SYNTHESIS OF INORGANIC AND POLYMERIC MEMBRANES WITH SAPO-44 ZEOLITE FOR GAS SEPARATION

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UNIVERSITI SAINS MALAYSIA
2015

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by

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Thesis submitted in fulfilment of the
requirements for the degree of
Master of Science

September 2015

ACKNOWLEDGEMENTS

In the name of Allah the Most Beneficent and the Most Merciful.

Alhamdulillah and thanks to ALLAH S.W.T for the blessing to me in completing my master degree project. This thesis is the symbolism of supports and guidance's that I acquired from my husband, parents, family and friends. Special thanks for their spiritual support, concern and encouragement.

I would like to express my sincerest gratitude and appreciation to my supervisor Dr Leo Choe Peng, for her continuous assistance, support, and invaluable guidance throughout this research. I would like to express my sincere thanks to my co-supervisor, Professor Abdul Latif Bin Ahmad for his support. I also would like to acknowledge the staffs and technicians of School of Chemical Engineering, USM for their kindness and supportive encouragement during the preparation of this project.

Lastly, I wish to express my acknowledgement to Kementerian Pengajian Tinggi for providing MyMaster. The fundings provided by MOSTI (Science Fund: 06-01-05-SF0579), Membrane Science and Technology Cluster (1001/PSF/8610013), Research University Individual Grant (1001/PJKMIA/811194) and RU-PRGS (1001/PJKIMIA/8035018) for conducting the research work gratefully acknowledged.

TABLES OF CONTENTS

CHAPTER 1 –INTRODUCTION

CHAPTER 2 - LITERATURE REVIEW

CHAPTER 3 –METHODOLOGY

CHAPTER 4 - RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

Al	Aluminium
Al_2O_3	Aluminium Oxide
APMS	3-aminopropyl trimethoxy
Ar	Argon
ATR	Attenuated Total Reflectance
BET	Brunauer-Emmett Teller
CH_4	Methane
CMS	Carbon molecular sieve
CO	Carbon Monoxide
CO_2	Carbon Dioxide
$C_6H_{13}N$	Cyclohexylamine
DC	Direct in-situ crystallization
DDR	Decadodecasil-3R
DI	Deionized water
DMAc	N, N-Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimetylsulfoxide
EDX	Energy Dispersive X-Ray
EtOH	Ethanol
FTIR	Fourier Transformed Infra Red
GC	Gas Chromatography
GPU	Gas Permeation Unit
He	Helium

HMA	2-hydroxy 5-methyl
H_2	Hydrogen
H_2O	Hydrogen Oxide
H_2S	Hydrogen sulphide
i-C_4H_{10}	isobutene
L-L	Liquid-liquid
LMWA	Low molecular weight additive
MeOH	Methanol
MMM	Mixed Matrix Membrane
MW	Microwave
NMP	N-Methyl-2-Pyrrolidone
N_2	Nitrogen
n-C_4H_{10}	n-butane
O_2	Oxygen
P	Phosphorus
PDMS	Polydimethylsiloxane
PES	Polyethersulfone
Poly (RTIL)	Solid Polymerized Room-Temperature Ionic Liquid
PSf	Polysulfone
SAPO	Silicoaluminophasphate
SDA	Structure Directing Agent
SEM	Scanning Electron Microscopy
SG	Secondary growth method
STP	Standard Operating Procedure
SS	Stainless Steel

THF	Tetrahydrofuran
UC	Uncalcined
XRD	X-ray Diffraction
α-Al_2O_3	Alfa-alumina

LIST OF SYMBOLS

Symbol	Description	Unit
T_g	Glass Transition Temperature	°C or K
Δp	Partial pressure difference across the membrane	bar or cmHg
P_i	Gas permeance of component *i*	GPU
Q_i	Volumetric flow rate of gas component	cm^3/s
A	Effective membrane area	cm^2
l	Effective membrane thickness	cm
J_i	Flux of component	$mol/m^2.s$
t	Time	s or min
T	Temperature	°C or K

Greek Letters

$\alpha_{i/j}$	Selectivity of component *i* over component *j*	-

Subscripts

i, j	Gas component CO_2, N_2, CH_4, H_2	-

SINTESIS MEMBRAN-MEMBRAN TAK ORGANIK DAN POLIMER DENGAN ZEOLIT SAPO-44 UNTUK PEMISAHAN GAS

ABSTRAK

Dalam kajian ini, membran jenis tak organik dan membran polimer yang melibatkan SAPO-44 telah dikaji. Membran jenis tak organik telah disintesis di atas penyokong α-alumina berbentuk cakera melalui kaedah pertumbuhan sekunder dan kesan pada suhu menyahkan templat telah dikaji. Manakala, dalam kajian membran polimer, polietersulfon (PES) dicampuri dengan kristal zeolit SAPO-44 disediakan melalui kaedah fasa balikan. Kesan pada membran PES sintesis berdasarkan parameter yang dijalankan, iaitu jenis pelarut, kepekatan polyethersulfone (17-27 %), masa penyejatan (30-2700 s) dan kepekatan polydimethylsiloxane (PDMS) (1-5 %) telah disiasat untuk kajianstruktur pada membran dan prestasi gas sebelum menambah kristal zeolit. Kesan penambahan zarah SAPO-44 (3-10 %) telah dikaji. Zeolit membran tak organic telah diuji untuk penyerapan gas tunggal CO_2 and N_2, manakala untuk membran polimer, tambahan gas CH_4 dan H_2 telah dijalankan. Pembuangan templat yang dijalankan di 375°C menghasilkan keputusannya membran yang bebas daripada retakan dan penyasingan gas yang optimum (CO_2/N_2 = 1.07). Pada suhu pembuangan templat yang lebih tinggi, penghabluran zeolit SAPO-44 telah hilang disebabkan oleh zeolit yang tidak teratur. Sebaliknya, dalam membran polimer PES, penambahan pelarut sampingan ke dalam larutan polimer didapati telah menurunkan kelikatan larutan dan menyebabkan tangguhan cecair-cecair berlaku semasa fasa penyongsangan. Liang-liang kecil telah terhasil di atas lapisan substruktur dan lapisan liang-liang menjadi tebal semasa peningkatan

penyejatan pelarut sebelum membrane mengeras dalam bukan pelarut. Lapisan PDMS di atas membran PES yang mempunyai lapisan kulit tebal mempamerkan keputusan yang lebih tinggi berbanding dengan membran yang tidak bersalut di atasnya. Membran polimer yang mengandungi THF bersama pelarut dengan masa penyejatan 60 saat dan 3% penyalutan PDMS didapati membran yang paling optimum antara membran yang lain dalam kerja-kerja ini dengan menghasilkan pengeluaran gas CO_2 sebanyak 44.86 GPU. Pengeluaran gas CO_2 telah meningkat kira-kira empat kali ganda apabila menambah 10% zeolit SAPO-44 di dalam membran PES/PDMS.

SYNTHESIS OF INORGANIC AND POLYMERIC MEMBRANES WITH SAPO-44 ZEOLITE FOR GAS SEPARATION

ABSTRACT

In the present research, inorganic and polymeric membranes involving SAPO-44 application were studied. Inorganic membranes were synthesized on α-alumina disc support by secondary growth method and the effect of calcination temperature of inorganic membrane was investigated. Meanwhile in polymeric membrane study, polyethersulfone (PES) membranes filled with SAPO-44 zeolite particles were fabricated via phase inversion method. The effects of PES membrane synthesis parameters, which are types of co-solvents, PES concentration (17-27 wt%), evaporation time (30 - 2700 s) and polydimethylsiloxane (PDMS) concentration (1 - 5 wt%) were investigated in order to study the changes in membrane morphology and gas performance before adding SAPO-44 particles. Then, the effects of SAPO-44 loading (3 - 10 wt%) were studied. The inorganic membranes were tested for single gas permeation of CO_2 and N_2, while for polymeric membrane, additional CH_4 and H_2 permeation tests were also conducted. Calcination temperature conducted at 375°C formed defect-free SAPO-44 membrane with CO_2 displayed more permeable through the SAPO-44 zeolite membrane compare to N_2 (CO_2/N_2 selectivity of 1.07). At the higher temperature, the crystallinity of SAPO-44 zeolite was lost due to the disorganization of zeolite. In contrast, the addition of co-solvent into the PES polymer solution decreased the dope viscosity and delayed liquid-liquid demixing during phase inversion. The microvoids were formed on top of substructure layer and the microvoids layer became thicker due to the increasing of solvent evaporation time. The PDMS coating on the PES membrane formed a dense skin layer and exhibited higher selectivity compared to the uncoated membrane. 20PT-3 is the optimum membrane among other fabricated polymeric membranes in this work with CO_2 permeance of 44.86 GPU. The CO_2 permeance was increased about four times when adding 10 wt% of SAPO-44 in PES/PDMS membrane.

CHAPTER 1

INTRODUCTION

1.1 Membranes for Gas Separation

Gas separation membrane units are widely used in industry for many applications. The rapid growing application are in natural gas treatment,refinery and petrochemical plant. In past few decades,more focus was on conventional methodswhich acquired high capital for the installation and operation units. By comparing with the conventional separation techniques of distillation, extraction, absorption and adsorption process, membrane separation has several advantages (Himeno et al., 2007). Membrane separation has drawn great attention in recent years because of its low energy consumption, environmental benignity and ease of operation (Shekhawat et al., 2003). The commercialized gas separation processes using membranes has been summarizedin Table 1.1(Bernardo et al., 2009, Goh et al., 2011).

Membranes are thin films that selectively permit the passage of gas molecules which can be explained by several transport mechanisms such as viscous flow, Knudsen diffusion, molecular sieving, solution diffusion and adsorption/surface diffusion (Mulder, 1997). Membranes are commonly categorized into inorganic, polymeric or composite membranes. Inorganic membranes can be prepared from zeolite, carbon molecular sieves, amorphous silica and metals.On the other hand, polymeric membranes are synthesized from various types of polymers or polymer blends. Meanwhile,composite membrane such as mixed matrix membranes (MMM) are designed to combine the benefits of inorganic and polymer materials(Iarikov and Oyama, 2011, D. D. Larikov and S. T. Oyama, 2011). By late 70s, inorganic and polymeric membranes were developed and tested at industrial scale (Kolsh and Schirmer, 1989).

Table 1.1: Main Industrial Applications of Membrane Gas Separation(Bernardo et al., 2009, Goh et al., 2011)

Separation	**Process**
H_2/N_2	Ammonia purge gas
H_2/CO	Syngas ratio adjustment
H_2/CH_4	Natural gas dehydration
H_2/hydrocarbons	Hydrogen recovery in refineries
O_2/N_2	Nitrogen generation, oxygen-enriched air production
CO_2/CH_4	Natural gas sweetening, landfill gas upgrading
H_2S/hydrocarbons	Sour gas treating
He/hydrocarbons	Helium separation
He/N_2	Helium recovery
Hydrocarbons/air	Hydrocarbon recovery, pollution control
H_2O/air	Air dehumidification
Volatile organic species (e.g., ethylene or propylene) Light gas (e.g., nitrogen)	Polyolefin purge gas purification

Inorganic membraneshave high demanddue to their highthermal and chemical stability. Three major types of inorganic membranes are currently available in the membrane market, namelyzeolite membranes, sol-gel microporous membranes and palladium (Pd)based membranes (Caro et al., 2000). Zeolites are always of great interest because they can be used in developingselective and strong adsorbents, selective ion resins or catalytically active thin films(Li, 2002). Due to its crystalline structure, zeolite membranes are able to withstand relatively high temperature compare to sol gel microporous membranes and Pd based membranes. Numerous zeolites are thermally stable above 500°C. They are also stable in alkaline or acidic media, depending on their chemical characteristic (Meinema et al., 2005). Despite the unique properties of zeolite membranes,they are expensive, difficult to be synthesied and handle. This hinders the application of inorganic membrane reactors in the process industry. However, in view of the significant potential advantages of inorganic membranes can guarantee that the zeolite membranes are under constant development. A thin and defect-free selective layer with high thermal and chemical stability and having small and homogeneously dispersed pores the main focus in the zeolite membrane based research (Saracco and Specchia, 1998).Zeolites are well defined as three dimensional, microporous and crystalline solids which contain aluminum, silicon, and oxygen in their regular framework. The silicon and aluminum atoms are tetrahedrally connected to each other through shared oxygen atoms. Therefore, the framework of zeolite is constructed from tetrahedral building blocks, TO_4 where T is tetrahedrally coordinated atom(Szostak, 1992). The zeolite emprirical formula is representedas:

$$M_{2/n}O \bullet Al_2O_3 \bullet x\ SiO_2 \bullet y\ H_2O$$

where M represents the counterion, n represents the counterion valence, x is equal to or greater than 2 since AlO_4tetrahedra are only joined to SiO_4tetrahedra and y indicates the degree of hydration(Li, 2002). Zeolites can be classified based on different frameworks. There are three major classes of zeolites in term of pore structure which are small, medium and large. Small pore framework structures with free diameter of 0.30 – 0.45 nm with 6-, 8-, and 9- membered ring are specifically suitable for gas separation. Potential zeolite membranes with small pore size for gas separations are T-type, SAPO-34, SAPO-44, NaA type, and DDR. The pore size of these zeolites is closer to the kinetic diameter of severalmoleculegases.Nowadays, SAPO zeolite is one of the potentially effective membranesto be apply as a membrane reactor due to its ability in adsorption, differences in diffusion rates and molecular sieving. Moreover, SAPO zeolite was commonly used as a catalyst in conversion of methanol to olefin (Chen and Thomas, 1991).

Polymeric membranes have also been commercialized for a widevariety of applications ranging from food and beverage processing, desalination of seawater,medical devices to gas separation. Polymeric membranes received considerable attention due to their excellent mechanical properties, low cost of materials andease of processing(Goh et al., 2011). Commercial polymeric membranes have an asymmetric structure with a very thin selective layer supported on a thicker porous layer. The thin selective layer permits higher gas fluxes through the membrane while the thick porous layer ensures structural integrity for the membranes. For gas separation, polymeric membranes can be separated into two general categories based on their glass transition temperature. Rubbery polymeric membranecan be operated above the glass transition temperature while glassy polymericmembrane can be operated below the glass transition temperature(Iarikov and Oyama, 2011, D. D. Larikov and S. T. Oyama, 2011).The glassy polymeric membraneis more effective in separating gas molecules based on size and shape than rubbery polymeric membrane. Meanwhile, the sorption coefficient of gases for rubbery polymeric membrane normally increased as the condensability of gases increased (Baker and Lokhandwala, 2008). The combination of glassy polymer and rubbery polymer could producemembrane with high permeation and high selectivity (Ghalei and Semsarzadeh, 2007). The domination of polymeric membranes in gas separation however has its limitation due to membrane plasticization at high pressure separation of natural gas. The most important plasticizing component in natural gas is carbon dioxide(Baker and Lokhandwala, 2008). Polymeric membranes also suffer from the limited choice of solvent, poor chemical stabilityand occurrence of swelling phenomenon that subsequently alter the membrane separation properties. Due to chemical degradation and thermal instability, their applications have been limited to separation processes (Goh et al., 2011).In addition, the performance of the polymeric membrane depends on the trade-off between selectivity and permeation. More permeable polymeric membranes are generally less selective. Consequently, polymeric membranes have not been able to significantly surpass the “upper bound” of the Robesonplot(Iarikov and Oyama, 2011).

In order to overcome the limitation of polymeric and inorganic membranes, MMM consisting of organic polymer and inorganic material has been developed and investigated. Inorganic materials with unique structure, surface chemistry and mechanical strength are used as the dispersed phase in MMM. The addition of inorganic materials in polymer matrix is expected to result in better membrane performance than the regular membranes(Aroon et al., 2010). The choice of polymer, inorganic phase and filler particle loading are the important parameters in preparing of MMM. Several factors that are important in designing the MMM are particle distribution and interfacial contact between polymer phase and dispersed fillersuch as a weak contact of particles in the polymer matrix and poor filler distribution which might cause particle agglomeration can affect the mixed matrix properties (Goh et al., 2011, Noble, 2011, Chung et al., 2007). Therefore, a comprehensive research on MMM should be conducted to obtain an optimum combination of the inorganic fillers to the polymeric phase.

1.2 Problem Statement

The synthesis of SAPO-44 zeolite as catalystfor the hydrocarbon cracking (Chen and Thomas, 1991) and oxygenate conversion process has been reported by several researchers (Liu et al., 2001). However, the fabrication of SAPO-44 zeolite membranein gas separationisa very challenging work. In the preparation of SAPO-44 zeolite membrane, template removal during calcinations process frequently results in crack crystals which may introduce large pores, affecting the actual molecular sieve effect of the membrane. About 0.5 – 0.9% contraction of the framework occurred at 340-400°C during template degradation and desorption(Geus and Van Bekkum, 1995). The thermal contraction may result in mechanical stress in zeolite layer and caused crack formation in zeolite membrane (Dong et al., 2000, Ahmad et al., 2010, Li et al., 2004). Dong et al. (2000) studied the template removal on MFI zeolite membrane. The MFI zeolite crystal framework shrinks during the template removal at 350-500°C. After template removal, the zeolite framework expands while the substrate shrinks upon cooling. A compression stress develops in the zeolite films during cooling process induce cracks. The thickness of the film is one of the factors responsible for defect formation during the calcinations process. Defects easily form in the thick membrane. Therefore, the synthesis conditions to control membrane thickness and template removal are essential to produce a good quality membrane(Dong et al., 2000).