SYNTHESIS, CHARACTERIZATION AND MODIFICATION OF SAPO-34 ZEOLITE MEMBRANE FOR SEPARATION OF CO_2 FROM BINARY GAS MIXTURES

by

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TABLE OF CONTENT

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

Symbol	Description
AFI	Aluminophosphate – five ($AlPO_4$-5)
α -Al_2O_3	alfa-alumina
$Al(i\text{-}C_3H_7O)_3$	Aluminium isopropoxide
ANOVA	Analysis of variance
Ar	Argon
ATN	$MgAlPO_4$ - thirty-nine (MAPO-39)
ATR	Attenuated Total Reflectance
Ba^{2+}	Barium cation
BEA	Zeolite Beta
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BPR	Back pressure regulator
Ca^{2+}	Calcium cation
CCD	Central composite design
CHA	Chabazite
CH_4	Methane
CMS	Carbon molecular sieve
CO_2	Carbon dioxide
CV	Check valve
DDR	Decadodecasil-3R
DI	Deionized
DOE	Design of experiment
EDI	Edingtonite
EDS	Energy Dispersive Spectroscopy
FAU	Faujasite

FCOM	Fluorescent confocal optical microscopy
FER	Zeolite Socony Mobil – thirty five (ZSM-35)
FTIR	Fourier Transformed Infra Red
FTM	Facilitated transport membrane
GC	Gas chromatography
H_2	Hydrogen
H_3PO_4	Phosphoric acid
HK	Horvath-Kawazoe
ITV	Instituto de Tecnologia Quimica Valencia – thirty seven (ITQ-37)
IZA-SC	International Zeolite Association Structure Commission
IRR	Instituto de Tecnologia Quimica Valencia – fourty four (ITQ-44)
IZA	International Zeolite Association
LTA	Linde A
MDES	Methyldiethoxysilane
MEA	Monoethanolamine
MEL	Zeolite Socony Mobil – eleven (ZSM-11)
MFI	Zeolite Socony Mobil – five (ZSM-5)
MLD	Molecular layer deposition
MMM	Mixed matrix membrane
Mg^{2+}	Magnesium cation
MOF	Metal-organic framework
MOR	Mordenite
M-S	Maxwell-Stefan
MW	Microwave
N_2	Nitrogen
NV	Needle valve
OFF	Offertite

PEEK	PolyEtherEtherKetone
PG	Pressure gauge
“Prob > F”	Probability
RTP	Rapid thermal processing
SAED	Selected area electron diffraction
SAPO-5	Silicoaluminophosphate – five
SAPO-34	Silicoaluminophosphate – thirty four
SDA	Structure directing agent
SEM	Scanning Electron Microscopy
SOD	Sodalite
Sr^{2+}	Strontium cation
TEAOH	Tetraethylammonium hydroxide
TEM	Transmission Electron Microscope
TGA	Thermal Gravimetric Analysis
TSA	Temperature swing adsorption
TWV	Three way valve
UWY	Institut Français du Pétrole and University of Mulhouse – twenty (IM-20)
VPT	Vapor phase transport
VSA	Vacuum and pressure swing adsorption
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbol	Description	Unit
A	Factor code of temperature in DOE	-
A_m	Effective area of the zeolite membrane	m^2
B	Factor code of pressure difference in DOE	-
b	Adsorption equilibrium constant	kPa^{-1}
C	Factor code of CO_2 % in the feed in DOE	-
D_{ms}	Maxwell-Stefan diffusivity	m^2/s
D_{ms0}	Infinite Maxwell-Stefan diffusivity	m^2/s
d, e, f	The lengths of crystallographic axes in different directions of a unit cell	Å
ΔH	Heat of adsorption	kJ/mol
ΔS	Entropy of adsorption	J/mol.K
E	Activation energy of Maxwell-Stefan diffusivity	J/mol
F_i	Gas flow of component i.	mol/s
M	Molecular weight	g/mol
N_i	Gas flux of component i	$mol/m^2.s$
n	Number of process variables in the model equation generated by DOE	-
p	Pressure	Pa
P_i	Gas permeance of component i	$mol/m^2.s.Pa$
Δp_i	Partial pressure difference of component i across the membrane	Pa
q_i	Molar loading of component i	mol/kg
R	Gas constant	J/mol.K
R^2	Regression coefficient	-

T	Temperature	^{o}C or K
t	Time	s or min
x_v and x_w	Process variables in the model equation generated by DOE	-
$x_v x_w$	First order interaction between x_v and x_w in the model equation generated by DOE	-
y	Response in the model equation generated by DOE	-
z	Distance from feed side of membrane	m

Greek Letters

φ_0	Regression coefficient for intercept terms in the model equation generated by DOE	-
φ_v	Regression coefficient for linear terms in the model equation generated by DOE	-
φ_{vv}	Regression coefficient for quadratic terms in the model equation generated by DOE	-
φ_{vw}	Regression coefficient for interaction terms in the model equation generated by DOE	-
ε , β , γ	The angles between the crystallographic axes of a unit cell	^{o}
$\alpha_{i/j}$	Selectivity of component i over component j	-
ζ	Error in the model equation generated by DOE	-
δ_{ij}	Kronecker delta	-
δ_m	The thickness of the membrane	m
θ_i	Fractional coverage of component i	-
ρ	Density of the membrane	kg/m^3
$(\nabla \mu_i)$	Chemical potential gradient causing driving force for diffusion	J/mol
Γ_i	Thermodynamic correction factor of component i	-

Subscripts

feed	Feed stream	-
i, *j*	Component gas CO_2, N_2, CH_4 or H_2	-
perm	Permeate stream	-
ret	Retentate stream	-

Superscripts

ideal	Ideal	-
s	Single gas	-
sat	Saturated	-
sep	Separation	-

SINTESIS, PENCIRIAN DAN PENGUBAHSUAIAN MEMBRAN ZEOLIT SAPO-34 UNTUK PEMISAHAN CO_2 DARIPADA CAMPURAN-CAMPURAN GAS PERDUAAN

ABSTRAK

Dalam kajian ini, membran zeolit silikoaluminofosfat – tiga puluh empat (SAPO-34) disintesis di atas penyokong α -alumina berbentuk cakera dengan menggunakan (1) penghabluran in-situ terus dan (2) pemanasan gelombang mikro (MW). Pemanasan MW membentuk membran SAPO-34 yang lebih nipis (ketebalan ~ 1.6 μm) dengan taburan saiz kristal zeolit (~ 0.6 μm) yang lebih kecil dalam masa sintesis sebanyak 2 jam pada 200 ^{o}C, yang lebih pendek daripada penghabluran in-situ terus. Membran SAPO-34 yang disintesis dengan menggunakan pemanasan MW telah diubahsuai dengan proses pertukaran ion dengan menggunakan kation Mg^{2+}, Ca^{2+}, Sr^{2+} dan Ba^{2+}. Sifat-sifat membran tersebut dicirikan dengan TEM, XRD, SEM, TGA, EDS, FT-IR dan penjerapan-penyahjerapan nitrogen. Membran zeolit SAPO-34 yang diubahsuai dengan Ba^{2+} meningkatkan kememilihan pemisahan CO_2/CH_4, CO_2/N_2 dan CO_2/H_2 masing-masing sebanyak 240, 217 dan 127 % dalam kajian penelapan dan pemisahan campuran gas sama molal. Membran zeolit SAPO-34 yang diubahsuai dengan Ba^{2+} diuji untuk penelapan satu gas CO_2, CH_4, N_2 dan H_2. Penelapan dan pemisahan gas perduaan CO_2/CH_4, CO_2/N_2 dan CO_2/H_2 juga dikaji. Kaedah permukaan gerak balas (RSM) digunakan untuk mengoptimumkan parameter proses untuk penelapan dan pemisahan gas perduaan CO_2/CH_4, CO_2/N_2 dan CO_2/H_2. Model matematik yang dibangunkan berdasarkan gabungan pendekatan perumusan Maxwell-Stefan dan garis sesuhu Langmuir, dapat mewakili penelapan satu gas, penelapan dan pemisahan gas perduaan dari segi telapan dan kememilihan pemisahan bagi gas melalui membran SAPO-34 yang diubahsuai dengan Ba^{2+} dengan ralat $\pm$ 10 %.

SYNTHESIS, CHARACTERIZATION AND MODIFICATION OF SAPO-34 ZEOLITE MEMBRANE FOR SEPARATION OF CO_2 FROM BINARY GAS MIXTURES

ABSTRACT

In the present research, silicoaluminophosphate – thirty four (SAPO-34) zeolite membranes were synthesized on α-alumina disc support using (1) direct in-situ crystallization and (2) microwave (MW) heating. MW heating formed thinner SAPO-34 membrane (thickness of ~ 1.6 μm) with narrower zeolite crystal size distribution (~ 0.6 μm) in much shortened synthesis time of 2 hours at 200 ^{o}C compared to direct in-situ crystallization. The SAPO-34 membranes synthesized using MW heating were modified by ion-exchange process with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}cations. The membranes were characterized using TEM, XRD, SEM, TGA, EDS, FT-IR and nitrogen adsorption-desorption. The Ba^{2+}-modified SAPO-34 zeolite membrane increased the CO_2/CH_4, CO_2/N_2 and CO_2/H_2 separation selectivity by 240, 217 and 127 % respectively in the equimolar gas mixture permeation and separation. The Ba^{2+}-modified SAPO-34 zeolite membrane was tested for single gas permeation of CO_2, CH_4, N_2, H_2. The binary gas permeation and separation of CO_2/CH_4, CO_2/N_2 and CO_2/H_2 was also studied. Response surface methodology (RSM) were used to optimize the process parameters for binary gas permeation and separation of CO_2/CH_4, CO_2/N_2 and CO_2/H_2. Mathematical models, developed based on combined approaches of Maxwell-Stefan formulation and Langmuir isotherm, were able to predict the single gas permeation, binary gas permeation and separation (in terms of permeance and selectivity) through the Ba^{2+}-modified SAPO-34 membrane within an error of $\pm$ 10 %.

CHAPTER 1

INTRODUCTION

1.1 Zeolite

Zeolites are crystalline silicates or aluminosilicates, based on a three-dimensional arrangement of TO_4 tetrahedral (SiO_4 or AlO_4), where T is silicon (Si) or aluminium (Al) atom, connected through their oxygen atoms to form subunits and finally large lattices by repeating identical building blocks (unit cells). The structural formula of zeolite is $M_{x/n}(AlO_2)_x(SiO_2)_y$ where n is the valence of cation M, x + y the total number of tetrahedral per unit cell and y/x the atomic Si/Al ratio varying from a minimal value of 1 to infinite (Guisnet and Gilson, 2002).

Most of the zeolites can be classified into three categories (Guisnet and Gilson, 2002):

- Small pore zeolites with 8 membered-ring pore apertures (8 tetrahedral atoms and 8 oxygen atoms) having free diameters of 0.30 – 0.45 nm.
- Medium pore zeolites with 10 membered-ring apertures having free diameters of 0.45 – 0.60 nm.
- Large pore zeolites with 12 membered-ring apertures having free diameters of 0.60 – 0.80 nm.

Each framework structure of zeolites were identified by the International Zeolite Association Structure Commission (IZA-SC) using a code consisting three capital letters. More than 130 zeolite framework structures have been listed by the Atlas of Framework Types in year 2011 (Baerlocher *et al.*, 2001). Table 1.1 presents

the examples of zeolite with their framework structure' codes reported in the literature. Those framework structures include Aluminophosphate – five (AFI), $MgAlPO_4$ - thirty-nine (ATN), Zeolite Beta (BEA), Chabazite (CHA), Decadodecasil-3R (DDR), Edingtonite (EDI), Faujasite (FAU), Zeolite Socony Mobil – thirty five (FER), Instituto de Tecnologia Quimica Valencia – thirty seven (ITV), Instituto de Tecnologia Quimica Valencia – fourty four (IRR), Linde A (LTA), Zeolite Socony Mobil – eleven (MEL), Zeolite Socony Mobil – five (MFI), Mordenite (MOR)< Offertite (OFF), Sodalite (SOD) and Institut Français du Pétrole and University of Mulhouse (UWY).

Table 1.1: Different zeolite framework structures reported in the literature (Bowen *et al.*, 2004; Julbe, 2007; Payra and Dutta, 2003)

Framework Structure	Corresponding Zeolite	Pore size (nm)
SOD	Sodalite	0.28
EDI	Edingtonite	0.28 x 0.38 and 0.8
CHA	SSZ-13, SAPO-34	0.38
ATN	MAPO-39	0.4
LTA	NaA	0.41
DDR	Decadodecasil	0.36 x 0.44
OFF-FER Intergrowth	T-type	0.36 x 0.51
MEL	ZSM-11	0.53 x 0.54
FER	ZSM-35	0.42 x 0.54 and 0.35 x 0.48
MFI	Silicalite-1, ZSM-5	0.53 x 0.56 and 0.51 x 0.55
OFF	Offertite	0.67 and 0.36 x 0.49
MOR	Mordenite	0.67 x 0.70 and 0.26 x 0.57
AFI	$AlPO_4$-5	0.73
FAU	NaX, NaY	0.74
BEA	Beta	0.73 x 0.60

Each framework structure displays distinctive pore structure and pore size. So far, the MFI framework structure is the most common zeolite used for various applications such as in catalysis and membrane separation. The MFI structure includes Silicalite-1 (pure silica zeolite) and ZSM-5 (alumino-silicate zeolite)

(Bowen *et al.*, 2004). Lately, three new zeolite framework structures have been approved by the IZA Structure Commission in the year of 2011 and these zeolites are classified as Instituto de Tecnologia Quimica Valencia – thirty seven (ITV), Instituto de Tecnologia Quimica Valencia – fourty four (IRR) and Institut Français du Pétrole and University of Mulhouse – twenty (UWY) (IZA-SC, 2011).

1.2 Zeolite Membrane

Generally, zeolite materials are prepared in the form of fine particles and agglomerate with desired shapes and sizes. The zeolite micropores in molecular size enable them to be used widely in applications such as adsorption, catalysis and ion exchange (Coronas, 2010). However, the zeolite materials in bulk form are not efficient for some applications and the preparation of zeolite materials as a thin layer is needed (Valtchev and Mintova, 2001). Zeolite membranes, are getting increasing importance in number of emerging applications such as chemical sensors, insulating layers in microprocessors, ion exchange electrodes, corrosion protection coatings, catalytic membrane reactor and membrane separator (Snyder and Tsapatsis, 2007; Choi *et al.*, 2009).

Zeolite membranes are generally formed by depositing zeolite layers on porous supports. Figure 1.1 shows the schematic of a supported zeolite membrane. The zeolite membrane acts as a selective barrier between two phases of fluid (Ismail *et al.*, 2002). When the fluid is fed to the supported zeolite membrane, the phase that passes through the zeolite membrane is called permeate while retentate is the phase that is unable to pass through the zeolite membrane.

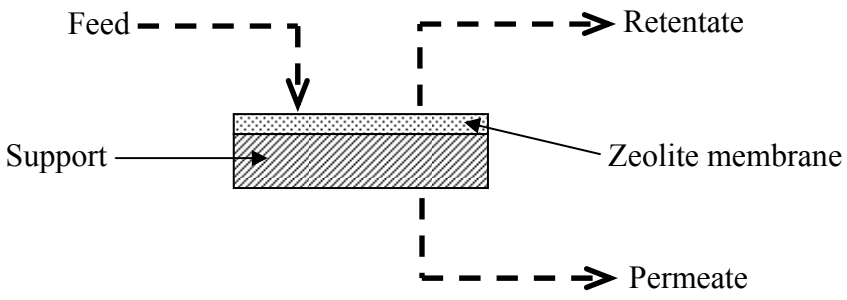

Figure 1.1: Schematic of a supported zeolite membrane

1.3 Gas Separation

1.3.1 Issue of CO_2 Gas Separation

The emission of carbon dioxide (CO_2) contributed to 80 % of current greenhouse gas emission to the atmosphere (Nair *et al.*, 2009). The increasing CO_2 concentration in the atmosphere in recent years and its implication on global warming has drawn attention of many researchers around the globe, creating the need for extensive investigation of CO_2 capture and separation (Li *et al.*, 2011a). Separation and recovery of CO_2 from large emission sources remained a great challenge nowadays in restricting the emission of greenhouse gas into the atmosphere. The CO_2 separation from methane (CH_4), nitrogen (N_2) and hydrogen (H_2) from the natural gas streams, power plant flue gas streams and fuel gas streams (i.e. in water-gas shift reaction) respectively, are among the main concerns nowadays for carbon dioxide removal and recovery to minimize its effect on the environment in terms of green house gases effect. CO_2 removal from these gas streams is also essential in the production of pure CH_4, N_2 and H_2 as industrially important energy and chemical sources. In view of this issue, there are increasing number of articles published by the researchers with the aim of finding potential processes for CO_2 capture, separation and CO_2 enrichment from exhaust gases to reduce carbon emissions directly at the source through greenhouse grown plant

uptake (Habib *et al.*, 2011; Scholes *et al.*, 2010; D'Alessandro *et al.*, 2010; Hasib-ur-Rahman *et al.*, 2010; Budd and McKeown, 2010; Mansourizadeh and Ismail, 2009; Krull *et al.*, 2008; Dion *et al.*, 2011; Jaffrin *et al.*, 2003).

1.3.2 Conventional Method for CO_2 Gas Separation

Figure 1.2 shows the common technologies available for separation of CO_2. Conventional methods for CO_2 separation include cryogenic distillation, absorption and adsorption processes. Cryogenic distillation enables CO_2 separation from relatively high purity (> 90 %) sources on the basis of cooling and condensation. However, it is expensive and energy intensive due to it's operation at very low temperature (lower than -73 ^{o}C for liquefaction of CO_2) and at elevated pressure (Li *et al.*, 2011a; Olajire, 2010; Leo *et al.*, 2009).

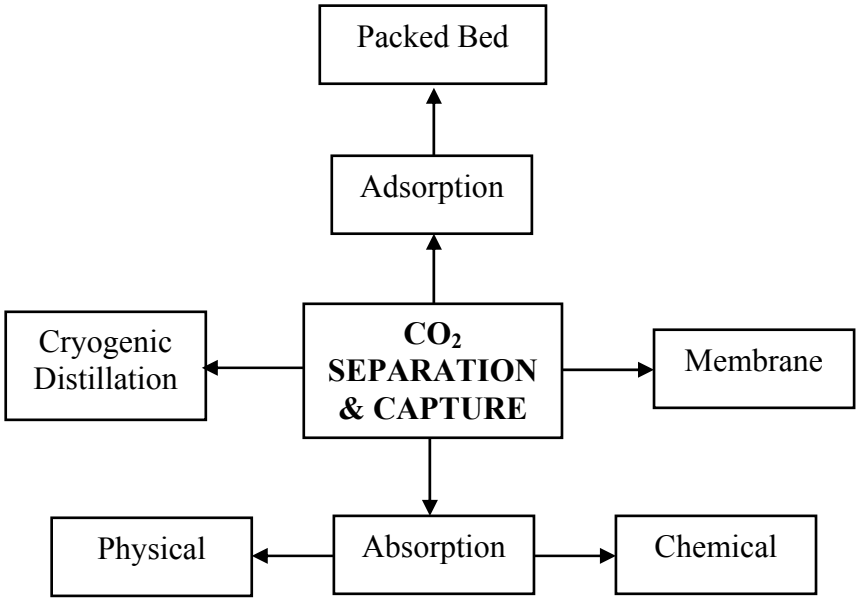

Figure 1.2: Common technologies for CO_2 separation (Li *et al.*, 2011a; Olajire, 2010)

Absorption, either chemical or physical, is another approach which is widely used for CO_2 separation. In chemical absorption, CO_2 is chemically captured through the acid-base neutralization reaction with caustic solvents such as

monoethanolamine (MEA) following by the driven-off of CO_2 by heating the aqueous solution comtaining amine-bound CO_2. The regeneration process required in the chemical absorption process is energy intensive (Bara *et al.*, 2009). Physical absorption, is another category of absorption in which CO_2 is bound selectively to the solvents (Fluor process, Rectisol process, ionic liquid etc) at high partial pressure and low temperature. However, physical absorption brings about drawback such as high capital cost of Fluor and Rectisol plant. In addition, the high viscosity of ionic liquid results in limited mass transfer and hence low absorption rates (D'Alessandro *et al.*, 2010; Hasib-ur-Rahman *et al.*, 2010; Olajire, 2010).

Adsorption is another well established method for CO_2 separation. Common solid adsorbents used include metal oxides, carbons, zeolites, ion exchange resins, activated alumina and metal-organic framework (MOF). The CO_2 separation is achieved by CO_2 adsorption to the solid adsorbents through physisorption (van der Waals) or chemisorption (covalent bonding), and followed by regeneration of the CO_2-adsorbed solid adsorbent through processes such as temperature swing adsorption (TSA), vacuum and pressure swing adsorption (VSA). The high power requirement for the adsorbent regeneration led to high capital cost of these processes (Li *et al.*, 2011a; D'Alessandro *et al.*, 2010).

1.3.3 Membrane-based CO_2 Gas Separation Technology

Membrane-based separation technology has attracted great deal of research interest for CO_2 separation in views of the requirement for reduction in the environmental impact, operation cost, energy utilization and waste generation (Bernardo *et al.*, 2009). Membrane offers advantages such as high energy efficiency

and operational simplicity compared to conventional CO_2 separation units (Lin and Freeman, 2005). It is mechanical robust as it needs no moving part and hence can be used in remote locations (Ismail *et al.*, 2009). Membrane enables continuous separation of gas by filtering one or more gases from the feed mixture based on the differences in physical and/or chemical interplays between the membrane and the gases (Olajire, 2010). Membrane can be categorized into organic (polymeric) and inorganic. Inorganic membranes include ceramic, carbon, oxides and different types of zeolites.

Polymeric membranes, are widely used for the membrane gas separation due to its low energy cost, ease in fabrication and scalability (Ismail *et al.*, 2009; Basu *et al.*, 2010). However, the application of polymeric membranes is limited to its loss in performance stability at high temperature, high pressure and in the highly acidic or alkaline environment (Koros and Mahajan, 2000). In addition, polymeric membranes, specially the type of glassy polymers, encounter plasticization problem in the presence of CO_2 even in low concentration. The swelling of polymer matrix occurs during plasticization resulted in permanent enlargement of interchain spacing in the polymer matrix. The matrix damage leads to reduced CO_2 gas separation performance of polymeric membrane (Bernardo *et al.*, 2009; Basu *et al.*, 2010; Baker, 2002).

Inorganic membranes are gaining increasing interest among the researchers for separation of CO_2 in view of their higher thermal, chemical and mechanical stability compared to organic membranes (Ismail *et al.*, 2009; Botias *et al.*, 2010). The porous inorganic membranes available commercially include carbon, glass,

oxide and zeolite membranes. The pore size of these membranes vary from microporous to mesoporous (< 25 nm) for carbon, oxide, zeolite and from mesoporous to macroporous (> 1 nm) for glass materials (Phair and Badwal, 2006). Besides, these membranes also differ in properties such as surface area, thermal and chemical stability (Meinema *et al.*, 2005). Carbon molecular sieve (CMS) membranes, prepared from carbonization of polymer precursors, have been widely investigated for its gas separation ability. Despite higher production cost of CMS membranes, they offer advantages such as higher permeance and separation performance compared to polymeric membranes (Hagg and He, 2011). However, careful handling is essential for CMS membranes since they suffer from the problem of brittleness (Bernardo *et al.*, 2009; Adhikari and Fernando, 2006; Ismail and David, 2001; Salleh *et al.*, 2011).

The development of facilitated transport membranes (FTMs) and mixed matrix membranes (MMMs) is another trend that emerges in the membrane-based gas separation technology. FTMs are good candidates for CO_2 separation on the basis of selective CO_2 transport using a carrier molecule with affinity to CO_2. Examples of FTMs are the immobilized liquids with facilitators such as amino species, polar polymers and ionic liquids, supported on polymeric or ceramic porous supports. However, FTMs face challenges with long-term stability and low tolerance in handling gas separation with high CO_2 partial pressure. The phenomenon of carrier saturation leads to decline in CO_2 separation performance of FTMs as the CO_2 partial pressure increases (Scholes *et al.*, 2010; Bernardo *et al.*, 2009). On the other hand, MMMs are formed by homogeneously incorporating the discrete phase (typically inorganic solids) in a continuous polymer phase. The combined strength

of two different phases, such as high selectivity of inorganic phase and low cost of polymer phase, makes MMMs attractive for CO_2 gas separation. However, MMMs encounter problems such as plasticization with CO_2 and easy formation of non-selective void spaces between polymer and inorganic phases (Li *et al.*, 2011a; Ismail *et al.*, 2009).

1.3.4 Zeolite Membrane for CO_2 Gas Separation

Zeolite membranes are the microporous inorganic membranes which are highly potential candidates for CO_2 gas separation. Besides possessing higher thermal, mechanical and chemical resistance compared to organic membranes, their well-defined, uniform and ordered molecular-sized pore structures make them attractive as shape-selective material for CO_2 gas separation (Shekhawat *et al.*, 2003; Sebastián *et al.*, 2007; Li *et al.*, 2006a; Jeong, 2010; Othman *et al.*, 2009). Choosing the suitable zeolite membrane with desired pore structure allows high gas separation performance by significantly discriminating the components in the gas stream on the basis of difference in molecular sieving, adsorption and diffusion effects (Caro *et al.*, 2000).

There have been extensive investigations on MFI and FAU zeolite membranes for the purpose of gas permeation and separation. MFI membrane with medium pore size (0.51-0.56 nm) and FAU membrane with large pore size (0.74 nm) enable satisfactory CO_2 separation performance. In recent years, the development of small-pore zeolite membrane (pore size < 0.45 nm) such as DDR and T-type, emerges as focus in research activities in exploring their ability in CO_2 gas separation. Silicoaluminophosphate – thirty four (SAPO-34), with CHA framework

structure consists of small pore structure. Figure 1.3 shows the framework structure of CHA. The SAPO-34 zeolite framework includes eight-ring apertures with an effective diameter of about 0.38 nm (Li *et al.*, 2004), which is close to the CO_2 gas molecule's kinetic diameter of 0.33 nm, make it potential candidate for CO_2 gas separation. Therefore, present study focused on synthesis of SAPO-34 zeolite membrane using novel method, modification of SAPO-34 zeolite membrane and its performance studies for CO_2 separation from CO_2/CH_4, CO_2/N_2 and CO_2/H_2 binary gas mixtures.

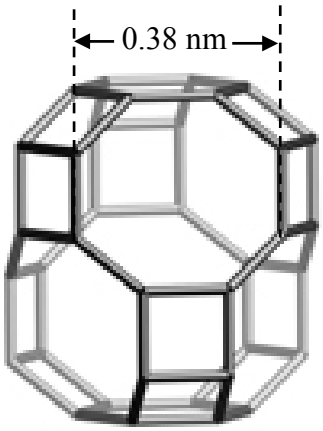

Figure 1.3: Framework structure of CHA (Li *et al.*, 2004; IZA-SC, 2008)

1.4 Problem Statement

Preparation of uniform and thin zeolite membrane is a very challenging work. There are number of factors and its combined effect influences the quality of the membrane produced. The choice of the right preparation method, suitability of the synthesis condition and dust free clean environment are essential for formation of high quality zeolite membrane. Mostly zeolite membranes were synthesized through direct in-situ crystallization. The preparation method reported so far in the literature for the synthesis of SAPO-34 membranes is direct in-situ crystallization and secondary growth method. Owing to non-uniformity in SAPO-34 zeolite

crystals (sized 0.1-4 μm) synthesized through the syntheses reported in previous studies, the SAPO-34 membranes have been formed with thickness of 5-25 μm (Li *et al.*, 2004; Poshusta *et al.*, 2000; Li *et al.*, 2005a; Li *et al.*, 2008). A good membrane should posses both high gas flux and separation selectivity for a gaseous component from the gaseous mixture. High gas flux is required for permeation and high separation selectivity is essential in confirming the high efficiency of the membrane separation system under low driving force, thus reducing the capital cost of the separation system (Lu *et al.*, 2007). However, membrane performance appears to be tradeoff between gas flux and separation selectivity. The increase in the thickness of the membrane layer generally increases the gas separation selectivity, but at the same time it attributed to the low flux of gaseous component. The preparation of a uniform and thin zeolite membrane with fewer defects, is desirable for both high gas flux and separation selectivity. This is one of the critical issue as well as challenge to the researchers nowadays to synthesize the membrane with the desired properties and characteristics.

The direct in-situ crystallization for SAPO-34 zeolite membranes brings about number of drawbacks and these include requirement of long synthesis time in addition to the problem of formation of non-uniform SAPO-34 zeolite crystals. The development of zeolite membrane for gas separation is still a subject of intensive research in the laboratory scale nowadays due to its high capital cost. In addition, another challenging task is the reproducibility of the synthesis method for the formation of zeolite membrane with desired thickness. Therefore, alternative methodology for synthesis of zeolite membrane with much shortened time is required in order to reduce the capital cost. The method need to be highly

reproducible and time-effective for the formation of SAPO-34 zeolite membrane with high quality (high gas flux and high separation selectivity). This will be the first step in the development of the zeolite membrane separation technology toward commercialization. In the present research, microwave (MW) heating appears to be potential technology for the synthesis of SAPO-34 zeolite membrane. The MW heating was reported to offer number of advantages such as rapid synthesis time of zeolite membrane and formation of zeolite crystals with higher uniformity compared to direct in-situ crystallization (Li and Yang, 2008).

Most of the CO_2 gas permeation and separation studies using zeolite membranes, including SAPO-34 zeolite membranes, were performed for equimolar binary gas mixtures which contains 50 % of CO_2 (Li *et al.*, 2004; Poshusta *et al.*, 2000; Li and Fan, 2010; Tian *et al.*, 2009; Hong *et al.*, 2008). Favre (2007) reported that in general the CO_2 concentration varies between 5-30 % in natural gas processing streams with mainly CH_4 gas and is 4-30 % in post combustion processing streams with mainly N_2. As for the concern of separation of CO_2 from H_2, the CO_2 concentration in the fuel gas streams (i.e. from steam reforming and gasification processes) may go as low as 4 % (Jeon *et al.*, 2008; Rajvanshi, 1986). The fuel gas compositions vary greatly depending on the process conditions and the feedstock compositions. This indicates that the CO_2 permeation and separation studies reported for SAPO-34 zeolite membranes so far did not reflect the real operation requirement in industrial separation systems. Therefore, it is highly desirable to study the performance of the SAPO-34 zeolite membranes for the separation of CO_2 from the feed gas mixtures with wide range of CO_2 concentration (as low as 5 %) in order to make the process more feasible for industrial application.

So far, high separation selectivities were achieved for gas mixtures CO_2/CH_4 and CO_2/N_2 using the reported SAPO-34 zeolite membranes. However, the SAPO-34 zeolite membranes showed very low separation selectivity, especially for gas mixture CO_2/H_2 at high temperature. Hong *et al.* (2008) reported CO_2/H_2 separation selectivity of more than 100 using SAPO-34 membrane at -20 ^oC. Such temperature was not applicable for the real industrial separation systems which are operated at temperature higher than room temperature. The SAPO-34 membrane separation performance dropped drastically with increase in temperature and it turned to be H_2-selective with H_2/CO_2 separation selectivity of only 2 at 200 ^oC (Hong *et al.*, 2008). Therefore, modification on the SAPO-34 zeolite membrane is required to further enhance its affinity toward CO_2, aims at improving the ability of the membrane for the separation of CO_2 from CO_2/CH_4, CO_2/N_2 and CO_2/H_2 gas mixtures, even at high temperature. Ion-exchange with different cations is among the methods that can be used to modify the SAPO-34 surface properties. There have been several studies reported for ion-exhange of SAPO-34 molecular sieve in the literature. Li *et al.* (2009) has studied the ion-exhange of SAPO-34 molecular sieve using cations Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} aimed at improving the methanol conversion to light olefin. On the other hand, ion-exchange of SAPO-34 molecular sieve with cations such as Ce^{3+}, Ti^{2+}, Mg^{2+}, Ca^{2+}, Ag^{+}, Na^{+} amd Sr^{2+} was found to change the properties of the molecular sieve including its pore width, surface area and light gases adsorption capability (Rivera-Ramos and Hernández-Maldonado, 2007; Rivera-Ramos *et al.*, 2008). Hence, the effect of modification (ion-exchange) towards CO_2 separation performance of the SAPO-34 zeolite membrane needs to be investigated in the present study.

There is no optimization study reported in the literature related with the process variables for gas permeation and separation using SAPO-34 zeolite membrane. The conventional approaches in the gas permeation and separation studies were conducted by running large number of experiments with only one process variable varied at a time. It is difficult to evaluate the possible interactions between the process variables by performing this one-factor-at-a-time approach (Montgomery, 2009). It is highly desirable to apply the statistical approach to determine the optimum conditions in permeation and separation studies of different gas mixtures containing CO_2, by performing minimum numbers of experiment runs. Design of experiment (DOE) is a useful statistical tool with it ability to evaluate the interactions between process variables, in addition to identification of optimum conditions for the membrane separation processes in order to maximize the flux and separation selectivity.

Mathematical models help in the better understanding of the transport phenomenon of different gas molecules through SAPO-34 zeolite membrane. The models should be able to predict the CO_2 permeation and separation performance of SAPO-34 membrane, in terms of gas fluxes, permeances and separation selectivity, for different gas mixtures. Determination of constants (i.e. adsorption constants and diffusivities) significantly helps in better understanding toward mechanisms of CO_2 permeation and separation in different gas mixtures. These models can be simulated and the simulated results could be compared with the experimental data in order to validate the models. The predictive models for CO_2 gas permeation and separation performance over wide range of process variables will be a useful tool in developing scalable membrane-based CO_2 separation technology.

1.5 Objectives

The present research aims at achieving the following objectives:

1. To synthesize SAPO-34 zeolite membrane through direct in-situ crystallization and MW heating.
2. To investigate the effect of MW heating time towards the formation of uniform and thin SAPO-34 membrane.
3. To modify the synthesized membrane using ion-exchange process with different cations and characterize the SAPO-34 zeolite membranes synthesized.
4. To study the performance of SAPO-34 membrane for the permeation and separation of CO_2 from CO_2/CH_4, CO_2/N_2 and CO_2/H_2 binary gaseous mixtures over wide range of process conditions (temperature, pressure difference across the membrane and CO_2 concentration in the feed).
5. To propose mathematical models for the prediction of gas fluxes, permeances and separation selectivities through SAPO-34 zeolite membrane in single gas permeation, binary gas mixture permeation and separation at different operating conditions. To compare the simulated results with the experimental data to verify the validity of the model.

1.6 Scope of the Study

1.6.1 Synthesis of SAPO-34 Zeolite Membranes

The SAPO-34 zeolite membrane was synthesized through direct in-situ crystallization following the procedures reported by Li *et al.* (2004). MW heating was adapted for the formation of SAPO-34 zeolite membranes. The effect of MW heating time (varied within 0.5-3 hours) was investigated towards quality of SAPO-34 zeolite membranes formed. Comparisons, in terms of properties and CO_2 separation performance, were made between the SAPO-34 zeolite membranes synthesized by direct in-situ crystallization and MW heating.

1.6.2 Modification of SAPO-34 Zeolite Membranes

Selected SAPO-34 zeolite membrane was subjected to modification (ion-exchange) with cations Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+}. The modified SAPO-34 zeolite membranes were compared for their properties and CO_2 gas separation from CO_2/CH_4, CO_2/N_2 and CO_2/H_2 gas mixtures.

1.6.3 Characterization of Unmodified and Modified SAPO-34 Zeolite Membranes

Various techniques were used to characterize the unmodified and modified SAPO-34 zeolites, either in the form of powder or membrane, as presented in Table 1.2. Single nitrogen permeation measurement at 30 ^{o}C and 3 bar pressure difference was performed for each coating of SAPO-34 zeolite layer before calcination process to determine the presence of defects in the membrane.

Table 1.2: Characterization techniques of SAPO-34 zeolite membrane

Method	Properties
Transmission Electron Microscopy (TEM)	Surface morphology and zeolite pore channel
Selected Area Electron Diffraction (SAED)	Presence of crystalline phase
X-ray Diffraction (XRD)	Crystallinity, structure and orientation
Scanning Electron Microscopy (SEM)	Microstructure, crystal size and membrane thickness.
Thermal Gravimetric Analysis (TGA)	Water content, template content and thermal stability.
Nitrogen Adsorption-Desorption Measurement	Surface area, pore width, micropore and mesopore volume and isotherm.
Fourier Transformed Infra Red (FTIR)	Characteristic framework vibration bands.
Energy Dispersive X-ray Spectroscopy (EDS)	Elemental composition.

1.6.4 Single Gas Permeation, Binary Gas Mixtures Permeation and Separation using SAPO-34 Zeolite Membranes

All the unmodified and modified SAPO-34 zeolite membranes were subjected to preliminary gas permeation and separation of equimolar CO_2/CH_4, CO_2/N_2 and CO_2/H_2 binary gas mixtures at 30 ^oC and 100 kPa. The modified SAPO-34 zeolite membrane with the highest preliminary CO_2 separation performance, was selected for single gas permeation studies of CO_2, CH_4, N_2 and H_2 over temperature of 30-180 ^oC and pressure difference of 100-500 kPa across the membrane. Thorough permeation and separation studies for the CO_2/CH_4, CO_2/N_2 and CO_2/H_2 binary gas mixtures were carried out using the selected modified SAPO-34 zeolite membrane over temperature of 30-180 ^oC, pressure difference of 100-500 kPa across

the membrane and 5-50 % CO_2 concentration in the feed. Determination of the ranges of process variables was based on the literature search and on the limitation of experimental membrane separator rig. The ability of the selected modified SAPO-34 zeolite membrane for separating CO_2 from the CO_2/CH_4, CO_2/N_2 and CO_2/H_2 binary gas mixtures containing CO_2 concentration in the feed as low as 5 %, was explored.

1.6.5 Optimization for Binary Gas Mixtures Permeation and Separation of Modified SAPO-34 Zeolite Membrane using DOE

DOE was selected for the permeation and separation studies of CO_2/CH_4, CO_2/N_2 and CO_2/H_2 binary gas mixtures using Design Expert software version 6.0.6 (STAT-EASE inc., Mineapolis, USA). In this statistical method, all variables were varied simultaneously in according to a set of experimental runs generated by Design Expert software. Response surface methodology (RSM) coupled with central composite design (CCD) was used to optimize the process variables for the CO_2 permeation and separation performance. Model equations were determined using quantitative data from the set of experimental runs. The effect of interaction between the process variables toward the responses was analyzed and the responses were optimized.

1.6.6 Modeling for Single Gas Permeation, Binary Gas Mixture Permeation and Separation of Modified SAPO-34 Zeolite Membrane

The single gas permeation, binary gas mixture permeation and separation of selected modified SAPO-34 zeolite membrane were modeled on the basis of combined effect of adsorption and diffusion. The adsorption and diffusion constants determined from the gas permeation data, were incorporated into the models. Single

gas fluxes, single gas permeances of different gas molecules (CO_2, CH_4, N_2, H_2) and the ideal selectivities (determined for single gas permeations) were modeled for temperature of 30-180 ^oC and 100-500 kPa pressure difference across the membrane. Models were also built to represent the gas fluxes, gas permeances and separation selectivities for equimolar CO_2/CH_4, CO_2/N_2, CO_2/H_2 binary gas mixture permeation and separation through selected modified SAPO-34 zeolite membrane at 30-180 ^oC and 100 kPa pressure difference across the membrane.

1.7 Organization of Thesis

In the first chapter (Introduction), the definition of zeolite membrane is introduced. Current issue of CO_2 and the approaches, including the membrane-based technologies, available for CO_2 separation are presented. The problem statements are elaborated, followed by determination of objectives and scope of study for present research project.

In the second chapter (literature review), reviews on the methods for synthesis of zeolite membranes, in addition to the modification approach for zeolite membranes, are presented. Characterization techniques used for analysis of chemical and physical properties of the zeolite membranes are elaborated. The gas permeation and separation studies reported for different zeolite membranes are discussed. At the end of this chapter, reviews of modeling and simulation process study for zeolite membranes are presented.

Chapter three (materials and methods) presents the list of all materials and chemicals used in present research project. Detailed procedures for the synthesis and modification of SAPO-34 zeolite membranes are presented. This chapter presents

the preparation of SAPO-34 zeolite sample for various characterization techniques. Operating procedures of the gas permeation and separation test rig in measuring the gas permeation and separation, gas sample collection and analysis are elaborated.

In the fourth chapter (results and discussion), the experimental results are presented and discussed. Firstly, the characterizations of unmodified and modified SAPO-34 zeolite membranes are presented. This is followed by preliminary equimolar binary gas mixture permeation and separation through SAPO-34 zeolite membranes. The selected modified SAPO-34 zeolite membrane was subjected to thorough single gas permeation of CO_2, CH_4, N_2 and H_2, followed by permeation and separation studies of CO_2/CH_4, CO_2/N_2 and CO_2/H_2 binary gas mixtures. In the next section, DOE approach was used to determine the effect of interaction between process variables towards the responses and optimization of the responses. At the last section, modeling studies for the single gas permeation (CO_2, CH_4, N_2 and H_2), binary gas mixture (CO_2/CH_4, CO_2/N_2 and CO_2/H_2) permeation and separation are presented. The models were built to predict the gas fluxes, gas permeances and separation selectivities through selected modified SAPO-34 zeolite membrane. The validity of the models was determined by performing comparison between simulated and experimental results.

Chapter 5 (conclusions and recommendations) presents the conclusive attainment of the major findings in the present study. Suggestions and recommendations are presented as improvement for the present study in the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Synthesis of Zeolite Membrane

The formation and properties of the zeolite products depend on large number of parameters, such as the synthesis conditions (i.e. temperature, pressure, stirring) and the compositions of the precursor solution required for synthesis (i.e. ratio between elements for framework formation, pH, content of the structure directing agent, water concentration) (Cubillas and Anderson, 2010). Figure 2.1 presents the phenomenon occurrence from nutrients to formation of zeolite crystals. The synthesis of zeolite starts with preparation of precursor solution consisting of required nutrients such as element for framework formation (Si, Al, P, O) and structure directing agent (SDA). By heating the precursor solution to desired temperature at autogenic pressure in an autoclave, entities with different size are formed through hydrolysis, oligomerization and condensation reactions catalyzed by hydroxyl ions. The amorphous phase is formed and is at pseudo-equilibrium with solution phase. After a period, breaking and remaking Si,Al-Si,Al bonds by the hydroxyl ions, results in formation of nuclei and followed by zeolite crystals (Cundy and Cox, 2005). Simultaneously, transformation of the amorphous phase into crystalline phase or dissolution of the amorphous phase into more stable product could happen. The zeolite crystals formed then grow with time in the autoclave (Coronas, 2010; Cubillas and Anderson, 2010).

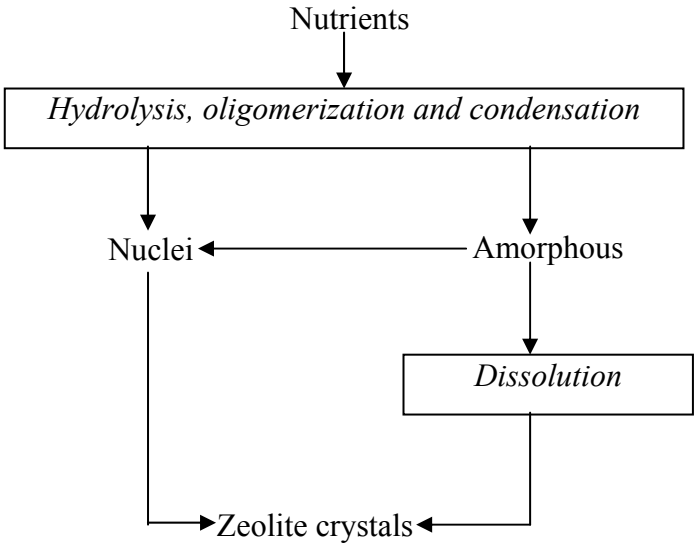

Figure 2.1: Phenomenon occurrence for transformation of nutrients into zeolite crystals (Coronas, 2010)

2.1.1 Methods of Zeolite Membrane Synthesis

There are numbers of report in the literature for the preparation of different types of zeolite membranes. These zeolite membranes includes MFI (ZSM-5 and silicalite-1), FAU (NaX and NaY), DDR, T-type, SAPO-34 and medernite membranes (Snyder and Tsapatsis, 2007). Figure 2.2 shows the common strategies being reported for the preparation of zeolite membranes in the literature. The thin zeolite membrane can be formed on top of a selected porous support using different techniques: (1) Liquid phase synthesis (direct in-situ crystallization and secondary (seeded) growth method) and (2) vapor phase synthesis (vapor phase transformation and steam-assisted crystallization).

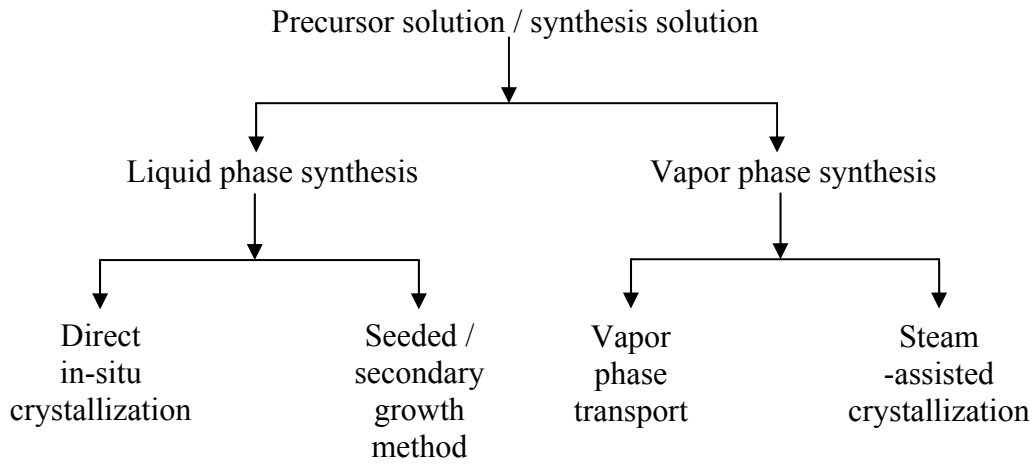

Figure 2.2: General methods for synthesis of zeolite membranes (Caro *et al.*, 2000)

The differences in the preparation of zeolite membranes following different methods are illustrated in Figure 2.3. In direct in-situ crystallization, the support is immersed in a precursor solution with known concentration under hydrothermal condition at given temperature. In secondary (seeded) growth method, a closely packed layer of zeolite crystal seeds is deposited onto the surface of a support before crystallization. Different techniques for the deposition of zeolite seeds on the support surface are reported in the literature such as rubbing, dip coating, slip casting and vacuum seeding. Subsequent hydrothermal synthesis is carried out to decouple the nucleation step and crystal growth (Pina *et al.*, 2004). Vapor phase synthesis is another method for the synthesis of zeolite membrane. The precursor is coated on the support via dipping technique, followed by drying. The dry, amorphous precursor is converted to crystalline material via contact with the vapor phase of an organic-water mixture (Parvelescu *et al.*, 2007).

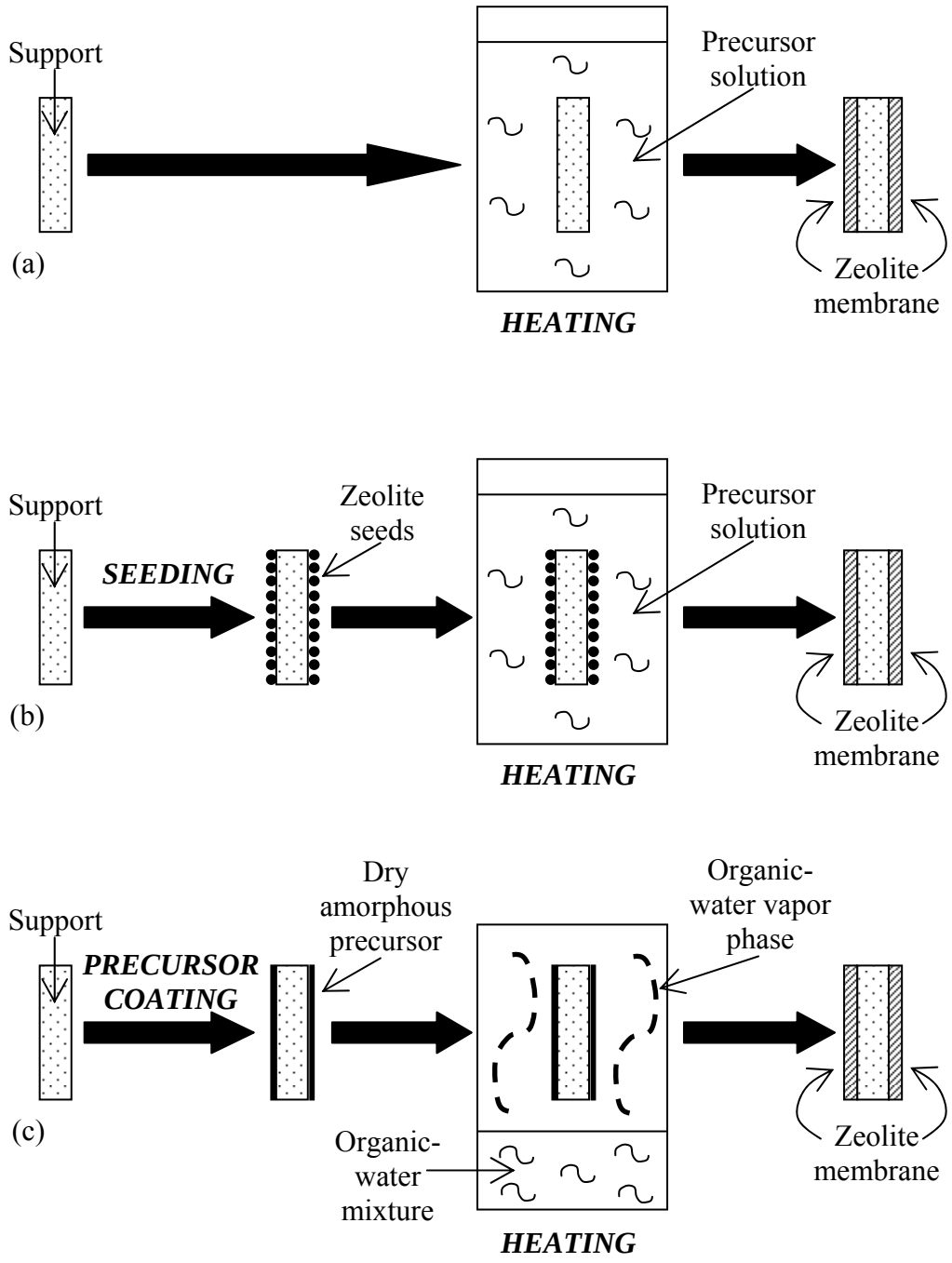

Figure 2.3: Steps in the preparation of zeolite membranes on double side of disc-shaped support for different methods: (a) direct in-situ crystallization hydrothermal synthesis, (b) secondary growth (seeded) hydrothermal synthesis and (c) vapor phase synthesis