SYNTHESIS AND CHARACTERIZATION OF ZEOLITE MEMBRANES FOR BINARY GAS SEPARATION

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SYNTHESIS AND CHARACTERIZATION OF ZEOLITE MEMBRANES FOR BINARY GAS SEPARATION

by

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LIST OF NOMENCLATURE

Symbol	**Description**	**Unit**
$\mathrm{I}_{(hkl)}$	Peak intensity of XRD crystallogram	Counts per second
-	Low level	-
+	High level	-
A	Factor code for temperature in DoE	-
B	Factor code for retentate total pressure in DoE	-
C	Factor code for CO_2 content in feed in DoE	-
CH_4	Methane gas	-
CO_2	Carbon dioxide gas	-
D	Factor code for sweep gas flowrate in DoE	-
F_{feed}	Total volumetric flowrate of the feed	cm^3/min
$F_{feed,CO2}$	Volumetric flowrate of CO_2 of the feed	cm^3/min
$F_{feed,N2}$	Volumetric flowrate of N_2 of the feed	cm^3/min
f_i	Molar fraction of gas species i in feed	-
$F_{permeate}$	Total volumetric flowrate of permeate stream	cm^3/min
$F_{permeate,CO2}$	Volumetric flowrate of CO_2 in the permeate	cm^3/min
$F_{permeate,N2}$	Volumetric flowrate of N_2 in the permeate	cm^3/min
$F_{retentate}$	Total volumetric flowrate in the retentate stream	cm^3/min
$F_{retentate,CO2}$	Volumetric flowrate of CO_2 in the retentate	cm^3/min
$F_{retentate,N2}$	Volumetric flowrate of N_2 in the retentate	cm^3/min
H_2	Hydrogen gas	-
R^2	Correlation coefficient	-
T	Silicon or Aluminum atom	-
x_i	Molar fraction of gas species i in retentate	-
y_i	Molar fraction of gas species i in permeate	-
Greek letters		
α	Alumina phase	
Ǻ	Angstrom, 10^{-8}	
Subscripts		
i	Gas species	

LIST OF ABBREVIATIONS

Symbol	**Description**
ANOVA	Analysis of variance
BEA	Zeolite Beta
BET	Brounar-Emmett-Teller
BR	Back pressure regulator
B-ZSM-5	Boron substituted Zeolite Socony Mobil 5
CCD	Center composite design
CCS	Catalytic cracking of silane
CVD	Chemical vapor deposition
DDI	Double distilled deionized
DDR	Zeolite Decadodelcasil 3-R
DoE	Design of experiments
EDX	Energy dispersive X-ray microanalysis
FAU	Zeolite Ferjausite
FER	Zeolite Ferrierite
GC	Gas chromatograph
IZA	International Zeolite Association
LTA	Zeolite Linde Type A
MA	Microwave assisted
MFC	Mass flow controller
MFI	Zeolite Mobil Five
MOR	Zeolite Mordenite
MR	Membered-ring
NaA	Zeolite Sodium contained Linde Type A
Na-ZSM-5	Sodium contained Zeolite Socony Mobil 5
NV	Needle valve

PVG	Pressure and vacuum gauge
R	Rotameter
RSM	Response surface methodology
S.S.	Stainless steel
SCCM	Standard Centimeter Cubic per Minute
SDA	Structure directing agent
SEM	Scanning electron microscopy
SOD	Zeolite Sodalite
TEOS	Tetraethyl orthosilicate
TGA	Thermal Gravimetric Analysis
TPA	Tetrapropylammonium
TPABr	Tetrapropylammonium bromide
TPAOH	Tetrapropylammonium hydroxide
XRD	X-ray diffraction

LIST OF APPENDICES

SINTESIS DAN PENCIRIAN MEMBRAN ZEOLIT UNTUK PEMISAHAN CAMPURAN GAS PERDUAAN

ABSTRAK

Tiga jenis membran zeolit MFI (ZSM-5 dan Silicalite-1) dengan kecacatan minimum telah disintesiskan dengan menggunakan cara yang berlainan. Membran tersebut adalah Silicalite-1 (Si/Al = ∞), Na-ZSM-5 (Si/Al = 25) and B-ZSM-5 (Si/B = 100). Zeolit membran Silicalite-1 disintesiskan dengan menggunakan cara penumbuhan sekundar manakala membran Na-ZSM-5 dan B-ZSM-5 disintesiskan dengan cara pengkristalan setempat. Semua membran disokong di atas α-alumina yang diubahsuai dengan salutan lapisan silica berliang meso.

Untuk menilai mikro struktur membran, membran zeolit dicirikan dengan XRD untuk phasa and orientasi kristal, SEM untuk cerapan pandangan morfologi permukaan and mengenalpasti ketebalan lapisan nipis zeolit. TGA digunakan untuk mentaksirkan kestabilan terma membran dan mengenalpasti pembuangan agen pengarahan struktur dari struktur zeolit. Biji berkoloid zeolit yang digunakan untuk menghasilkan membran zeolit Silicalite-1 dicirikan dengan TEM untuk saiz biji dan morfologi struktur.

Campuran gas perduan yang mengandungi CO_2/N_2, CO_2/CH_4 dan H_2/CO_2 digunakan untuk menilai prestasi pemisahan membran. Pemisahan CO_2/N_2 dan CO_2/CH_4 berlaku kerana penjerapan terutama CO_2 atas liang zeolit MFI. Kesan penjerapan bersaingan tidak wujud untuk permisahan sistem H_2/CO_2. Nilai kememilihan pemisahan yang tertinggi bagi campuran perduan CO_2/N_2 dan CO_2/CH_4 diperolehi dengan menggunakan membran B-ZSM-5 pada suhu rendah dan tekanan tinggi. Kememilihan pemisahan tertinggi bagi campuran perduan H_2/CO_2 diperolehi pada suhu dan tekanan tinggi. Nilai kememilihan yang diperolehi adalah 9.27, 8.17 dan

1.39 dengan fluks kemeresapan 13.14, 14.52 dan 6.98 cm^3/min bagi pemisahan CO_2/N_2, CO_2/CH_4 dan H_2/CO_2 masing-masing.

Rekabentuk komposit tengah (CCD) digunakan untuk menilai sumbangan parameter pengendalian ke atas kedua-dua respons (kememilihan dan fluks kemeresapan) untuk pemisahan CO_2/N_2, CO_2/CH_4 dan H_2/CO_2 dengan menggunakan membran B-ZSM-5. Metodologi permukaan sambutan (RSM) digunakan untuk mendapatkan nilai optimum bagi perameter pengendalian tersebut. Keadaan optimum bagi pemisahan sistem CO_2/N_2, adalah: suhu = 25 ^oC, jumlah tekanan buangan = 5 bar, kandungan CO_2 dalam suapan = 44.03% dan kadar aliran gas sapu = 300 cm^3/min dengan kememilihan = 8.89 dan fluks kemeresapan sebanyak 13.50 cm^3/min. Keadaan optimum bagi pemisahan CO_2/CH_4 adalah: suhu = 25 ^oC, jumlah tekanan buangan = 4.74 bar, kandungan CO_2 dalam suapan = 45.73% dan kadar aliran gas sapu = 300 cm^3/min dengan kememilihan = 8.05 dan fluks kemeresapan sebanyak 14.36 cm^3/min. Bagi pemisahan H_2/CO_2, keadaan optimum yang didapati adalah: suhu = 150 ^oC, jumlah tekanan buangan = 4.09 bar, kandungan CO_2 dalam suapan = 16.52% dan kadar aliran gas sapu = 213.34 cm^3/min dengan kememilihan = 1.65 dan fluks kemeresapan sebanyak 9.19 cm^3/min.

SYNTHESIS AND CHARACTERIZATION OF ZEOLITE MEMBRANES FOR BINARY GAS SEPARATION

ABSTRACT

Three types of MFI zeolite membranes (ZSM-5 and Silicalite-1) with minimum defect were synthesized using different synthesis approach. These membranes were Silicalite-1 (Si/Al = ∞), Na-ZSM-5 (Si/Al = 25) and B-ZSM-5 (Si/B = 100). Silicalite-1 zeolite membrane was synthesized using secondary growth method whereas Na-ZSM-5 and B-ZSM-5 membranes were synthesized using in-situ crystallization method. All the membranes were supported over surface modified α-alumina coated with mesoporous silica layer.

To evaluate the membrane microstructure, zeolite membranes were characterized by XRD for their crystalline phase and crystal orientation, SEM for visual observation of the membrane surface morphology and to obtain the thickness of the zeolite thin film. TGA was conducted to assess the thermal stability of the membrane as well as to confirm the removal of the structure directing agent (SDA) from the zeolite structure. Zeolite colloidal seeds used for the synthesis of Silicalite-1 zeolite membrane were characterized by TEM for its seed size and structure morphology.

Binary gas mixtures containing CO_2/N_2, CO_2/CH_4 and H_2/CO_2 were used to evaluate the membrane separation performance. The separation of CO_2/N_2 and CO_2/CH_4 took place due to the preferential adsorption of CO_2 on MFI zeolite pores. This competitive adsorption effect was not present for the separation of H_2/CO_2 system. The highest separation selectivity for CO_2/N_2 and CO_2/CH_4 binary mixture was obtained over B-ZSM-5 membrane at low temperature and high pressure. The highest separation selectivity for H_2/CO_2 binary gas mixture was obtained at high temperature and high pressure. The selectivity obtained was 9.27, 8.17 and 1.39 with the

permeation flux of 13.14, 14.52 and 6.98 cm^3/min for the separation of CO_2/N_2, CO_2/CH_4 and H_2/CO_2 respectively.

Centre composite design (CCD) was used to evaluate the contribution of the operating parameters to the two responses (selectivity and permeation flux) for the separation of CO_2/N_2, CO_2/CH_4 and H_2/CO_2 using B-ZSM-5 membrane. A response surface methodology (RSM) was used to obtain the optimum values of the operating parameters. The optimum conditions for the separation of CO_2/N_2 system were: temperature = 25 °C, retentate total pressure = 5 bar, CO_2 content in feed = 44.03% and sweep gas flowrate = 300 cm^3/min with selectivity = 8.89 and CO_2 permeation flux of 13.50 cm^3/min. The optimum conditions for separation of CO_2/CH_4 were: temperature = 25 °C, retentate total pressure = 4.74 bar, CO_2 content in feed = 45.73% and sweep gas flowrate = 300cm^3/min with selectivity = 8.05 and CO_2 permeation flux of 14.36cm^3/min. For the separation of H_2/CO_2, the optimum conditions obtained were: temperature = 150 °C, retentate total pressure = 4.09 bar, CO_2 content in feed = 16.52% and sweep gas flowrate = 213.34cm^3/min with selectivity = 1.65 and H_2 permeation flux of 9.19 cm^3/min.

CHAPTER 1

INTRODUCTION

1.1 Membrane based gas separation

Gas separation is a common and yet important operation in the chemical and gas processing industries. Conventional methods for gas separation such as cryogenic distillation, absorption and adsorption are energy intensive due to high heating and cooling load and installation of the units usually requires a very high capital cost. Over the past half century, there has been a great interest in alternative methods for gas separation in the industries and this has led to the development of membrane based separation. Membrane separation is a cost effective and simple unit operation compare to the traditional separation unit. During the past 20 years, sales of membrane gas separation equipment have increased to become a USD 150 million/year business. More than 90% of this business involves the separation of noncondensable gases: nitrogen from air, carbon dioxide from methane; and hydrogen from nitrogen, argon, or methane (Baker, 2002).

Generally, any material that can be made into sufficiently thin and stable films can be used as membrane. This includes metal, glass, ceramics and polymers as well as ordered molecular monolayers of liquids (Pandey and Chauhan, 2001). The organic polymers are the most widely used materials in the membrane area. The polymeric membranes dominate the membrane market was mainly due to the availability of different types of low cost polymer materials which can be easily processed into a thin film membrane that give a good separation and sufficient permeation flux. Metal based inorganic membranes (e.g. palladium) have been used for hydrogen separation on a commercial scale since 1950s (Baker, 2004). However, the high cost of materials and complex synthesis procedure and lower separation selectivity compared with organic polymer membrane has put inorganic membrane on the brink of commercialization. Some of the most commonly used materials for gas separation membranes are listed in Table 1.1. For the inorganic materials listed, most of them are still in the stage of scientific research purposes used for small scale gas separation.

Table 1.1: Materials for gas separating membranes (Poling *et al*., 2001)

Organic polymers	**Inorganic materials**
Polysulfone, polyethersulfone	Zeolites
Celluloseacetate	Nanoporous carbon
Polyimide, polyetherimide	Carbon molecular sieves
Polycarbonate (brominated)	Ultramicroporous amorphous silica
Polyphenyleneoxide	Palladium alloys
Polydimethylsiloxane	Mixed conducting pervoskites
Polyvinyltrimethylsilane	

Although the polymeric membranes have been widely used in the field of separation for decades, it has come to their limitation due to the properties of the materials. The major problem of polymeric membrane is the low operating temperature limits and weak chemical resistant. Majority of polymeric membrane started to deteriorate around 80 – 100 ^{o}C. In other word, it is not economical to use polymeric membrane for the separation of process gases at high temperature. The chemical processes in highly acidic or alkaline environment have limited the usage of polymeric membrane since most of the polymer materials deteriorated in such conditions. Another important issue which hindered the use of polymeric membrane is the phenomena of fouling and concentration polarization. Concentration polarization is the accumulation of the solutes, molecules or particles retained or rejected by the membrane near its surface. It is deleterious to the purity of the product and responsible for the decline of the permeate flux (Hsieh, 1996). To overcome these entire problems of the polymeric membrane, inorganic membrane started to gain more attention of the researchers. The major advantages and disadvantage of inorganic membrane as compared to polymeric membrane is summarized in Table 1.2.

Table 1.2: Advantages and disadvantages of inorganic membranes in comparison with polymeric membranes (Caro *et al*., 2000)

Arguments for inorganic membranes	**Arguments against inorganic membranes**
Long-term stability at high temperatures	High capital costs
Resistance to harsh environments	Brittleness
Resistance to high pressure drops	Low membrane surface per module volume
Inert towards microbiological degradation	Difficulty in achieving high selectivities in large scale microporous membranes
Easy cleanability after fouling	Generally low permeability of the highly selective (dense) membranes at medium temperatures
Easy catalytic activation	Difficult membrane-to-module sealing at high temperatures

Along with others inorganic membranes, zeolite membrane possess advantages not only of its thermal and chemical stability but also high selectivity for certain important separations due to the highly uniform pore size at molecular dimension of this crystalline materials. (Yampolskii *et al*., 2006). Another key feature of zeolite membrane is the catalytic property that makes it highly potential to be used as catalytic membrane reactor. The use of zeolite as catalyst has been extensive in the chemical and petroleum industries. A large volume of information regarding zeolite science has been developed for decades and can be easily obtained which give an advantage for the development and commercialization of zeolite membrane as compared to other type of inorganic membranes (Cundy and Cox, 2005, Caro *et al*., 2000)

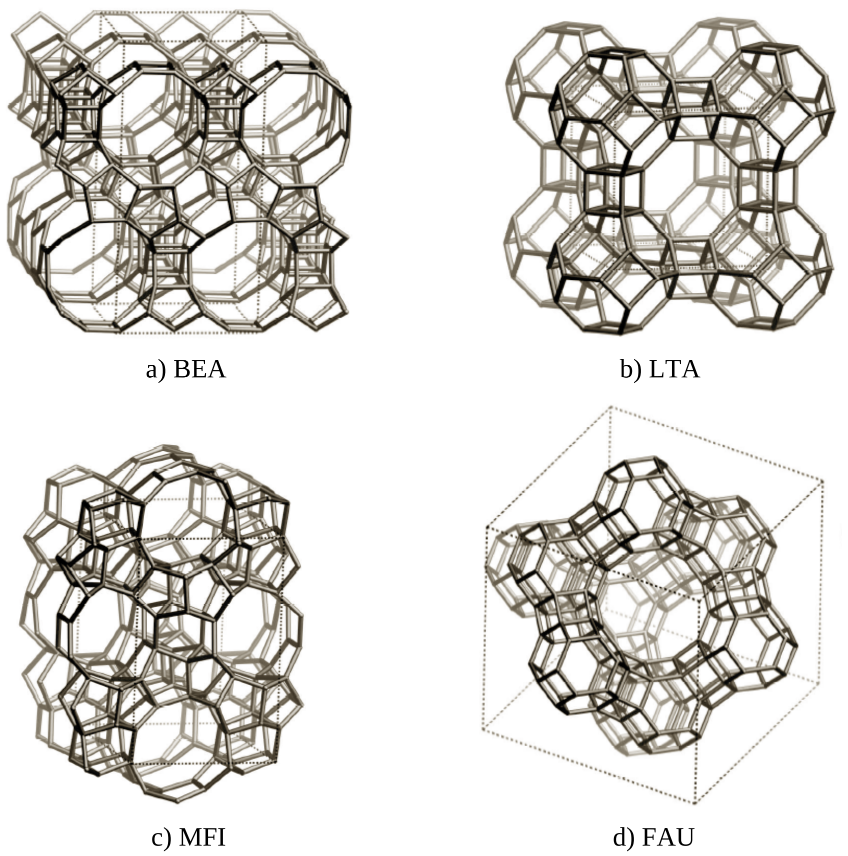
1.2 Zeolites

Zeolites are microporous crystalline silicates or aluminosilicates composed of TO_4 tetrahedra (T= Silicon or Aluminum atom) with oxygen atoms connecting neighboring tetrahedral (Auerbach *et al.*, 2003). Silicon may be considered as the principal or key element of the framework. Elements which substitute for silicon must accept a tetrahedral coordination with oxygen. If the Aluminum atom presented in the zeolite framework, it become negatively charged due to the +3 charge on the Aluminum. In order to make the overall framework neutral it required an extra framework cation (such as Na^+, NH_4^+ and K^+ etc.) presented within the structure. Due to these ions exchangeable extra framework cations, it gives rise to the rich ion-exchange chemistry of zeolites which play an important role in catalysis, adsorption and ion exchange processes.

Most of the natural zeolites are in the form of low silica contained and highly impure that gives low/no application on the industrial scale. The pioneering works of Milton (Union Carbide), Barrer and coworkers and researchers at Mobil Oil Corp. in the 1950s and 1960s had led to the vast advance in producing synthetic zeolites with high purity and flexibility of zeolite chemical compositions which give a bright future of zeolite science (Weitkamp and Puppe, 1999). Since then various types of zeolite have been used in the laboratories and industries as catalyst, adsorbent, ion exchange and molecular sieve materials etc.

1.2.1 Structure, pore size and nomenclature

The zeolite structure consists of a three dimensional network of SiO_4 and AlO_4 linked to each other tetrahedral by sharing oxygen atoms forming cavities or cages that can be connected by ring or pore openings of defined size and sharp (Ramsay and Kallus, 2000). The most common method to categorize zeolites is based on their framework structure. The Structure Commission of the International Zeolite Association (IZA) identifies each framework with a three-letter mnemonic code. Currently there are about 160 zeolites with different framework structure has been recorded in the Atlas of Zeolite Framework Types which can be accessed through the IZA website. Figure 1.1 shows the 3-D stick structure for some of the most commonly used zeolite in the industries and their three-letter code. Beside the framework structure, zeolite can be subdivided according to their framework compositional characteristics, thus the MFI framework encompasses ZSM-5, Silicalite-1 (the aluminium free counterpart) as well as its ion-exchanged forms with Na^+, B^{3+} and Fe^{3+} etc.


a) BEA

b) LTA

c) MFI

d) FAU

Figure 1.1: 3D structure of zeolite crystal a) zeolite beta (BEA), b) zeolite Linde type A (LTA), c) zeolite Zocony Mobill 5 (MFI), d) zeolite Ferjausite (FAU) (Auerbach *et al.,* 2003)

The zeolite pore is formed by the connection of tetrahedral atoms apertures. A name of membered-ring (MR) is defined for the ring formed by the tetrahedral atoms and oxygen atoms. Thus most of the zeolites can be broadly classified into three categories according to their pore size (Guisnet and Gilson, 2002):

- Small pore zeolites with 8 MR (8 tetrahedral atoms and 8 oxygen atoms) having free diameters of 3.0 – 4.5 Ǻ.
- Medium pore zeolites with 10 MR having free diameters of 4.5 – 6.0 Ǻ.
- Large pore zeolites with 12 MR having free diameters of 6.0 – 8.0 Ǻ.

Some of the common types of zeolites with different pore sizes are presented in Figure 1.2. The pore size value given in Figure 1.2 is based on the smallest value in the pore opening (some of the MR is in oval shape). To categorize zeolite based on pore size is very subjective, since some of the newly synthesized zeolites have ultra large/small pores which are out of the range of the above category (Guisnet and Gilson, 2002).

1.3 Zeolite membrane

For years, zeolites in the form of powder or compressed pellets have been utilized as adsorbent for gas separation in the industries. The idea of making polycrystalline zeolite film supported by a porous substrate used for separation was first patented in 1987 by H. Suzuki (Suzuki, 1987). Since then, vast research has been reported by coating zeolite film on different substrates such as porous glass, ceramic and porous stainless steel. Basically zeolite membrane is a composite membrane with a thin layer of polycrystalline zeolite film coated on top of a macropore inorganic substrate (Figure 1.3). The zeolite film acts as a selective layer whereas the substrate provides the mechanical strength to the fragile zeolite film.

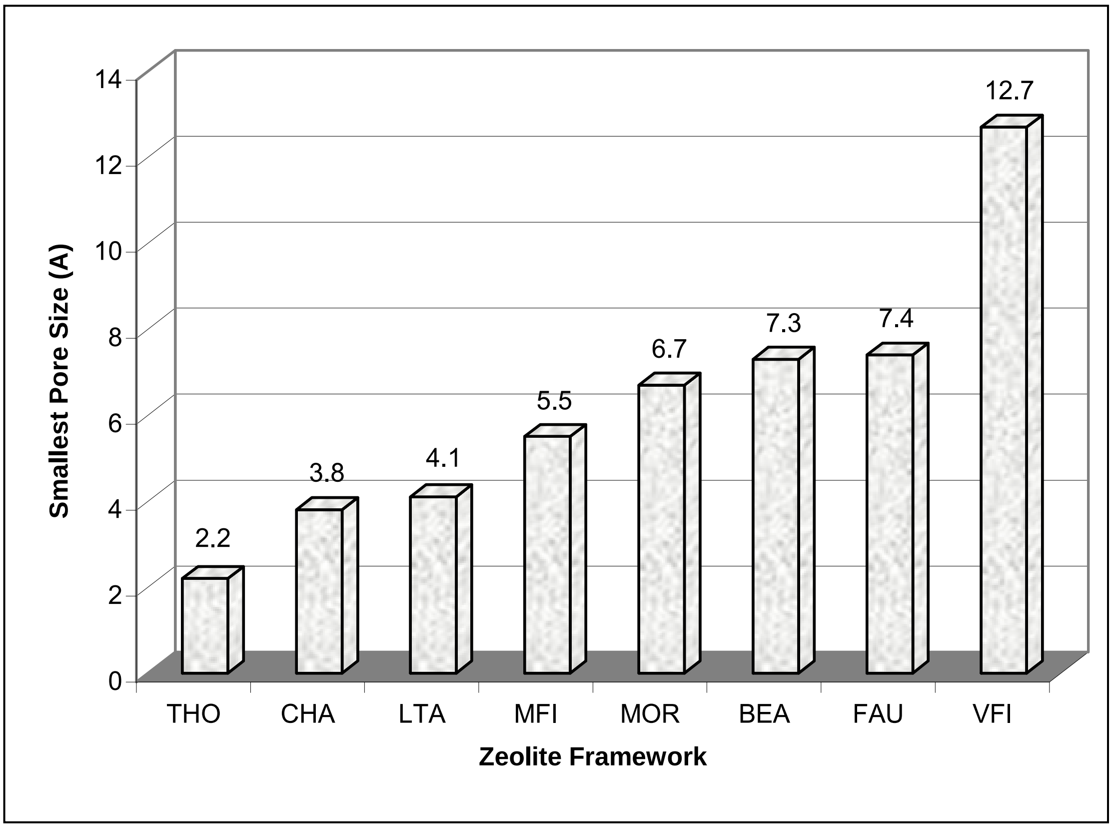


Figure 1.2 Comparison of pore size of different zeolite framework

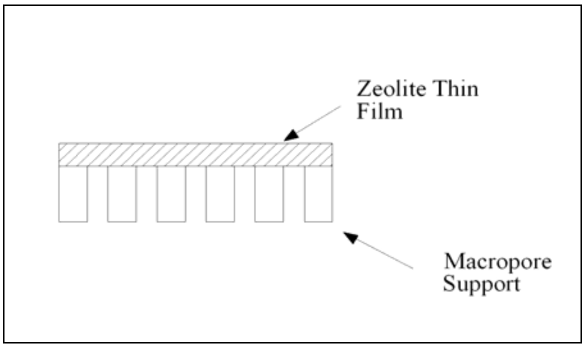


Figure 1.3 Schematic diagram of supported zeolite membrane

The reason for using zeolite film as membrane is mainly because the zeolite in the form of polycrystalline film can be made as thin as 1 – 50 μm, this extremely thin layer not only can act as selective layer but also possess high permeation rate which is better than the powder and pellet form. Due to its unique properties such as highly uniform and molecular dimension pore sizes, high thermal and chemical stability;

zeolite membrane has been considered as one of the most potential candidate to replace polymeric membrane in the industries.

The developments of zeolite membrane are still at the level of laboratory research. The first and the only commercial large scale zeolite membrane was developed by Yoshio Morigami in year 2001 (Morigami *et al*., 2001) for ethanol dehydration using pervaporation process. The use of zeolite membrane for gas and vapor separation in the industries still remained as a hurdle to overcome. The reason zeolite membrane fail to be commercialized was due to the difficulties in the synthesis of a large surface area high quality polycrystalline zeolite thin film and also the high materials cost required to synthesize the membrane. Furthermore, the reproducibility of the membrane synthesis method developed still not adequate to fully commercialize the product. A large number of researches have been carried out by academic researchers worldwide to make zeolite membrane commercially viable. Some of the potential applications of zeolite membrane which have been carried out in the laboratory scale are summarized in Table 1.3.

Table 1.3: Applications of zeolite membrane in the laboratory scale

Zeolite Membrane	**Separation**	**Reference**
MFI	n-hexane/dimethylbutane	(Flanders *et al*., 2000)
NaA	Water/ethanol	(Okamoto *et al*., 2001)
FAU	Benzene/cyclohexane	(Jeong *et al*., 2003)
MFI	Xylene isomers	(Gu *et al*., 2006)
DDR	CO_2/CH_4	(Tomita *et al*., 2004)
MFI	CO_2/N_2	(Bernal *et al*., 2004)
MFI	CO_2/H_2	(Masuda *et al*., 2001)
SOD	H_2/N_2	(Zheng *et al*., 2005)
MFI	H_2/CH_4	(Welk and Nenoff, 2005)
SOD	H_2/n-butane	(Xu *et al*., 2004)
MOR/MFI bilayer	Water/acidic acid	(de la Iglesia *et al*., 2006)
MFI	C5/C6 hydrocarbon mixture	(Arruebo *et al*., 2006)

1.3.1 Type of zeolite

Although there are more than 160 different type of zeolite have been synthesized, not all these zeolites can be made into membranes. Currently there are only 10 types of zeolites have been synthesized as zeolite membrane. These zeolite are: MFI (Choi *et al*., 2006, Hong *et al.*, 2005, Gu *et al*., 2006), CHA (Jia and Murad, 2005), MOR (Bernal *et al.*, 2000, Navajas *et al.*, 2006) , FAU (Giannakopoulos and Nikolakis, 2005, Hasegawa *et al*., 2001), LTA (Li *et al*., 2006, Aoki *et al.*, 2000), BEA (Maloncy *et al*., 2005) , SOD (Xu *et al*., 2004), FER (Jia and Murad, 2005), DDR (Tomita *et al*., 2004) and MEL (Li *et al*., 2002). The reason for only a few zeolites were synthesized into membranes was mainly due to the fact that the recipe and synthesis methodology developed for zeolite powder synthesis does not guarantee the formation of a continuous polycrystalline thin film. Therefore there is need of new methods to be explored to modify the existing method to crystallize zeolite into membrane. In other word it also shows that there are still a plenty of rooms for the zeolite membrane development since a large number of available zeolites are not explored to be converted into thin films.

1.4 Carbon dioxide scenario

Global warming and climate change has become one of the serious environment issues in our world. By year 2100 it is estimated that global temperature will increase between 1.4 to 5.8 ^{o}C if climate change policies are not implemented (Houghton, 2001). Green house gases such as carbon dioxide, methane and nitrous oxide have been identified as the cause of the global climate change. The increase in global temperature will bring a numbers of negative effects such as rising of sea levels due to melting of iceberg at the pole, changes in ecosystems, lost of biodiversity and reduction of crop yield (McCarthy *et al.*, 2001). The situation is getting worst day by day due to the increase demand of energy produced from oil, gas and coal around the world. According to ExxonBil energy outlook (2005), the global CO_2 emission has increased from 18 billion tons in year 1980 to 27 billion tons in 2005. It projected that this number will climb to 40 billion tons by year 2030 with 1.7% average growth per year and close to 80% of the CO_2 emission will come from developing countries where economic growth and improved living standard are major contributions for the large increase in energy demand. The emission of green house gases can be reduced by numbers of methods such as improve in energy efficiency, replacement of fossil fuel to green fuel and sequestration of CO_2 from its source. The main source of CO_2 emission is from the fossil fuel power station and hydrocarbon processing plant where the CO_2 with the flue gases coming out at high temperature. Traditional adsorption unit is not a cost effective method to remove CO_2 from flue gases and commercially available polymeric membrane cannot stand the harsh conditions at the emission point. Therefore zeolite membrane gained great interest from academic researchers and considered to be one of the most suitable candidates for the task.

Beside the environmental issues mentioned, the separation of CO_2 is an important process in the chemical reaction field and hydrocarbon processing in the industries. One good example is the CO_2 reforming of methane into syngas (i.e. CO + H_2) on ZSM-5 supported catalyst (Zhang *et al*., 2005) where the reaction take place at 700 ^{o}C. The product stream is a mixture of CO_2, CH_4, H_2, and CO, once H_2 was separated from the product stream the reaction equilibrium will shifted to increase the yield. Another well known example is the removal of CO_2 from natural gas (mainly methane). The removing of CO_2 will increase the calorific value and transportability of the natural gas therefore before a natural gas rich in carbon dioxide can be transported, it must be pre-processed so as to meet the typical specification of 2–5% carbon dioxide (Datta and Sen, 2006).

1.5 Problem statement

Theoretically, a continuous polycrystalline zeolite film has great advantages over other materials as an effective membrane layer due to its uniform pore structure at the molecular level. However it is difficult to synthesize a low defect zeolite film of large surface area. As the membrane surface area increases, defects such as microcracks and intercrystalline boundary layer which deteriorates membrane quality tend to form during the synthesis and template removal step. The gas separation usually requires higher quality membrane than liquid separation and pervaporation, because the presence of liquid phase in a membrane have often involved preferential sorption effects and pore blocking processes due to surface tension which somehow suppresses the effect of defects (Ramsay and Kallus, 2000). But for gas separation, a minor defect in the membrane structure will dramatically destroy the separation performance. Therefore development for zeolite membrane for gas separation still remains a challenge for the researcher.

The methods to produce high quality (minimum defects) zeolite membrane have been reported in the literature (Coronas *et al*., 1997, Hedlund *et al*., 2002, Bernal *et al*., 2004) but the results are not reproducible which mainly due to the complex mechanism of zeolite crystal growth that has not been fully understood. Hence, reproducibility of the synthesis method is one of the key features in the synthesis of zeolite membrane.

The separation of carbon dioxide from gas mixture using different type of zeolite membranes has been reported by number of researchers in the literature. The binary gas system studied mainly: CO_2/N_2 (Sebastian *et al*., 2006, Shin *et al*., 2005, Seike *et al*., 2002), CO_2/H_2 (Bonhomme *et al*., 2003, Zheng *et al*., 2005) , CO_2/CH_4 (Li et al., 2005, Tomita et al., 2004). Some of the zeolite membranes used has small pores so that molecular sieve becomes the main separation mechanism. There are a large number of research work reported using medium pore MFI zeolite membranes for the task. The reason is simply because MFI zeolite is the most important catalyst for number of industrial processes such as methanol to gasoline, syngas production, Fischer-Tropsch synthesis, xylene isomerization and steam reforming (Bhatia, 1990). Carbon dioxide, hydrogen, nitrogen and methane are some of the main gaseous components in these processes. MFI zeolite membrane could act as a separator as well as reactor for number of industrial reaction. The MFI catalytic membrane reactor (CMR) is still at the beginning stage. Even though some work has been reported in the literatures (van Dyk *et al*., 2003, Rohde *et al*., 2005), but yet there are still many problems and issues not solved related with the development of MFI zeolite CMR. For a CMR to be applicable, the mass transfer of gas components through membrane have to be fully understood, thus vast research work has been conducted using MFI zeolite membrane for the removal of CO_2 from binary gas mixture containing CO_2.

The transport mechanism of gases in zeolite membrane is complex; a number of steps have been observed during the movement of gas molecule in the pore of zeolite membrane and showed the selectivity and flux is a function of operating temperature, feed loading, feed and permeate pressure, use of sweep gas, presence of water in the feed and membrane module configuration (Burggraaf, 1999, Bernal *et al*., 2004). This is especially true for separation based on adsorption and surface diffusion mechanisms where the absorption rate is a function of pressure and temperature. However all of the gas separation process studies reported in the literature were conducted using one-factor-at-a-time approach which one chosen factor was successively varied over its range while other factors were held constant. This one-factor-at-a-time method fail to consider the possible interactions between the factors (Montgomery, 2005). Therefore a statistical Design of Experiment (DoE) approach to fully evaluate the effect of operating variables and interactions between the factors to the membrane separation performance is much needed.

1.6 Objectives

The present research has the following objectives:

1) To design and fabricate a permeation test rig which is capable to perform separation of binary gas mixture using zeolite membrane at different operating conditions.
2) To synthesize low defects MFI zeolite membrane with different chemical composition.
3) To characterize the MFI zeolite membranes for its chemical composition, surface and morphology characteristics, separation and permeation properties.
4) To study and compare the performance of MFI zeolite membranes with different chemical composition for the separation of: CO_2/N_2, CO_2/CH_4 and CO_2/H_2 binary gas mixtures.
5) To study the performance of MFI zeolite membrane and evaluate the effects of important variables in the separation of CO_2 from binary gas mixtures using statistical design of experiment (DoE) approach.

1.7 Scope of the study

In the first part of the present study, a membrane permeation test rig was designed and fabricated for finding the performance of disc type membrane. The test rig was designed to conduct separation study for binary gas mixture using zeolite membrane at different operating conditions. The operating parameters that can be varied using this test rig were: feed composition, temperature, pressure and sweep gas flowrate.

The second part of this study was to synthesize a low defect zeolite membrane using different synthesis approach and it was limited to the synthesis of MFI type zeolite membranes (ZSM-5 and Silicalite-1). Three types of MFI zeolite membranes with different Si/Al ratio and extra framework cation were synthesized. MFI zeolite membranes Silicalite-1 (Si/Al = ∞), Na-ZSM-5 (Si/Al = 25) and B-ZSM-5 (Si/B = 100) were synthesized. Silicalite-1 membrane was synthesized using secondary growth method whereas Na-ZSM-5 and B-ZSM-5 membranes were synthesized using in-situ crystallization method and α-alumina was used as support for all the membranes.

All the membranes synthesized were characterized using SEM, XRD, TGA and TEM respectively. For evaluation of the membrane quality, separation of different binary gas mixture was conducted. The binary gas mixtures: CO_2/N_2, CO_2/CH_4 and CO_2/H_2 were studied for separation of CO_2 from these mixtures. For each of this binary gas mixture, the separation performance of different MFI zeolite membranes was compared at various operating conditions.

The last part of the present study focused at the investigation of the effect of operation parameters (feed concentration, pressure, temperature and sweep gas) on the selectivity and permeance of the membrane for the separation of CO_2 present in the binary gas mixtures. The type of MFI zeolite membrane which performed best in the preliminary study was chosen for further study using DoE analysis. Four factors were identified and chosen for separation process study using DoE approach. These were feed pressure (1 – 5 bars), operating temperature (25 ^oC – 150 ^oC), sweep gas flowrate (0 – 300 cm^3/min) and feed composition (5 – 50 % CO_2 in feed). The range of the factors was decided based on literature search and practical viability of the experimental test rig.

1.8 Organization of the thesis

This thesis contains six chapters. In the first chapter, a brief introduction about membrane technologies and its prospects for gas separation, zeolite membrane and its recent developments, recent application of zeolite membrane, carbon dioxide scenario and it impact to the environment are presented. A problem statement list out some of the problems unsolved in the field of zeolite membrane research, especially problems related to the removal of carbon dioxide from binary gas mixture, thus giving a direction of the present research work.

Chapter two presents literature review on the synthesis methods for zeolite membrane which were developed for the last decade. Beside that, some of the membrane modification and fine tuning methods applied by various researchers are presented as well. This is followed by the review of the different membrane module design and mode of gas separation reported in the literature. At the end of the chapter, a review of experimental data for the separation of CO_2/N_2, CO_2/CH_4 and CO_2/H_2 binary gas mixtures reported is presented for the purpose of comparison.

In chapter three, a detailed description of the experimental works is elaborated. The materials and procedure applied for the synthesis of different type of zeolite membranes, design of the membrane permeation cell and sealing method, design and operation procedure of the membrane permeation test rig, method of gas permeation measurement and samples collection and analysis are included. At the end of the chapter the procedure of sample preparation for various characterization methods used in the present study are given.

Chapter four covers the results and discussions of the experimental data obtained in the present study. This chapter is divided into 3 sections; the first section presented and discussed the reproducibility of the membrane synthesis methodology.

The second section covers the characterization of the zeolite membrane, where the XRD crystallograms, SEM micrographs, TGA analysis and TEM micrographs are shown to reveal the microstructure and topology of the zeolite membrane. The last section of this chapter covers the membrane performance study where the separation data for different binary gas mixture using different type of zeolite membranes are presented. For each of the binary mixture, the performance of different type of zeolite membranes is compared. Finally the Design of Experiment (DOE) results for the selected MFI zeolite membrane based on preliminary studies is presented and discussed.

Chapter five covers meaningful conclusions obtained in the present study. At last, some suggestions and recommendations to improve the present research work as well as the future direction of the currently study are presented.

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CHAPTER 2

LITERATURE REVIEW

2.1 Synthesis of zeolite membrane

2.1.1 Synthesis methods

The synthesis of zeolite membrane was derived from zeolite powder synthesis methodology. The basic concept of zeolite formation is identical for both zeolites in thin film and powder form. The hydrothermal synthesis is the most common method for preparation of zeolites. After over 50 years of developments, the hydrothermal synthesis techniques have reached a very high level of advancement but yet the understanding of the complex chemical formation of zeolite crystal remained unclear to the researcher. It is reported that number of factors such as temperature, composition of the reaction mixture, the nature of the reactants, and pretreatment of the amorphous precursors can influence not only the reaction kinetics but also the type of zeolite that formed (Schuth *et al*., 2002). Typically the synthesis of zeolite is carried out in a batch system where an aluminates solution and silicate solution is mixed together. The mixture solution is held at temperature above ambient at autogenous pressure for a certain period of time. The proposed mechanism for zeolite crystallization is given in Figure 2.1 (Dokter *et al*., 1995). As the temperature increased, silicate particles start clustering around the template molecules to form the primary units. Aggregation of these primary units continues until nucleation takes place. These nuclei grow larger by the assimilation of aluminosilicates material from the solution phase. Once the nucleuses grow to its critical size, it will transform into macroscopic crystal of zeolite.

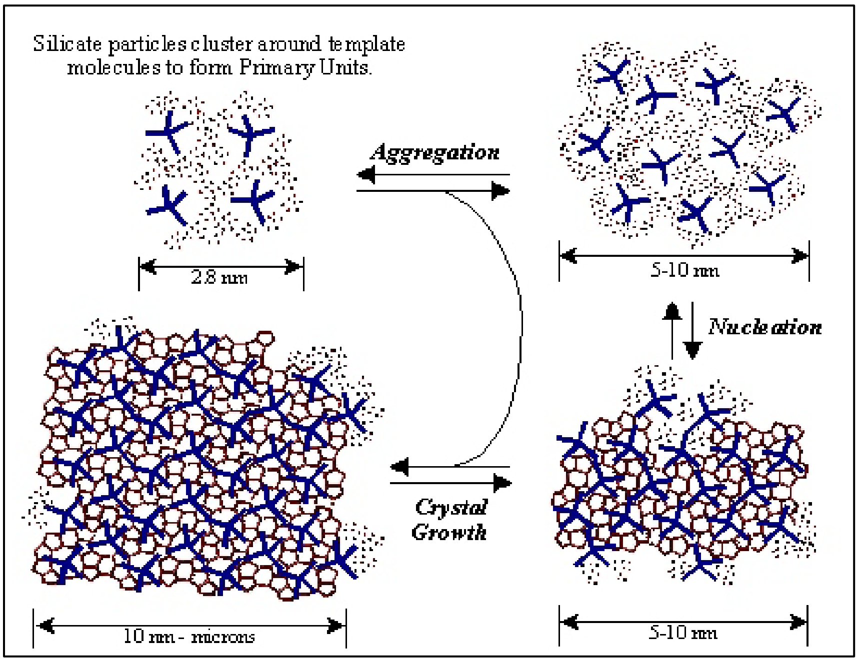

Figure 2.1: Mechanism of zeolite crystallization (Dokter et al., 1995)

In the synthesis of zeolite, one of the main components is the cationic organic structure directing agent. As shown in Figure 2.1, these organic molecules serve as void filler, charge balancer, structure directing agent and also a true template for the zeolite formation (Helmkamp and Davis, 1995). Without this structure directing agent it is difficult to obtain the desire zeolite structure, especially for the synthesis of high silica contained zeolite. After the synthesis of zeolite, this organic cations molecule is removed by calcination to activate the zeolite pore.

To transform the zeolite into a continuous polycrystalline layer growth on macroporous support, there are two most widely used methods namely: in-situ crystallization and secondary growth method (or sometime referred as seeding method). Both methods have some common steps in the synthesis procedure where a support was put inside a closed container containing zeolite synthesis gel and undergo the hydrothermal synthesis process by heating the system to a specific temperature for a certain period of time at autogenous pressure. The difference between the two methods is that for the in-situ method, the nucleation and crystallization take place in the bulk solution and slowly leads to deposition of nuclei and crystals on the support surface. Therefore a simultaneous and abundant heterogeneous nucleation is the prerequisite for the formation of good quality zeolite membrane using in situ crystallization method and thus this method generally requires stringent synthesis conditions (Lin et al., 2002). Yan et al. has conducted extensive experimentation to optimize the compositions of synthesis solution for the in-situ synthesis of ZSM-5 zeolite membranes. In term of practical viable this method is simple and convenient for coating of zeolite film although the film thickness is usually thicker than those prepared using the second method.

The secondary growth method, a zeolite nuclei (referred as seed) solution is first prepared and the seed is coated on the support using various coating methods to form a monolayer of seed thin film. The seed thin film is then transformed into zeolite crystal by immersing the seed coated support into a zeolite synthesis gel and undergoes for hydrothermal synthesis. Compared to the in situ crystallization scheme, seeded growth method offers significant advantages such as better control over membrane microstructure (thickness, orientation), higher reproducibility, and a wider range of hydrothermal synthesis conditions leading to continuous film formation (Auerbach *et al*., 2003). Furthermore, elimination of the constraints imposed by the need for crystal nucleation, due to the pre-existence of nuclei on the support surface, this method renders crystal growth as the main film formation mechanism and thus adds improved flexibility in zeolite film and membrane preparation (Lovallo *et al*., 1998). Several reports have proved that membranes made by secondary growth can exhibit distinct microstructure as compared to membranes grown by the in situ technique (Lovallo and Tsapatsis, 1996, Bonilla *et al*., 2001, Xomeritakis *et al*., 2000, Nair *et al*., 2001). Since secondary growth method required an extra step for the coating of the seed layer, it makes this method complicated and time consuming as compared to the former method. Beside that, if seeds are used, a high coverage of the support with seeds has to be achieved, otherwise dome-like defects will form in areas where continuity of the seed layers are interrupted (Xomeritakis *et al*., 1995). However, it is difficult to obtain a continuous seed layer with high coverage for an enlarged-area synthesis, especially on complex supports such as multi-channels, honeycomb and hollow fibers. Furthermore, in view of industrial mass production, the procedure of in-situ synthesis is simpler and thus more preferable than secondary growth. A typical MFI zeolite membrane synthesis procedure is presented in Figure 2.2.

After the coating of zeolite thin film, a procedure was carried out to check the quality of the thin film. This procedure is commonly named as leak test. Since organic molecules were employed as structure directing agent (SDA) in zeolite synthesis, prior to the removal of this SDA, the zeolite thin film should be a dense layer due to the pore blocking of the organic molecules. Nitrogen or helium gas is used to check the permeability of the film. If the thin film is impermeable to the inert gases, it shows that a high quality (without defect) layer of zeolite is obtained. Once the defect is found, repeat coating of second or third layer of zeolite film is carried out until the membrane is impermeable. After the leak test, the SDA molecules are removed by calcination at a very low heating and cooling rate to avoid the thermal crack formation which could deteriorate the quality of the membrane.

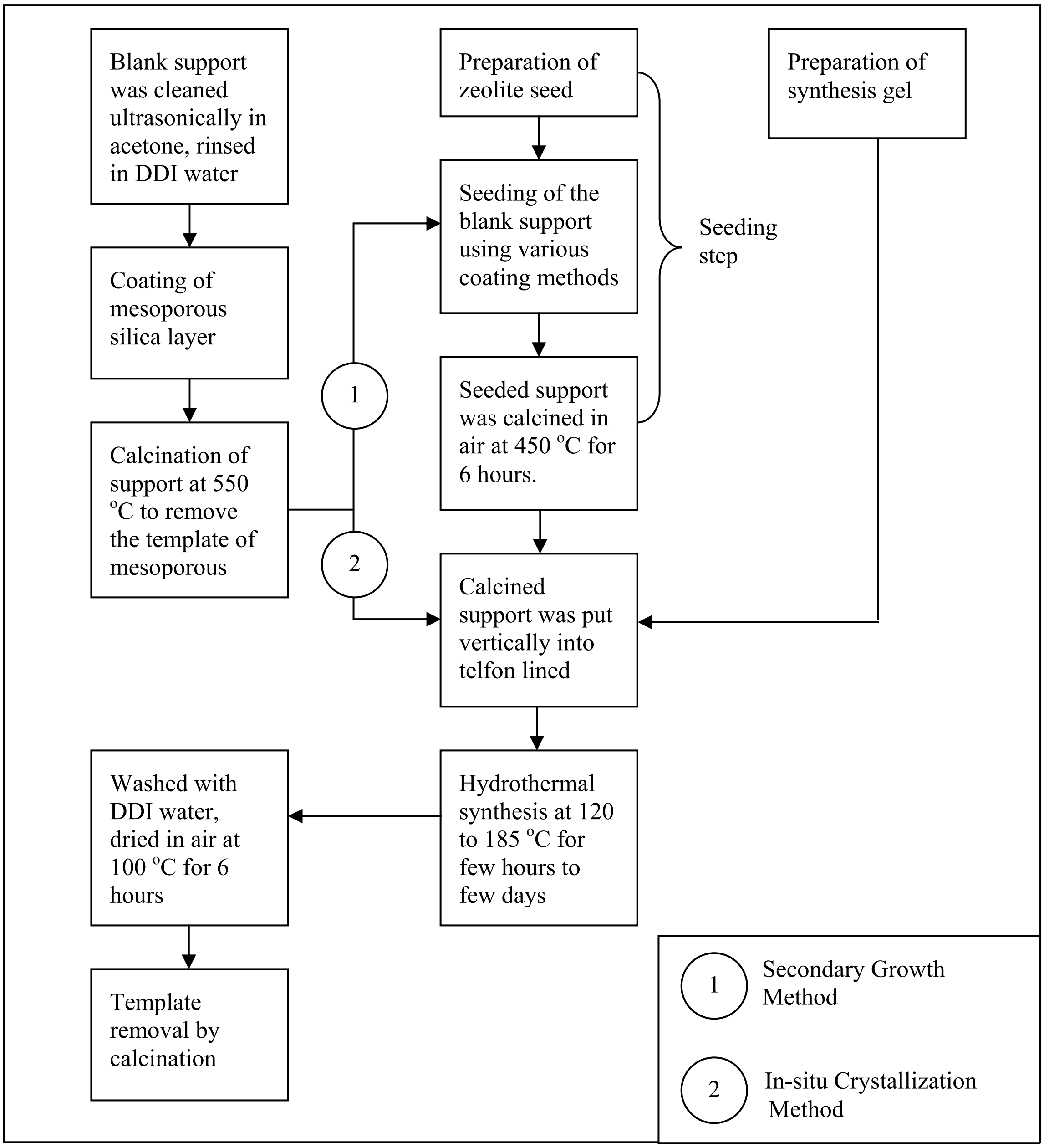

Figure 2.2: Typical MFI zeolite membrane synthesis procedures

Other than these two most widely used methods, zeolite membrane has been synthesized using methods such as chemical vapor deposition (CVD) (Li and Long, 2001, Kikuchi *et al*., 1997, Nishiyama *et al*., 1996) and microwave assisted hydrothermal synthesis method (Motuzas *et al*., 2006, Julbe *et al*., 2005, Motuzas *et al*., 2007). Chemical vapor deposition or dry gel conversion method in synonymic have been developed a decade ago for synthesis of zeolites. This method was first developed by Xu *et al*. (1990) who reported that MFI zeolite was crystallized from an amorphous dry gel under the vapors of triethylamine (Et_3N) and ethylenediamine (EDA) and water. Kim *et al.* (1993) and Matsukata *et al.* (1993) followed this report and successfully synthesized different kinds of zeolites, such as analcime (ANA), mordenite (MOR) and ferrierite (FER) as well as MFI by the CVD method and confirmed the promising potential of this new synthetic method. In CVD method, an amorphous gel containing silica, aluminium is first coated on the support. The crystallization occurs in a second step, the water for the hydrothermal synthesis coming as saturated vapor from the bottom of the autoclave. The template may be present either in the water or in the gel. This approach allows a strict control of the zeolite amount deposited and it is possible to prepare membranes even on supports having complicated shapes like honeycombs. A drawback is the high chances of cracks formation in the amorphous gel layer and finally caused the present of defect in the zeolite thin film formed (Nishiyama *et al*., 1996). The crack formation problem remained as a great hurdle for this synthesis method and because of this, CVD method has gained less attention of researchers for the pass few years.

The conventional hydrothermal synthesis method to prepare zeolite membranes usually required a long time for heating, nucleation and crystallization to take place. This time consuming procedure is not preferable for scaling up process. Thus a new synthesis method that combines hydrothermal synthesis and microwave heating technique has been developed (Xu *et al.*, 2000, Julbe *et al*., 2003, Motuzas *et al*., 2006, Julbe *et al*., 2005). The microwave assisted (MA) hydrothermal synthesis has the advantages of very short time, broad composition, small zeolite particle size, narrow zeolite particle size distribution, and high purity (Xu *et al*., 2000). These advantages could be attributed to fast homogeneous nucleation and the easy dissolution of the gel (Jansen *et al*., 1992). In spite of all these advantages, only few studies on the microwave synthesis of zeolite membranes have been reported to date and most of the studies were carried out for the synthesis of zeolite LTA membranes through secondary growth method (Chen *et al*., 2004, Chen *et al*., 2005, Li *et al*., 2006, Kita, 2003) and it was reported that continuous LTA zeolite membrane could not be microwave-synthesized without seeding. Thus further studies yet to be conducted to fully understood the crystallization process under microwave condition.

2.1.2 Membrane support

The main purpose of the membrane support is to provide the mechanical strength to the fragile zeolite thin layer. Inert porous material such as α-alumina (Zhang *et al*., 2005b, Pera-Titus *et al*., 2006, Gopalakrishnan *et al*., 2006), stainless steel (Arruebo *et al*., 2006, Mabande *et al*., 2004), glass (Wong *et al*., 2001) and mullite (Komarneni *et al*., 1998, Mirfendereski *et al*., 2006) are some of the commonly used supports reported in the literature. Stainless steel (S.S) support has an advantage of ease of sealing where the S.S support can be welded directly on to dense S.S tubing. But on the other hand S.S support may not be suitable when operated at high temperature and corrosive environment. Therefore α-alumina still remains as the most widely used support in the literature due to it inert properties and high thermal stability. One of the issues in choosing membrane support material is the different thermal expansion between the support and the zeolite thin film at higher temperature. Due to the different thermal expansion coefficient, the support and zeolite thin film will expand at different rate and tendency of crack formation are high especially at the intermediate layer. One of the disadvantages of S.S support is due to its very high thermal expansion compare to alumina support, therefore operation at high temperature the S.S support will expand more rapidly than the zeolite thin film and it will crack the thin layer. For alumina support, it has a lower thermal expansion coefficient but a good sealing of the membrane to the module for this type of support still remain a challenge. Beside that, during the hydrothermal synthesis process, aluminium oxide will leach out from the support and alter chemical composition (Si/Al ratio) of the zeolite synthesis gel which is not desirable. Furthermore, the α-alumina support has a macroporous structure with typical pore size of around 200 nm. During the synthesis process, a portion of zeolite synthesis gel will penetrate into the alumina support and crystal growth inside the support. This phenomenon will dramatically decrease the permeation flux. In order to improve the quality of the zeolite membrane, some modification on the support is usually done by coating a mesoporous silica layer on the surface of the blank support (Zhang *et al*., 2005a, Lai *et al*., 2004). This mesoporous silica layer will act as a masking material to prevent the penetration of the zeolite synthesis gel to enter the support pores and also prevent the aluminium oxide leach out from the support, thus a distinguish layer of zeolite film is obtained. Other than being a masking layer, the mesoporous silica layer gives an extra advantage to prevent thermal crack during calcination step to remove the organic template due to it intermediate thermal expansion coefficient between the zeolite and alumina support (Lai *et al*., 2003).

2.1.3 Template removal

The use of structure directing agent (SDA) provides better control of zeolite crystallization, but the SDA was trapped inside the zeolite pore after the synthesis process and this SDA have to be removed in order to activate the zeolite pores. The most commonly used method to remove SDA is by calcination in air to burn off these organic molecules at high temperature. MFI zeolite is the most widely studied zeolite membrane in the literature, the most commonly used SDA for the formation of MFI zeolite is the tetrapropylammonium (TPA^+) organic template. The removal of TPA^+ ion from MFI zeolite membrane was studied by different authors. Pachtova *et al*. (2002) reported the pyrolytic and oxidative removal of TPA^+ from Silicalite-1 zeolite crystal and found that cracks are usually formed during calcination of zeolites. Dong *et al*. (2000) reported that the MFI zeolite structure shrinks during template removal at 350 – 500 ^oC. In contrast after template removal, the MFI zeolite framework expands while the substrate shrinks upon cooling. A compression stress develops in the zeolite film during the cooling process when the zeolite crystallites are chemically bonded to the