

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

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SAPO-44 ZEOLITE FOR GAS SEPARATION**

**by**

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## LIST OF ABBREVIATIONS

Al	Aluminium
Al <sub>2</sub> O <sub>3</sub>	Aluminium Oxide
APMS	3-aminopropyl trimethoxy
Ar	Argon
ATR	Attenuated Total Reflectance
BET	Brunauer-Emmett Teller
CH <sub>4</sub>	Methane
CMS	Carbon molecular sieve
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
C <sub>6</sub> H <sub>13</sub> N	Cyclohexylamine
DC	Direct in-situ crystallization
DDR	Decadodecasil-3R
DI	Deionized water
DMAc	N, N-Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
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 <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Hydrogen Oxide
H <sub>2</sub> S	Hydrogen sulphide
i-C <sub>4</sub> H <sub>10</sub>	isobutene
L-L	Liquid-liquid
LMWA	Low molecular weight additive
MeOH	Methanol
MMM	Mixed Matrix Membrane
MW	Microwave
NMP	N-Methyl-2-Pyrrolidone
N <sub>2</sub>	Nitrogen
n-C <sub>4</sub> H <sub>10</sub>	n-butane
O <sub>2</sub>	Oxygen
P	Phosphorus
PDMS	Polydimethylsiloxane
PES	Polyethersulfone
Poly (RTIL)	Solid Polymerized Room-Temperature Ionic Liquid
PSf	Polysulfone
SAPO	Silicoaluminophosphate
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
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	Alfa-alumina

## LIST OF SYMBOLS

<b>Symbol</b>	<b>Description</b>	<b>Unit</b>
$T_g$	Glass Transition Temperature	°C or K
$\Delta p$	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 <sup>3</sup> /s
$A$	Effective membrane area	cm <sup>2</sup>
$l$	Effective membrane thickness	cm
$J_i$	Flux of component	mol/m <sup>2</sup> .s
$t$	Time	s or min
$T$	Temperature	°C or K
<b>Greek Letters</b>		
$\alpha_{i/j}$	Selectivity of component $i$ over component $j$	-
<b>Subscripts</b>		
$i, j$	Gas component CO <sub>2</sub> , N <sub>2</sub> , CH <sub>4</sub> , H <sub>2</sub>	-

**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  $\alpha$ -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<sub>2</sub> and N<sub>2</sub>, manakala untuk membran polimer, tambahan gas CH<sub>4</sub> dan H<sub>2</sub> telah dijalankan. Pembuangan templat yang dijalankan di 375°C menghasilkan keputusannya membran yang bebas daripada retakan dan penyasingan gas yang optimum (CO<sub>2</sub>/N<sub>2</sub> = 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 tanggahan 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<sub>2</sub> sebanyak 44.86 GPU. Pengeluaran gas CO<sub>2</sub> 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  $\alpha$ -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<sub>2</sub> and N<sub>2</sub>, while for polymeric membrane, additional CH<sub>4</sub> and H<sub>2</sub> permeation tests were also conducted. Calcination temperature conducted at 375°C formed defect-free SAPO-44 membrane with CO<sub>2</sub> displayed more permeable through the SAPO-44 zeolite membrane compare to N<sub>2</sub> (CO<sub>2</sub>/N<sub>2</sub> 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<sub>2</sub> permeance of 44.86 GPU. The CO<sub>2</sub> 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 methods which 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 summarized in 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

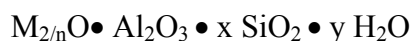
polymeric membranes were developed and tested at industrial scale (Kolsh and Schirmer, 1989).

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

<b>Separation</b>	<b>Process</b>
H <sub>2</sub> /N <sub>2</sub>	Ammonia purge gas
H <sub>2</sub> /CO	Syngas ratio adjustment
H <sub>2</sub> /CH <sub>4</sub>	Natural gas dehydration
H <sub>2</sub> /hydrocarbons	Hydrogen recovery in refineries
O <sub>2</sub> /N <sub>2</sub>	Nitrogen generation, oxygen-enriched air production
CO <sub>2</sub> /CH <sub>4</sub>	Natural gas sweetening, landfill gas upgrading
H <sub>2</sub> S/hydrocarbons	Sour gas treating
He/hydrocarbons	Helium separation
He/N <sub>2</sub>	Helium recovery
Hydrocarbons/air	Hydrocarbon recovery, pollution control
H <sub>2</sub> O/air	Air dehumidification
Volatile organic species (e.g., ethylene or propylene) Light gas (e.g., nitrogen)	Polyolefin purge gas purification

Inorganic membranes have high demand due to their high thermal and chemical stability. Three major types of inorganic membranes are currently available in the membrane market, namely zeolite 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 developing selective 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 synthesised 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 empirical formula is represented as:



where M represents the counterion, n represents the counterion valence, x is equal to or greater than 2 since  $AlO_4$  tetrahedra are only joined to  $SiO_4$  tetrahedra 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 several molecule gases. Nowadays, SAPO zeolite is one of the potentially effective membranes to be applied 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 wide variety 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 and ease 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 membranes can be operated above the glass transition temperature while glassy polymeric membranes can be operated below the glass transition temperature (Larikov and Oyama, 2011, D. D. Larikov and S. T. Oyama, 2011). The glassy polymeric membrane is 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 produce membrane 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 stability and 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 Robeson plot (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 fillers such 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 catalyst for 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 membrane in gas separation is a very challenging work. In the preparation of SAPO-44 zeolite membrane, template removal during calcination 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 calcination 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).