniaxial cold pressing at 40,000 lb. The starch was burnt out by heating the substrates at 450°C for 3-6 hours and supports with a disk shape were placed into a high temperature furnace and heat-treated at 1400°C for 2 hours with heating rate of 5°C/min resulting in the formation of a porous alumina substrate with good mechanical strength with following characteristics: 25.3 mm in diameter, 2.5 mm in thickness, ~1 μ m pore diameter, ~40% porosity. The surface of the alumina supports were then treated mechanically and chemically in order to enhance the growth of MFI zeolite layer on those substrates.

The fabrication of MFI zeolite layer on top of porous alumina substrate was performed using two techniques, namely in-situ crystallization and secondary growth. Although being relatively simple, the in-situ crystallization technique did not yield a continuous zeolite layer making it inadequate for processing such membranes.

Continuous MFI zeolite thin layer, defect free, with good morphology was grown on porous alumina substrate using secondary growth technique with the assistance of microwave irradiation at 160°C for 2h. For seeding the zeolite nano-sized crystals on the surface of porous alumina substrates, spin-coating technique showed much better results, as compared to dip coating technique, in term of uniform seeds distribution and short

process time. The uniform morphology of MFI zeolite layer was improved as the number of seeding runs was increased from one to three times, and the orientation of the grown crystals was controlled with their crystallographic preferred orientation (CPO) (1 0 1). Thermo-gravimetric analysis (TGA) showed that 500°C was required for the removal of Tetrapropylammonium hydroxide (TPAOH) from the channels/pores of MFI zeolite crystals and the calcination step was one of the most sensitive steps due to the reported contradictory behavior of expansion and contraction between the zeolite crystals and the alumina substrate. Hence, MFI zeolite membrane was calcinated at very low heating and cooling rate 1°C/min at 500°C for 6 hours. The results revealed that the MFI zeolite layer was crystalline, and using three seeding layers with a thickness of 120 nm was appropriate to prevent the diffusion of aluminum ions towards the top surface of MFI zeolite crystals.

Further work in this research is proposed to investigate several additional aspects. For instance, the optimum amount and size of zeolite seeds required for enhance the seeding conditions and the correlation between the seeding parameters and substrate's surface roughness will allow a better understanding and control on the subsequent zeolite layer morphology. It is also important to consider such membranes for separation/filtration applications, and for that testing such membranes using the dedicated test flow cells developed in the research group of Prof. Laoui will be very valuable and may open new avenues for tailoring the processing of these membranes for specific applications.

References

- [1] V. Belessiotis, E. Delyannis. Water shortage and renewable energies (RE) desalination with possible technological applications. *Desalination* 139 (2001) 133-138.
- [3] Sabine Lattemann, Thomas Höpner. Environmental impact and impact assessment of seawater desalination. *Desalination* 220 (2008) 1–15.
- [4] K.V. Reddy, N. Ghaffour. Overview of the cost of desalinated water and costing methodologies. *Desalination* 205 (2007) 340–353
- [5] Mohammed Abdulaziz A1-Sahlawi Seawater desalination in Saudi Arabia: economic review and demand projections. *Desalination* 123 (1999).
- [6] Takeshi Matsuura. Progress in membrane science and technology for seawater desalination a review. *Desalination* 134 (2001) 47-54.
- [7] T. Uemura, K. Kotera, M. Henmi*, H. Tomioka. Membrane technology in seawater desalination: History, recent developments and future prospects. *Desalination and Water Treatment* 33 (2011) 283–288
- [8] JONAS HEDLUND. Control of the Preferred Orientation in MFI Films Synthesized by Seeding. *Journal of Porous Materials* 7, 455–464 (2000)
- [9] Liangxiong Li; Junhang Dong; Tina M. Nenoff. Transport of water and alkali metal ions through MFI zeolite membranes during reverse osmosis. *Separation and Purification Technology* 53. (2007-02). 42-48
- [10] Griselda Bonilla, Isabel Díaz, Michael Tsapatsis, Hae-Kwon Jeong, Yongjae Lee, and Dionisios G. Vlachos. Zeolite (MFI) Crystal Morphology

Control Using Organic Structure-Directing Agents. *Chem. Mater.*, 2004, 16 (26), pp 5697–5705.

[11] Zhengbao Wang and Yushan Yan. Controlling Crystal Orientation in Zeolite MFI Thin Films by Direct In Situ Crystallization. *Chem. Mater.* 2001, 13, 1101-1107.

[12] Zhengbao Wang, Yushan Yan. Oriented zeolite MFI monolayer films on metal substrates by in situ crystallization. *Microporous and Mesoporous Materials*, Volume 48, Issues 1-3, 1 November 2001, Pages 229-238.

[13] Fa-Zhi Zhang, Masayoshi Fuji, and Minoru Takahashi. In Situ Growth of Continuous b-Oriented MFI Zeolite Membranes on Porous γ -Alumina Substrates Precoated with a Mesoporous Silica Sublayer. *Chem. Mater.* 2005, 17, 1167-1173

[14] Z.A.E.P. Vroon, K. Keizer, M.J. Gilde, H. Verweij, A.J. Burggraaf. Transport properties of alkanes through ceramic thin zeolite MFI membranes. *Journal of Membrane Science* 113(1996) 293-300.

[15] K. Keizer^{1,a}, A.J. Burggraaf^a, Z.A.E.P. Vroon^{2,b}, H. Verweij^a. Two components permeation through thin zeolite MFI membranes. *Journal of Membrane Science* 147 (1998) 159-172.

[16] Yushan Yan, Mark E. Davis, George R. Gavalas. Preparation of highly selective zeolite ZSM-5 membranes by a post-synthetic coking treatment. *Journal of Membrane Science* 123 (1997) 95-103.

- [17] Jonas Hedlund, Johan Sterte, Marc Anthonis, Anton-Jan Bons, Barbara Carstensen, Ned Corcoran, Don Cox, Harry Deckman, Wim De Gijnst, Peter-Paul de Moor, Frank Lai, Jim McHenry, Wilfried Mortier, Juan Reinoso, Jack Peters. High-flux MFI membranes. *Microporous and Mesoporous Materials* 52 (2002) 179–189
- [18] George Xomeritakis, AnastasiosGouzinis, Sankar Nair, Tatsuya Okubo, Mingyan He, Rene M. Overney, Michael Tsapatsis. Growth, microstructure, and permeation properties of supported zeolite (MFI) films and membranes prepared by secondary growth. *Chemical Engineering Science* 54 (1999) 3521-3531.
- [19] Mark C. Lovallo, AnastasiosGouzinis, Michael Tsapatsis. Synthesis and characterization of oriented MFI membranes prepared by secondary growth. *AIChE Journal* Volume 44, Issue 8, pages 1903–1913, August 1998. Volume 142, Issue 1, June 2011, Pages 154-160
- [20] Wei Xiao, Jianhua Yang, Jinming Lu, JinquWang. synthesis and property of silicate-1 membranes by restricting growth method with dilute solution. *Microporous and Mesoporous Materials* 129 (2010) 22-29.
- [21] J.Motuzas; A. Julbe; R.D. Noble; A. van der Lee; Z.J. Beresnevicus. Rapid synthesis of oriented silicalite-1 membranes by microwave-assisted hydrothermal treatment. *Microporous and Mesoporous Materials* 92 (2006) 259–269.
- [22] Wei Xiao; Zhan Chen; Liang Zhou; Jianhua Yang; Jinming Lu; Jinqu Wang. A simple seeding method for MFI zeolite membrane synthesis on

macroporous support by microwave heating. Microporous and Mesoporous Materials, Volume 142, Issue 1, June 2011, Pages 154-160

[23] J.Motuzas; S. Heng; P.P.S. Ze Lau; K.L. Yeung; Z.J. Beresnevicius; A. Julbe.Ultra-rapid production of MFI membranes by coupling microwave-assisted synthesis with either ozone or calcination treatment. Microporous and Mesoporous Materials.Volume 99, Issues 1-2, 1 February 2007, Pages 197-205.

[24] Víctor Sebastian; Reyes Mallada; Joaquín Coronas; Anne Julbe; Rinse A. Terpstra; Ruud W.J. Dirrix. Microwave-assisted hydrothermal rapid synthesis of capillary MFI-type zeolite–ceramic membranes for pervaporation application. Journal of Membrane Science, Volume 355, Issues 1-2, 15 June 2010, Pages 28-35.

[25] Zhong Tang; Seok-Jhin Kim; XuehongGu; Junhang Dong. Microwave synthesis of MFI-type zeolite membranes by seeded secondary growth without the use of organic structure directing agents.Microporous and MesoporousMaterialsVolume 118, Issues 1-3, 1 February 2009, Pages 224-231.

[26] Q. Li, D. Creaser and J. Sterte The synthesis of small colloidal crystals of TPA-silicalite-1 with short synthesis times and high yields. Porous Materials in Environmentally Friendly Processes. Studies in Surface Science and Catalysis, Vol. 125.

[27] Q. Li, D. Creaser, J. Sterte.The nucleation period for TPA-silicalite-1 crystallization determined by a two-stage varying-temperature synthesis.

Microporous and Mesoporous Materials, Volume 31, Issues 1-2, October 1999,
Pages 141-150

[28] A.E. Persson, B.J. Schoeman, J. Sterte, and J.-E.Otterstedt. The synthesis of discrete colloidal particles of TPA-silicalite-1. *Zeolites*, 1994, 14 557-567.

[29] Cheng-Ye Hsu, Anthony S. T. Chiang, Rosilda Selvin, Robert W. Thompson. Rapid Synthesis of MFI Zeolite Nanocrystals. *J. Phys. Chem. B* 2005, 109, 18804-18814.

[30] Christine E. A. Kirschhock, Raman Ravishankar, Frederik Verspeurt, Piet J. Grobet, Pierre A. Jacobs, and Johan A. Martens. Identification of Precursor Species in the Formation of MFI Zeolite in the TPAOH-TEOS-H₂O System. *J. Phys. Chem. B* 1999, 103, 4965-4971.

[31] C. E. A. Kirschhock, R. Ravishankar, L. Van Looveren, P. A. Jacobs, and J. A. Martens. Mechanism of Transformation of Precursors into Nanoslabs in the Early Stages of MFI and MEL Zeolite Formation from TPAOH-TEOS-H₂O and TBAOH-TEOS-H₂O Mixtures. *J. Phys. Chem. B* 1999, 103, 4972-4978.

[32] Christine E. A. Kirschhock, Sebastien P. B. Kremer, Piet J. Grobet, Pierre A. Jacobs, and Johan A. Martens. New Evidence for Precursor Species in the Formation of MFI Zeolite in the Tetrapropylammonium Hydroxide-Tetraethyl Orthosilicate-Water System. *J. Phys. Chem. B*, Vol. 106, No. 19, 2002.

- [33] R. Van Grieken *, J.L. Sotelo, J.M. Menéndez, J.A. Melero. Anomalous crystallization mechanism in the synthesis of nanocrystalline ZSM-5. *Microporous and Mesoporous Materials* 39 (2000) 135±147.
- [34] Joseph Lik Hang Chau, Carlos Tellez, King LunYeung, Kachun Ho. The role of surface chemistry in zeolite membrane formation. *Journal of Membrane Science*. Volume 164, Issues 1-2, 4 January 2000, Pages 257-275
- [35] Wan Cheong Wong, Louisa Tak Yin Au, Carlos Tellez Ariso, King LunYeung. Effects of synthesis parameters on the zeolite membrane growth. *Journal of Membrane Science* 191 (2001) 143–163
- [36] Margaret E. Welk, Tina M. Nenoff. H₂ SEPARATION THROUGH ZEOLITE THIN FILM MEMBRANES. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 2004, 49(2), 889.
- [37] JIANG Haiyang¹, ZHANG Baoquan¹, Y. S. Lin^{1,2} & LI Yongdan¹. Synthesis of zeolite membranes. *Chinese Science Bulletin* 2004 Vol. 49 No. 24 2547-2554
- [38] O. Pachtová, M. Kocirik, A. Zikánová, B. Bernauer, S. Miachon, J.-A. Dalmon, A comparative study of template removal from silicalite-1 crystals in pyrolytic and oxidizing regimes, *Micropor. Mesopor. Mater.* 55 (2002) 285.
- [39] H.-K. Jeong, Z. Lai, M. Tsapatsis, J.C. Hanson, Strain of MFI crystals in membranes: an in situ synchrotron X-ray study, *Micropor. Mesopor. Mater.* 84 (2005) 332.

- [40] J.Dong, Y.S. Lin, M.Z.-C. Hu, R.A. Peascoe, E.A. Payzant, Template-removal-associated microstructural development of porousceramic- supported MFI zeolite membranes, *Micropor. Mesopor.Mater.* 34 (2000) 241.
- [41] E.R. Geus, H. van Bekkum, Calcination of large MFI-type single crystals, Part 2. Crack formation and thermomechanical properties in view of the preparation of zeolite membranes, *Zeolites* 15 (1995) 333.
- [42] M.J. den Exter, H. van Bekkum, C.J.M. Rijn, F. Kapteijn, J.A. Moulijn, H. Schellevis, C.I.N. Beenakker, Stability of oriented silicalite-1 films in view of zeolite membrane preparation, *Zeolites* 19 (1997) 13.
- [43] J. Hedlund, F. Jareman, A.-J.Bons, M. Anthonis, A masking technique for high quality MFI membranes, *J. Membr.Sci.* 222 (2003) 163.
- [44] J.Motuzas; A. Julbe; R.D. Noble; A. van der Lee; Z.J. Beresnevicius. Rapid synthesis of oriented silicalite-1 membranes by microwave-assisted hydrothermal treatment. *Microporous and Mesoporous Materials* 92 (2006) 259–269.
- [45] Wei Xiao; Zhan Chen; Liang Zhou; Jianhua Yang; Jinming Lu; Jinqu Wang. A simple seeding method for MFI zeolite membrane synthesis on macroporous support by microwave heating. *Microporous and Mesoporous Materials*, Volume 142, Issue 1, June 2011, Pages 154-160
- [46] Yanshuo Li, Weishen Yang. Microwave synthesis of zeolite membranes: A review. *Journal of Membrane Science*, Volume 337, Issues 1-2, 15 July

2009, Pages 47-54.

[47] METAXAS, A. C. and MEREDITH, R. J. Industrial microwave heating. IEE, 1983, reprinted 1988 and 1993.

[48] I. Girnus, M.M. Pohl, J. Richtermendau, M. Schneider, M. Noack, D. Venzke, J. Caro, Synthesis of AlPO₄-5 aluminum phosphate molecular-sieve crystals for membrane applications by microwave-heating, Adv. Mater. 7 (1995) 711–714.

[49] L.X. Zhang, H.T. Wang, In situ synthesis of AlPO₄-14, CoAPO-44 and ZnAPO-34 films on alumina substrates, J. Mater. Sci. 37 (2002) 1491–1496.

[50] C.D. Madhusoodana, R.N. Das, Y. Kameshima, K. Okada, Preparation of ceramic honeycomb filter supported zeolite membrane modules by microwave-assisted in situ crystallization, Sci. Eng. Ceram. 3 317–318 (2006) 697–700.

[51] Y.S. Li, J. Liu, W.S. Yang, Formation mechanism of microwave synthesized LTA zeolite membranes, J. Membr. Sci. 281 (2006) 646–657.

[52] Y.S. Li, J. Liu, H.L. Chen, W.S. Yang, L.W. Lin, Preparation of LTA zeolite membranes with few non-zeolite pores using microwave heating, Chin. J. Catal. 27 (2006) 544–546.

[53] Y.S. Li, H.L. Chen, J. Liu, W.S. Yang, Microwave synthesis of LTA zeolite membranes without seeding, J. Membr. Sci. 277 (2006) 230–239.

- [54] A. Julbe, J. Motuzas, F. Cazevielle, G. Volle, C. Guizard, Synthesis of sodalite/ α Al_2O_3 composite membranes by microwave heating, *Sep. Purif. Technol.* 32 (2003) 139–149.
- [55] D. Baek, U.Y. Hwang, K.S. Lee, Y. Shul, K.K. Koo, Formation of zeolite A film on metal substrates by microwave heating, *J. Ind. Eng. Chem.* 7 (2001) 241–249.
- [56] S. Mintova, S. Mo, T. Bein, Nanosized AlPO_4 -5 molecular sieves and ultrathin films prepared by microwave synthesis, *Chem. Mater.* 10 (1998) 4030–4036.
- [57] J. Caro, F. Marlow, K. Hoffmann, C. Striebel, J. Kornatowski, I. Girnus, M. Noack, P. Kolsch, News from AlPO_4 -5: microwave synthesis, application as medium to organize molecules for spectroscopy and nonlinear optics, material for one-dimensional membranes, *Stud. Surf.Sci. Catal.* 105 (1997) 2171–2178.
- [58] C.D. Madhusoodana, R.N. Das, Y. Kameshima, K. Okada, Microwave-assisted hydrothermal synthesis of zeolite films on ceramic supports, *J. Mater. Sci.* 41 (2006) 1481–1487.
- [59] D. Coutinho, J.A. Losilla, K.J. Balkus, Microwave synthesis of ETS-4 and ETS-4 thin films, *Microporous Mesoporous Mater.* 90 (2006) 229–236.
- [60] X.B. Chen, W.S. Yang, J. Liu, L.W. Lin, Synthesis of zeolite NaA

membranes with high permeance under microwave radiation on mesoporous-layer-modified macroporous substrates for gas separation, *J. Membr. Sci.* 255 (2005) 201–211.

[61] X.C. Xu, Y. Bao, C.S. Song, W.S. Yang, J. Liu, L.W. Lin, Microwave-assisted hydrothermal synthesis of hydroxy-sodalite zeolite membrane, *Microporous Mesoporous Mater.* 75 (2004) 173–181.

[62] Z.L. Cheng, Z.S. Chao, W.P. Fang, H.L. Wan, Synthesis regularity of NaA zeolite membrane in microwave field, *J. Inorg. Mater.* 18 (2003) 1306–1312.

[63] Z.L. Cheng, H.Q. Lin, Z.S. Chao, H.L. Wan, NaY zeolite membrane prepared by using pre-absorbed nanosized NaY zeolite synthesized by microwave heating, *Chem. J. Chin. Univ.* 24 (2003) 1857–1861.

[64] Z.L. Cheng, Z.S. Chao, H.L. Wan, Synthesis of compact NaA zeolite membrane by microwave heating method, *Chin. Chem. Lett.* 14 (2003) 874–876.

[65] K. Weh, M. Noack, I. Sieber, J. Caro, Permeation of single gases and gas mixtures through faujasite-type molecular sieve membranes, *Microporous Mesoporous Mater.* 54 (2002) 27–36.

[66] X.H. Xu, W.H. Yang, J. Liu, L.W. Lin, Synthesis of NaA zeolite membrane by microwave heating, *Sep. Purif. Technol.* 25 (2001) 241–249.

[67] Z.L. Cheng, Z.S. Chao, H.L. Wan, Research of A type zeolite as well as

zeolite membrane by microwave heating, *Chin. J. Inorg. Chem.* 18 (2002)528–532.

[68] X.C. Xu, W.S. Yang, J. Liu, L.W. Lin, Fast formation of NaA zeolite membrane in the microwave field, *Chin. Sci. Bull.* 45 (2000) 1179–1181.

[69] X.C. Xu, W.S. Yang, J. Liu, L.W. Lin, Synthesis of a high-permeance NaA zeolite membrane by microwave heating, *Adv. Mater.* 12 (2000) 195–196.

[70] T.G. Tsai, H.C. Shih, S.J. Liao, K.J. Chao, Well-aligned SAPO-5 membrane: preparation and characterization, *Microporous Mesoporous Mater.* 22 (1998) 333–341.

[71] S.M. Bradshaw, E.J. van Wyk, and J.B. de Swardt. Microwave heating principles and the application to the regeneration of granular activated carbon . *The Journal of The South African Institute of Mining and Metallurgy* JULY/AUGUST 1998.

[72] M Pan, Y.S Lin .Template-free secondary growth synthesis of MFI type zeolite membranes. *Microporous and Mesoporous Materials*. Volume 43, Issue 3, May 2001, Pages 319-327

[73] Georgios N. Karanikolos, James W. Wydra,, Jared A. Stoeger, Hermenegildo Garcí'a, Avelino Corma, and Michael Tsapatsis. Continuous c-Oriented ALPO4-5 Films by Tertiary Growth. *Chem. Mater.* 2007, 19, 792-797.

- [74] F. Krumeich. "Electron Microscopy Method: Scanning Electron Microscopy (SEM)" microscopy.ethz.ch. n.p. May 17, 2011.
- [75] Swapp, Susan. "Geochemical Instrumentation and Analysis: Brose Collection: Scanning Electron Microscopy (SEM)".serc.carleton.edu. n.p. January 28, 2012.
- [76] L.J. Poppe, V.F. Paskevich, J.C. Hathaway, and D.S. Blackwood. "U. S. Geological Survey Open-File Report 01-041: A Laboratory Manual for X-Ray Powder Diffraction: X-Ray Diffraction Primer" .n.p. 11 Oct 2001
- [77] A. W. HULL. A New Method of Chemical Analysis.1919.
- [78] Kirschhock, C. E. A.; Ravishankar, R.; Verspeurt, F.; Grobet, P.J.; Jacobs, P. A.; Martens, J. A. J. Aggregation Mechanism of Nanoslabs with Zeolite MFI-Type Structure Phys. Chem. B 1999, 103, 4965.
- [79] Li, Q.; Creaser, D.; Sterte, J. Microporous Mesoporous Mater. 1999,31, 141
- [80] Cundy, C. S.; Forrest, J. O. Microporous Mesoporous Mater. 2004,72, 67
- [81] Teruoki Tago and Takao Masuda. Zeolite nanocrystals-synthesis and application.2010
- [82] JIANG Haiyang, ZHANG Baoquan¹, Y. S. Lin, Yongdan. Synthesis of zeolite membranes.Chinese Science Bulletin 2004 Vol. 49 No. 24 2547-2554.

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