SILICALITE-1 MEMBRANE: SYNTHESIS, MODIFICATION, CHARACTERIZATION AND ITS PERFORMANCE FOR THE REACTIVE SEPARATION OF PARA-XYLENE FROM XYLENE ISOMERS

by

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LIST OF ABBREVIATIONS

Symbol	Description
AEL	Silicoaluminophosphate (SAPO-11)
AFI	Aluminophosphate (AIPO-5)
ANOVA	Analysis of variance
BEA	Zeolite Beta
BET	Brounar-Emmett-Teller
BPR	Back pressure regulator
CaO-ZSM-5	Calsium oxide loaded zeolite ZSM-5
^{13}C CP-MAS NMR	Carbon-13 cross polarization- magic angle spinning nuclear magnetic resonance
CCD	Central composite design
CHE	Ethylcyclohexenyl trimethoxysilane
CLD	Chemical liquid deposition
CMR	Catalytic membrane reactor
Cor total	Totals of all information corrected for the mean
CV	Check valve
CVD	Chemical vapor deposition
DDI	Double distilled deionized
DDR	Zeolite Decadodelcasil 3-R
DF	Degrees of freedom for the model
DMT	Dimethyl terephthalate
DoE	Design of experiments
DSL	Dual Site Langmuir
DTG	Derivative thermal gravity

EA	Elemental analysis
EDA	Ethylenediamine
Et_3N	Triethylamine
EPD	Electrophoretic deposition
FAU	Zeolite Faujausite
FER	Zeolite Ferrierite
FID	Flame ionization detector
FT-IR	Fourier transform infrared spectroscopy
F-value	Test for comparing model variance with residual (error) variance
GC	Gas chromatograph
HR-TEM	High resolution transmission electron microscopy
HR-XRD	High resolution X-ray diffraction
HZSM-5	Acid-loaded zeolite ZSM-5
IAST	Ideal Adsorbed Sorption Theory
LTA	Zeolite Linde Type A
MEL	Zeolite Socony Mobil-11 or ZSM-11
MFC	Mass flow controller
MFI	Zeolite Mobil Five (ZSM-5)
MgO-ZSM-5	Magnesium oxide loaded zeolite ZSM-5
MOR	Zeolite Mordenite
MP	Mercaptopropyltrimethoxysilane
3MP	3-Mercaptopropyltrimethoxysilane
MR	Membered-ring
MS	Maxwell–Stefan
MW	Molecular weight

NaA	Zeolite Sodium contained Linde Type A
NH_3-TPD	Ammonia temperature-programmed desorption
NV	Needle valve
ODE	Ordinary differential equation
OS	Organosilane source
PDE	Partial differential equation
PE	Phenethyltrimethoxysilane
PET	Polyethylene terephthalate
PG	Pressure gauge
PP	Polypropylene
Prob	Probability
Prob >F	Probability of seeing the observed F value if the null hypothesis is true (there is no factor effect)
PTA	Terephthalic acid
PV	Pervaporation
RAST	Real Adsorbed Sorption Theory
RSM	Response surface methodology
SAED	Selected area electron diffraction
SCCM	Standard centimeter cubic per minute
$SCCO_2$	Supercritical fluid silanation process
SDA	Structure directing agent
SEM	Scanning electron microscopy
^{29}Si MAS NMR	Silicon-29 magic angle spinning nuclear magnetic resonance
SOD	Zeolite Sodalite
SS	Stainless steel
SSR	Sum of squares of residuals

TBACl	Chloride tetrabutylammonium chloride
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TEOS	Tetraethylorthosilicate
TGA	Temperature gravimetric analysis
TMACl	Tetramethylammonium
TMB	Trimethylbenzene
TMMPS	Tris(methoxy)mercaptopropylsilane
TMS	Tetramethylsilane
TOS	Time on stream
TPA	Tetrapropylammonium
TPD	Temperature-programmed desorption
TPABr	Tetrapropylammonium bromide
TPAOH	Tetrapropylammonium hydroxide
VG	Vacuum gauge
VP	Vapor permeation
WHSV	Weight hourly space velocity
ZSM-5	Zocony Mobil Five

Greek Letters

p-xylene	para-xylene
m-xylene	meta-xylene
o-xylene	ortho-xylene

LIST OF SYMBOL

Symbol	Description	Unit
-	Low level	-
+	High level	-
a	Crystal orientation of silicalite-1	-
a_s	Surface area of the adsorbent	m^2/kg
A	Factor code for temperature in DoE	-
b	Crystal orientation of silicalite-1	-
B	Factor code for *p*-xylene feed partial pressure in DoE	-
[B]	Matrix of Fick's diffusivities	m^2/s
c	Crystal orientation of silicalite-1	-
c_i^F	Concentration of species *i* in feed	mol/m^3
c_i^P	Concentration of species *i* in permeate	mol/m^3
c_i^R	Concentration of species *i* in retentate	mol/m^3
c_{mx}	Concentration of *m*-xylene	mol/m^3
$c_{mx,r}$	Reference concentration of *m*-xylene	mol/m^3
c_{ox}	Concentration of *o*-xylene	mol/m^3
$c_{ox,r}$	Reference concentration of *o*-xylene	mol/m^3
c_{px}	Concentration of *p*-xylene	mol/m^3
$c_{px,r}$	Reference concentration of *p*-xylene	mol/m^3
C	Factor code for *p*-xylene feed composition in feed in DoE	-
C_{mx}	Dimensionless *m*-xylene concentration	-
C_{ox}	Dimensionless *o*-xylene concentration	-
C_{px}	Dimensionless *p*-xylene concentration	-

d_i	Individual desirability in DoE	-
d_p	Average pore diameter	nm
D_e	Total desirability in DoE	-
D_i	Diffusivity of component *i*	m^2/s
$Đ_i$	Maxwell–Stefan's diffusivity of species *i* in the membrane	m^2/s
$Đ_{ij}$	Maxwell–Stefan's diffusivity for interchange between *i* and *j*	m^2/s
$Đ_{12}$	Maxwell–Stefan's diffusivity of 1–2 binary mixture	m^2/s
[*D*]	Square matrix of inverse Maxwell–Stefan coefficients	s/m^2
E_a	Activation energy in Eyring's equation	kJ/mol
E_1	Activation energy of *m*-xylene to *p*-xylene	kJ/mol
E_2	Activation energy of *m*-xylene to *o*-xylene	kJ/mol
E_3	Activation energy of *o*-xylene to *p*-xylene	kJ/mol
E_{-1}	Activation energy of *p*-xylene to *m* –xylene	kJ/mol
E_{-2}	Activation energyof *o*-xylene to *m*-xylene	kJ/mol
E_{-3}	Activation energy of *p*-xylene to *o*-xylene	kJ/mol
F_{px}	Actual code for p-xylene feed composition in DoE	-
(h0h)	Crystal orientation of silicalite-1	-
ΔH_{iA}	Adsorption enthalpy for site A	kJ/mol
ΔH_{iB}	Adsorption enthalpy for site B	kJ/mol
k_1	Rate constant of *m*-xylene to *p*-xylene	min^{-1}
k_2	Rate constant of *m*-xylene to *o*-xylene	min^{-1}
k_3	Rate constant of *o*-xylene to *p*-xylene	min^{-1}
k_{-1}	Rate constant of *p*-xylene to *m* –xylene	min^{-1}
k_{-2}	Rate constant of *o*-xylene to *m*-xylene	min^{-1}

k_{-3}	Rate constant of *p*-xylene to *o*-xylene	min^{-1}
k_o	Frequency factor in reaction kinetic	min^{-1}
$K_{i,A}$	Equilibrium constant of component *i* at adsorption site A	kPa^{-1}
$K_{i,B}$	Equilibrium constant of component *i* at adsorption site B	kPa^{-1}
M	Mole of xylene	mol/s
M_{ox}	Moles of *o*-xylene transferred per unit time	mol/s
M_{px}	Moles of *p*-xylene transferred per unit time	mol/s
N_{cal}	Predicted flux	$mol/m^2.s$
N_{exp}	Experimental flux	$mol/m^2.s$
N_i	Molar flux of species *i*	$mol/m^2.s$
n	Number of diffusing species	-
p/p_o	Relative pressure for nitrogen adsorption-desorption measurement	-
p/p_s	*p*-xylen*e* activity	-
p_i	Partial pressure of species *i*	kPa
$p_i^0(\Pi)$	The equilibrium gas-phase pressure (IAST)	kPa
P	System pressure	kPa
P_{px}	Actual code for p-xylene feed partial pressure in DoE	kPa
q_i	Amount adsorbed in molecular loading of species *i*	mol/kg
$q_{i,sat}$	Saturation loading of species *i*	mol/kg
$q_{i,sat,A}$	Saturation molecular loading of site A	mol/kg
$q_{i,sat,B}$	Saturation molecular loading of site B	mol/kg
$[q_{sat}]$	Diagonal matrix with the saturation loading	mol/kg
q_i^o	Amount of single component adsorbed in molecular loading	mol/kg

Q^F	Total volumetric flow rate of feed	m^3/min
Q^P	Total volumetric flow rates of permeate	m^3/min
Q^R	Total volumetric flow rate of retentate	m^3/min
r_{mx}	Rate of reaction of *m*-xylene	mol/m^3min
r_{ox}	Rate of reaction of *o*-xylene	mol/m^3min
r_{px}	Rate of reaction of *p*-xylene	mol/m^3min
R	Universal gas constant	J//mol.K
R^2	Correlation coefficient	-
ΔS_{iA}	Adsorption entropy for site A	J/mol.K
ΔS_{iB}	Adsorption entropy for site B	J/mol.K
S_{BET}	BET surface area	m^2/g
$S_{px/ox}$	Predicted Separation factor of *p*-/*o*-xylene	-
t	Time	min
T	Temperature	K
V	Sample volume	ml
V_{mic}	Micro-pore volume	cm^3/g
V_{tot}	Total pore volume	cm^3/g
W	Membrane weight	g
x_i	Molar fraction of component *i* in adsorbed phase	-
X_{mx}	Mole fraction of *m*-xylene	-
X_{ox}	Mole fraction of *o*-xylene	-
X_{px}	Mole fraction of *p*-xylene	-
y_i	Molar fraction of component *i* in gas phase	-
Y	Predicted response	-
z	Distance coordinate along membrane, m	m

Greek letters

a	Membrane area	m^2
α	Catalyst deactivation constant	min^{-1}
α_1	Distance of the axial point from center in DoE	-
$\alpha_{px/ox}$	*p-/o*-xylene separation factor	-
$\alpha_{px/mx}$	*p-/m*-xylene separation factor	-
β_o	Offset term in DoE model	-
$\beta_1, \beta_2, \beta_3$	Linear terms in DoE model	-
$\beta_{11}, \beta_{22}, \beta_{33}$	Quadratic terms in DoE model	-
$\beta_{12}, \beta_{13}, \beta_{23}$	Interaction terms in DoE model	-
X	Dimensionless membrane thickness	-
δ	Thickness of membrane	m
ε	Dimensionless volumetric flow rate for permeate	-
Γ	Thermodynamic correction factor	-
$[\Gamma]$	Matrix of thermodynamic factors	-
γ	Dimensionless volumetric flow rate for retentate	-
μ_i	Molar chemical potential, J/mol	-
Φ^2_{mx}	Thiele modulus for *m*-xylene	-
Φ^2_{ox}	Thiele modulus for *o*-xylene	-
Φ^2_{px}	Thiele modulus for *p*-xylene	-
ψ_{ox}	Dimensionless reference *o*-xylene concentration	-
ψ_{px}	Dimensionless reference *p*-xylene concentration	-
ρ	Density of silicalite-1 membrane	kg/m^3
Π	Spreading pressure (IAST)	kPa
τ	Residence time	min

θ_i	Fractional occupancy of component *i*	-
τ_{mx}	Dimensionless diffusion coefficient for *m*-xylene	-
τ_{ox}	Dimensionless diffusion coefficient for *o*-xylene	-
τ_{px}	Dimensionless diffusion coefficient for *p*-xylene	-
ζ	Dimensionless reaction rate constant	-
Subscripts		
A	Refer to site A	-
B	Refer to site B	-
1	Component 1 (*p*-xylene) in binary mixture	-
2	Component 2 (*o*-xylene) in binary mixture	-
sat	Saturation loading conditions	-
i, j	Component in the mixture, *p*-xylene, *o*-xylene and *m*-xylene	-
Superscripts		
F	Feed	-
P	Permeate	-
R	Retentate	-
Operators		
∇	Gradient	-
Vector and matrix notation		
( )	Component vector	-
[ ]	Square matrix	-

MEMBRAN SILIKALIT-1: SINTESIS, MODIFIKASI, PENCIRIAN DAN PRESTASI BAGI PEMISAHAN REAKTIF PARA-XILENA DARI ISOMER-ISOMER XILENA

ABSTRAK

Pemisahan reaktif para-xilena dari isomer-isomer xilena dalam reactor membran bermangkin adalah bergantung kepada pilihan membran bermangkin yang sesuai. Membran ini seharusnya memangkinkan tindak balas pengisomeran xilena, dan juga memisahkan para-xilena (*p*-xylene) dari isomer-isomernya (*ortho*-xilena (*o*-xilena) dan *meta*-xilena (*m*-xilena)). Dalam kajian ini, membran silicalit-1 dan dua jenis membran silikalit-1 berfungsikan asid: (1) membran silicalit-1 berfungsikan asid propilsulfonik dan (2) membran silicalit-1 berfungsikan asid arenasulfonik telah disintesiskan di atas α-alumina yang berbentuk cakera, yang dipra-salut dengan lapisan silika berliang meso. Sifat-sifat fizik dan kimia membran-membran telah dikaji dengan menggunakan teknik-teknik yang berbeza seperti XRD, SEM, TEM, ^{29}Si MAS NMR, ^{13} CCP-MAS NMR, FTIR, TGA, EA, NH_3-TPD, pentitratan asid-bes, penjerapan-penyahjerapan nitrogen. Penerapan nitrogen and ujian permporosimetri dijalankan untuk menilai kualiti dan kewujudan liang-liang bukan-zeolit dalam membran.

Reka bentuk eksperimen diaplikasikan dalam proses pengoptimuman pemisahan *p*-xilena daripada campuran dedua *p-/o*-xilena dan campuran tetiga *p-/o-/m*-xilena dengan menggunakan membran silikalit-1. Fluks *p*-xilena yang optimum sebanyak 3.83 x 10^{-6} mol/m^2.s dan faktor pemisahan *p-/o*-xilena sebanyak 46 telah diperolehi pada suhu 198 ^{o}C, tekanan separa *p*-xilena dalam suapan sebanyak 0.15 kPa dan komposisi suapan *p*-xilena sebanyak 0.80. Fluks *p*-xilena yang optimum

sebanyak 5.94 x 10^{-6} mol/m^2s, faktor pemisahan *p-/o*-xilena sebanyak 19 and pemisahan faktor *p-/m*-xilena sebanyak 20 telah dicapai pada suhu 198 ^{o}C, tekanan separa *p*-xilena sebanyak 0.22 kPa dalam pemisahan campuran tetiga isomer xilena. Model resapan *Maxwell-Stefan*, dengan kombinasi teori larutan jerap unggul dan parameter penjerapan satu-komponen telah digunakan untuk meramalkan fluks penerapan *p*-xilena dan *o*-xilena dalam campuran *p-/o*-xilena melalui membran silicalit-1 pada julat suhu 150 ^{o}C- 250 ^{o}C.

Aktiviti bermangkin dalam tindak balas pengisomeran *m*-xilena bagi membran silicalit-1 berfungsikan asid telah diuji dalam julat suhu dari 355 ^{o}C ke 450 ^{o}C. Pada suhu 450 ^{o}C, penukaran *m*-xilena adalah sebanyak 57 % dengan hasil *p*-xilena sebanyak 33 % bagi membran silicalit-1 berfungsikan asid arenasulfonik yang disintesis dengan menggunakan 15 mol% pheniltiltrimetoksisilana sebagai sumber organosilana. Peningkatan dalam hasil xilena adalah disebabkan oleh pemisahan produk tindak balas melalui membran bermangkin, yang menunjukkan kestabilan struktur selepas beroperasi selama 120 jam. Skim tindak balas segitiga berdasarkan model masa aliran telah digunakan untuk menentukan parameter kinetik bagi pengisomeran *m*-xilena dalam julat suhu 355 ^{o}C ke 450 ^{o}C dengan menggunakan membran silicalit-1 berfungsikan asid. Suatu model berdasarkan kinetik-kinetik tindak balas dan kadar resapan berkombinasi dengan persamaan-persamaan imbangan jisim isomer-isomer xilena dalam reaktor membran bermangkin telah dicadangkan. Model persamaan-persamaan itu telah disimulasikan untuk mendapatkan susuk kepekatan merentasi membran. Model itu menerangkan kombinasi tindak balas pengisomeran xilena dan pemisahan dalam reaktor membran bermangkin menggunakan membran silicalit-1 berfungsikan asid.

SILICALITE-1 MEMBRANE: SYNTHESIS, MODIFICATION, CHARACTERIZATION AND ITS PERFORMANCE FOR THE REACTIVE SEPARATION OF PARA-XYLENE FROM XYLENE ISOMERS

ABSTRACT

Reactive separation of para-xylene from xylene isomers in a catalytic membrane reactor depends on the right choice of catalytic membrane. This membrane should not only catalyze xylene isomerization reaction but also separate para-xylene (*p*-xylene) from its isomers (ortho-xylene (*o*-xylene) and meta-xylene (*m*-xylene)). In the present study, silicalite-1 and two types of acid-functionalized silicalite-1 membranes: (1) propylsulfonic acid-functionalized silicalite-1 membrane and (2) arenesulfonic acid-functionalized silicalite-1 membrane were synthesized on disc type α-alumina support, pre-coated with mesoporous silica layer. The physical and chemical properties of the membranes were characterized using different techniques such as XRD, SEM, TEM, ^{29}Si MAS NMR, ^{13}C CP-MAS NMR, FTIR, TGA, EA, NH_3-TPD, acid-base titration and nitrogen adsorption–desorption. The nitrogen permeation and permporosimetry tests were conducted to evaluate the quality and the presence of non-zeolite pores in the membranes.

Design of experiments (DoE) was applied in the optimization process of *p*-xylene separation from *p*-/*o*-xylene binary mixture and *p*-/*o*-/*m*-xylene ternary xylene mixture using silicalite-1 membrane. The optimum *p*-xylene flux of 3.83 x 10^{-6} mol/m^2.s and *p*-/*o*-xylene separation factor of 46 were obtained at a temperature of 198 ^{o}C, *p*-xylene feed partial pressure of 0.15 kPa and *p*-xylene feed composition of 0.80. The optimum *p*-xylene flux of 5.94 x 10^{-6} mol/m^2.s, *p*-/*o*-xylene separation factor of 19 and *p*-/*m*-xylene separation factor of 20 were achieve at

temperature of 198 ^{o}C and *p*-xylene feed partial pressure of 0.22 kPa in ternary xylene mixture separation. The Maxwell-Stefan diffusion model, in combination with the Ideal Adsorbed Solution (IAS) theory and single-component adsorption parameter were used to predict the permeation flux of *p*-xylene and *o*-xylene for binary xylene mixture through a silicalite-1 membrane in the temperature range of 150 ^{o}C – 250 ^{o}C.

Acid-functionalized silicalite-1 membranes were tested for their catalytic activity in *m*-xylene isomerization reaction in the temperature range of 355 ^{o}C to 450 ^{o}C. At 450 ^{o}C. *m*-xylene conversion was 57 % with 33 % *p*-xylene yield over arenesulfonic acid-functionalized silicalite-1 membrane, synthesized using 15 mol% of phenelthytrimethoxysilane as an organosilane source. The enhancement in *p*-xylene yield was due to the continuous separation of the reaction products through the catalytic membrane, which exhibited good structural stability for 120 hours of operation. A triangular reaction scheme based on time on stream (TOS) model was used to determine the kinetic parameters for *m*-xylene isomerization in the temperature range of 355 ^{o}C to 450 ^{o}C using acid-functionalized silicalite-1 membranes. A model based on the reaction kinetics and rate of diffusion combined with the mass balance equations of xylene isomers in catalytic membrane reactor was proposed. The model equations were simulated to obtain concentration profile of xylene isomers across the membrane. The model described the combined xylene isomerization reaction and separation in the catalytic membrane reactor using acid-functionalized silicalite-1 membrane.

CHAPTER 1

INTRODUCTION

Xylene has three isomers namely *p*-xylene, *m*-xylene and *o*-xylene and used as industrial solvents or intermediates for many derivatives (Xomeritakis *et a*l., 2001; Lai *et al*., 2003). Isophthalic acid is produced from the oxidation of *m*-xylene and used in the manufacturing of unsaturated polyester resins. *o*-xylene is the raw material for the synthesis of phthalic anhydride which is used in the production of phthalate plasticizers. Among the three xylene isomers, *p*-xylene is the most industrially used isomer and therefore, has the largest commercial market. The isomer *p*-xylene is the feed for the production of pure terephthalic acid (PTA) and dimethyl terephthalate (DMT). PTA as well as DMT are the feed stocks for polyethylene terephthalate (PET) synthesis which in turn is used in the polyester resin and fibers production. The world wide demand for *p*-xylene increased from 19.3 million tons in year 2003 (US$535/metric tonne) to 30.3 million tonnes (US$1,140/metric tonne) in year 2009, with an average growth rate of 7.8% (Online Library, 2003; Online Library, 2009a). Due to increase in the global demand of *p*-xylene and current expensive industrial processes, researchers have been searching for alternatives to decrease the energy consumption and operating cost for *p*-xylene production.

1.1 Industrial Production of *p*-xylene

The industrial production and recovery of *p*-xylene is an important operation in a large petrochemical plant. *p*-xylene is currently produced through two different routes: 1) separation of *p*-xylene from its isomers and 2) isomerization of isomer *m*-xylene or *o*-xylene to *p*-xylene. Separation of *p*-xylene from its isomers is difficult

because of their close boiling points (*p*-xylene: 138 ^{o}C, *m*-xylene: 139 ^{o}C and *o*-xylene:144 ^{o}C). Xylenes isomers are currently separated by cryogenic crystallization, or selective adsorption process such as UOP's Parex and IFP's Eluxyl processes, which are highly energy intensive (Online Library, 2006a).

UOP's Parex-Isomar and ExxonMobil's XyMax are the processes for *p*-xylene production based on isomerization of mixed xylenes using advanced catalyst (Online Library, 2002; Online Library, 2006b). Toluene disproportionation is an alternative route to produce *p*-xylene, but, benzene is produced as a co-product. The current technology for *p*-xylene production involves complex operations with high capital cost and high energy consumption.

1.2 Membrane Based Technology

1.2.1 Membrane Separation Processes

Membrane-based separation processes were first introduced at the early 18th century and found their applications in petrochemical, food and pharmaceutical industries, biotechnology and variety of environmental abatement processes (Marcano and Tsotsis, 2002). The advantages of membrane separation process over most of the conventional separation processes are reported to be energy savings as well as reduction in the initial capital investment cost (Marcano and Tsotsis, 2002). A membrane is a permeable or semi-permeable phase in a form of thin film made from the variety of materials ranging from inorganic materials to different types of polymers. The membrane is able to act as a barrier to separate different species by controlling the exchange of species between two adjacent fluid phases. The basic membrane separation process is shown in Figure 1.1; where the species retained in

the fluid stream defined as retentate, and another fluid stream is defined as permeate contains species passing through the membrane.

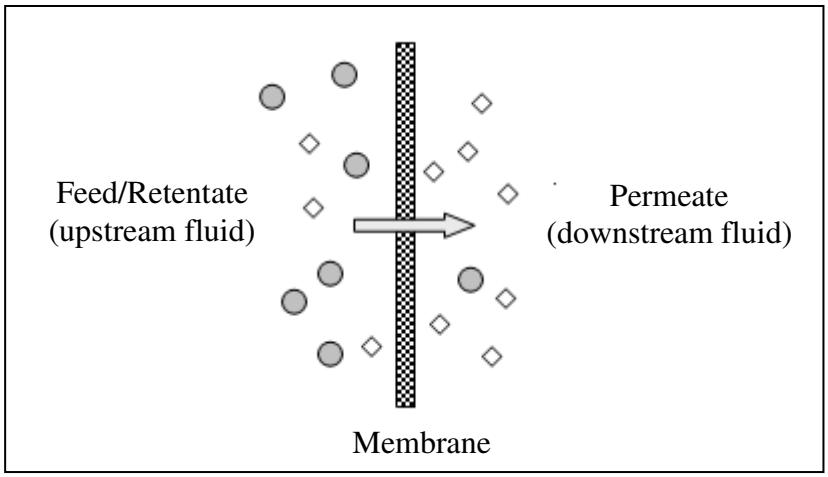

Figure 1.1: Schematic of the basic membrane separation principle (Hsieh, 1996)

The factors that contribute to the transport process across the membrane are driving force, associated with a gradient of concentration, pressure and temperature. Permeability and permselectivity are the two important parameters in evaluating the membrane performance. Permeability is defined as the flux (molar or volumetric) flow through the membrane with respect to its thickness and driving force; whereas the permselectivity is the ability of the membrane to separate the given species, which is also defined as the ratio of individual permeabilities for the two species.

1.2.2 Membrane Separation Process with Catalytic Reaction

There has been significant interest in the membrane-based reactive separation processes. In reactive separation process, there are two distinct processes, (i) reaction and (ii) separation in a single unit operation. Catalytic membrane reactor has attracted attention in catalytic reaction application due to their potential for

substantial savings in the processing cost and less capital investment in these types of arrangement.

The conventional-type packed bed reactor and fluidized bed reactor are usually operated below equilibrium conversion in order to minimize undesired reactions. In membrane-based reactive separation processes, the synergistic effect of separation and reaction occurs simultaneously within a single unit and results in the enhancement of:

i) Conversion. Moles of reactant converted/moles of reactant in the feed. The role of the membrane is to act as a catalyst (Tarditi *et al*., 2008a).

ii) Yield. Moles of desired products form/moles of reactant in the feed. The role of the membrane is principally to remove a reaction product selectively from the reactor for equilibrium-limited reactions. This is particularly useful for reactions limited by thermodynamic equilibrium reactions (Marcano & Tsotsis, 2002).

iii) Selectivity. Moles of desired products form/moles of reactant converted. The role of the membrane is to dose a reactant that may react in successive reactions (feed distribution). The concentration of the reactants is kept low by controlled addition through the membrane. In this way, the side reactions and further reaction of the desired product to the undesired one could be minimized (Ozdemir *et al*., 2006).

1.3 Zeolite Membrane

Zeolites are crystalline, microporous aluminosilicates which find extensive industrial use as catalysts, adsorbents, and ion exchangers with high capacities and

selectivities (Bhatia, 1990; Motuzas *et al*., 2005). When zeolite is grown as films, zeolite membrane is formed. Zeolite membranes or films have been in focus in recent years because of their well-defined micropore structure, good thermal and structural stability. The characteristics of zeolite membrane have opened up its potential application in membrane reactor, catalytic membrane reactor and chemical and gas sensors (Keizer *et al*., 1998; Bonilla *et al*., 2001; Nair *et al*., 2001; Bernal *et al*., 2001; Lai *et al*., 2004). One particular process in which zeolite membrane might offer significant advantage compared to existing technology is the separation of close-boiling point hydrocarbons that are difficult to be separated by distillation or other complex and energy-intensive processes (Nair *et al*., 2001). Currently, zeolite membrane is also reported for application in corrosion protection and antimicrobial coatings (Cheng *et al*., 2001, McDonnell *et al*., 2005). Figure 1.2 shows the path from zeolite to zeolite membrane and its application. Three common types of zeolite used for industrial processes, i.e. ZSM-5 (Zocony Mobil Five), FAU (Faujausite) and BEA (beta) are shown in the Figure 1.2.

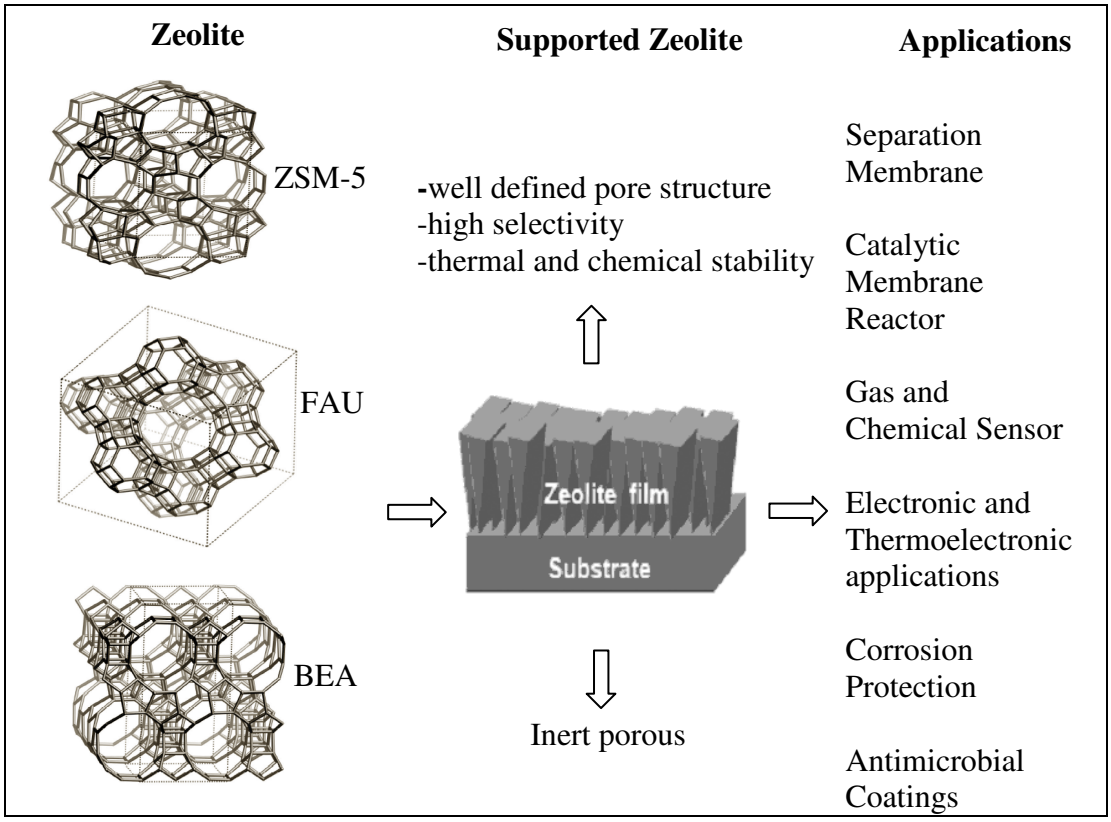

Figure 1.2: Path from zeolites to zeolite membranes and their application (Tsapatsis, 2004)

Zeolite composed of different types of framework structure and pore size. Table 1.1 shows the pore openings of different types of zeolite used in the industry (Baerlocher *et al*., 2001). Although there are more than 160 types of zeolites being synthesized, not all these zeolites can be grown into membranes. The synthesis methodology developed for zeolite powder does not guarantee the formation of a continuous polycrystalline thin film. A number of zeolites that have been synthesized as zeolite membrane include MFI (Lai *et al*., 2004; Tarditi *et al.*, 2006a; Gu *et al*., 2006), FAU (Nikolakis *et al*., 2001; Jeong *et al*., 2003), BEA (Wang *et al*., 2001; Maloncy *et al*., 2005) , MOR (Navajas *et al*., 2006) , LTA (Aoki *et al*., 2000), FER (Jia and Murad, 2005), DDR (Tomita *et al*., 2004), MEL (Li *et al*., 2002) and SAPO-34 (Li *et al*., 2004).

Table 1.1: Code and kinetic diameter of selected zeolites (Baerlocher *et al*., 2001)

Zeolite (code)	**Kinetic diameter (Å)**
Zeolite Socony Mobil-5 or ZSM-5 (MFI)	5.3 x 5.6
Ferrierite (FER)	3.5 x 4.8
Faujasite (FAU)	7.4 x 7.4
Mordenite (MOR)	6.5 x 7.0
Linde Type A (LTA)	4.1 x 4.1
Zeolite Socony Mobil-11 or ZSM-11 (MEL)	5.3 x 5.4
Beta (BEA)	7.3 x 6.0
Deca-dodecasil 3R (DDR)	3.6 x 4.4
Aluminophosphate (AIPO-5, AFI)	7.3 x 7.3
Silicoaluminophosphate (SAPO-11, AEL)	3.9 x 6.3

Among the zeolite membranes, zeolite MFI membranes (ZSM-5 and Silicalite-1) are the most common membranes studied by the researchers and thus, relatively large information available for its synthesis and application in the literature. The pore structure of MFI zeolite is near to the size of many industrially important organic molecules. Therefore, its membrane can be used for the separation of organic compounds with kinetic diameters close to its pores. Zeolite MFI membrane has the pore structure of straight (b-oriented), circular pores (0.54 x 0.56 nm) interconnected with sinusoidal (a-oriented), elliptical pores (0.51 x 0.54 nm) and a tortuous path along the c-direction (Lai *et al*., 2004). Figure 1.3 shows a schematic of the 3-dimensional pore structure of MFI zeolites (ZSM-5 and Silicalite-1). The pore diameters of the important organic molecules are presented in Table 1.2.

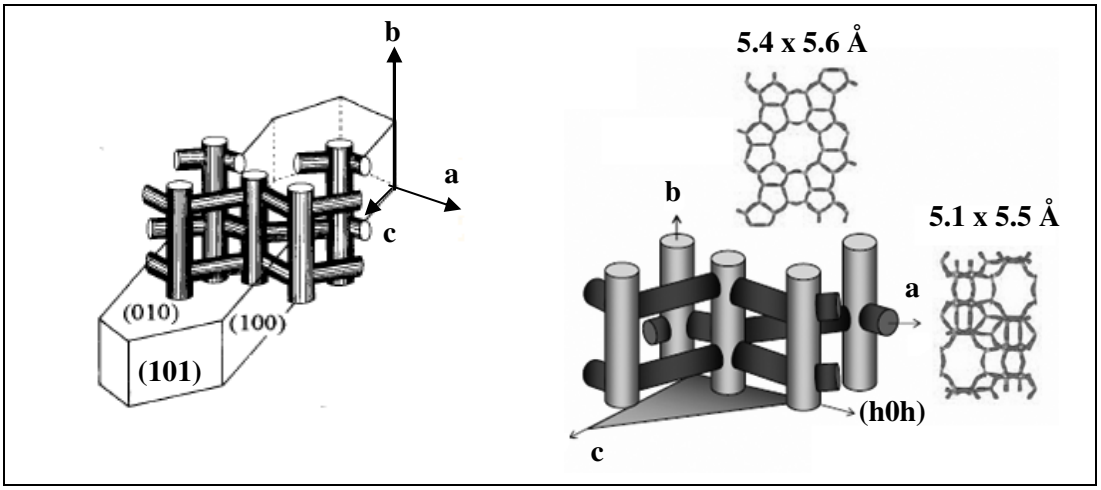

Figure 1.3: 3-dimensional pore structure of MFI zeolites (ZSM-5 and Silicalite-1) (Lai *et al*., 2004b, Tsapatsis, 2004)

Table 1.2: Kinetic diameter of selected organic molecules (Lai *et al*., 2004a)

Molecule	**Kinetic Diameter (angstrom,Å)**
p-xylene	5.85
m-xylene	6.80
o-xylene	6.80
cyclohexane	6.00
n-hexane	4.30
benzene	5.85
dimethylbutane	6.20

1.3.1 Separation of Xylene Isomers using Zeolite Membrane

MFI-type zeolite membrane could be used to separate close boiling point xylene isomers due to the kinetic diameters of xylene molecules are close to the pore structure of the membrane (Table 1.1). Unlike distillation processes, the separation mechanism in zeolite membrane is not based on the relative volatility of components, but on the difference in sorption and diffusion properties of the feed substances as well as molecular sieve effect of the membrane (Hedlund *et al*., 1999; Nikolakis *et al*., 2001; Jeong *et al*., 2003; Lai *et al*., 2003; Dyk *et al*., 2005). The

typical molecular structure of xylene isomers is shown in Figure 1.4. During the past few years, separation of xylene isomers using MFI-type zeolite membrane has been reported by various researchers and achieved only a little success due to the microscopic defects present in the membrane (Xomeritakis *et al*., 2001; Lai *et al*., 2003; Taridit *et al*., 2006). Therefore, high flux and high selectivity zeolite membranes should be developed.

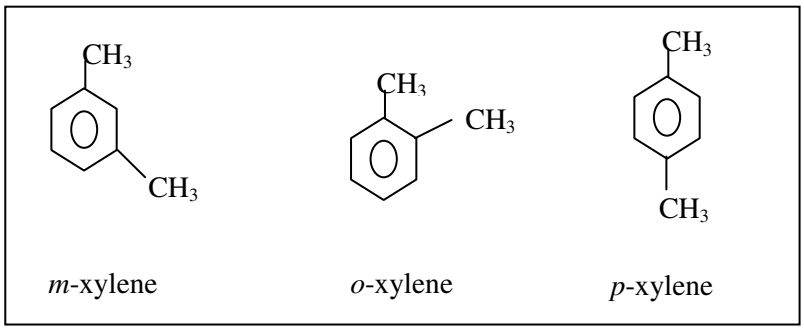

Figure 1.4: Typical molecular structure of xylenes (Morin *et al*., 1997)

1.3.2 Catalytic Zeolite Membrane for Combined Xylene Isomerization and Separation

In order to meet the *p*-xylene demand, ortho- and meta-xylenes are converted via the xylene isomerization reaction, a major industrial process for the production of *p*-xylene. Xylene isomerization is a thermodynamic equilibrium restricted reaction, and therefore, 100% conversion is not possible under conventional conditions. The xylene isomerization is an acid-catalyzed reaction and most of the isomerization plants are using zeolite based catalysts. It is well-known that xylenes undergo two main competitive reactions, i.e. isomerization and disproportionation (Figure 1.5) over zeolite catalysts (Morin *et al*., 1996; Yu *et al.*, 1996; Morin *et al*., 1998; Guisnet *et al*., 2000). Thus, it is desired to minimize disproportionation in favor of isomerization reaction, especially to para-isomer.

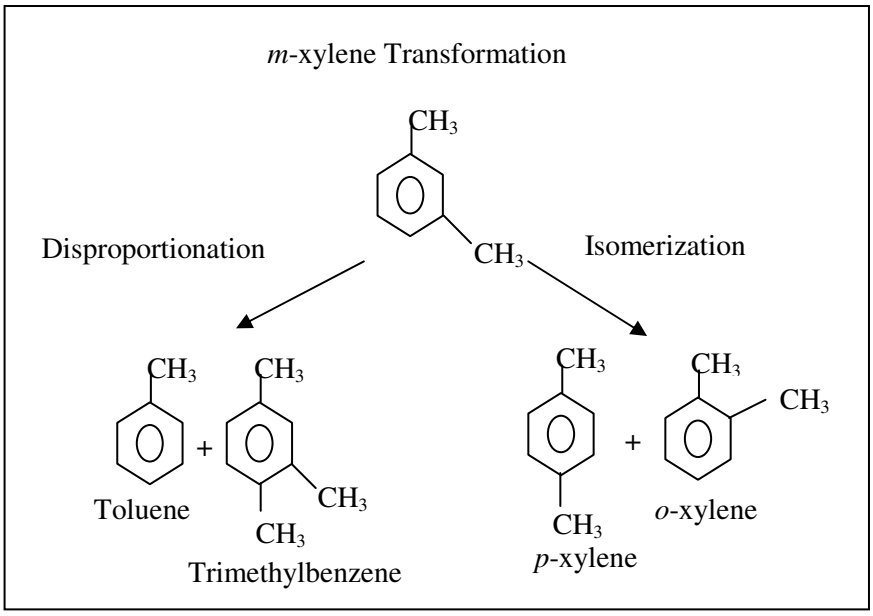

Figure 1.5: *m*-xylene transformation (Morin *et al*., 1997)

The application of zeolite membrane as catalytic membrane reactor for xylene isomerization and simultaneous separation could be a good alternative to increase conversion, selectivity and yield by selective removal of the product from the reactor (Dyk *et al*., 2005; Stephane Haag *et al*., 2006; Tarditi *et al*., 2008a; Zhang *et al*., 2009). The combined separation and reaction in a single unit provides better flexibility of operation and enhancement in the reaction process as well as reducing energy consumption, improving operation safety, and miniaturizing the reactor system (Tarditi *et al.*, 2008a). The zeolite-based catalytic membrane reactor generally consists of a supported permselective layer (membrane) that simultaneously acts as catalyst (catalytic membrane reactor, CMR). The prospects of catalytic zeolite membrane reactor need to be studied so that the technology is economically competitive.

1.4 Modification of Zeolite for Combined Xylene Isomerization and Separation

Recently, researchers have explored the possibility of adding chemical functionalities into the zeolites structure with organic groups, to develop organic-functionalized molecular sieve material, a new class of catalysts with organic active sites (Jones *et al*., 2001). Therefore, the acid functionalized zeolite crystal has been studied as heterogeneous catalyst for number of reactions (Shin *et al*., 2000; Monique *et al*., 2004).

Acid-functionalized zeolite membrane can be used as catalytic membrane for combined xylene isomerization reaction and separation in a single reactive separation step. The acidic functional group present in the membrane could become the active reaction site for the isomerization reaction. This type of process intensification could increase yield of *p*-xylene. At the same time, more efficient heat integration along with the simultaneous reaction and separation could be achieved in a single unit resulting in substantial savings. Figure 1.6 shows schematic of the combined reaction and membrane separation process. *m*-xylene is used as feed reactant and isomerization reaction occurred in the acid-functionalized silicalite-1 membrane to produce *p*-xylene and *o*-xylene. The reaction products are subsequently removed from the retentate.

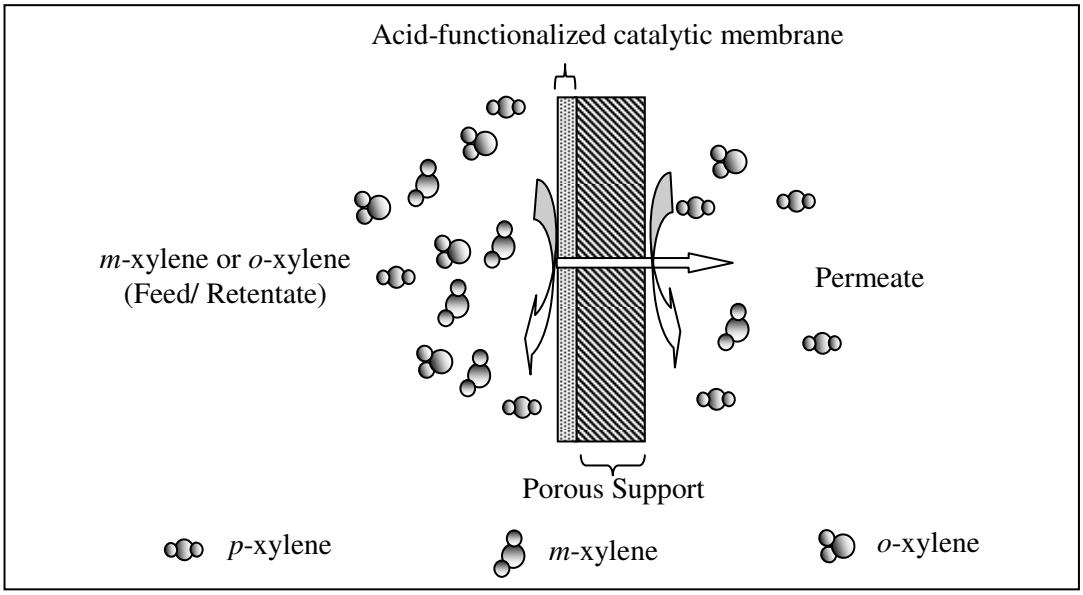

Figure 1.6: Schematic of combined xylene isomerization and separation in a single stage of operation using acid-functionalized catalytic membrane reactor

1.5 Problem Statement

The current technologies for *p*-xylene production and recovery consume high energy and incur high operating cost. Due to the increasing demand and rising price of *p*-xylene over the global market, researchers have devoted considerable effort over the past 10 years in finding economic process route for the production and recovery of *p*-xylene. MFI-type zeolite membrane emerged as a potential effective alternative to be used in a membrane reactor.

The synthesis of a well-intergrown and high quality (thin, compact and low defects) silicalite-1 (MFI type zeolite) membrane still poses many challenges for various researchers. During the synthesis and template removal steps, defects such as intercrystalline boundary and cracks can easily form. A high quality membrane is needed for the separation of xylene isomers because a minor defect in the membrane structure will affect the separation performance. Although the methods to produce minimum defects zeolite membrane have been reported in the literature (Hedlund *et*

al., 2002, Bernal *et al*., 2004), the results are not reproducible which are mainly due to the complex mechanism of zeolite crystal growth that has not been fully understood. Hence, reproducibility of the synthesis method is another challenging task for the synthesis of zeolite membrane.

Most of the xylene separation studies using MFI type zeolite membrane reported in the literature have focused on the effect of membrane quality such as orientation, thickness, microstructure and defects. The effect of separation process variables such as temperature, xylene feed composition and feed partial pressure, as well as their interactions are not systematically investigated. To the best of our knowledge, optimization of the operating process variables in xylene separation has not been reported. Therefore, there is a need to use the statistical approach to study the separation performance of the membrane. This approach with minimum number of experiments will provide information about i) interactions between the process variables, ii) important variables in the separation process and iii) identification of the optimum operating condition. The conventional approach reported in the literature for the study needs large number of experiments using one process variable studied at a time and keeping other variables constant. This one-factor-at-a-time method generally fails 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.

Although the reported results show the potential of H-ZSM-5 in membrane reactors for xylene isomerization; the membrane shows moderate to low selectivity

of *p*-xylene (Kim *et al*., 1998; Zheng *et al*., 2006). There is a need to synthesize a catalytic membrane with improved conversion, *p*-xylene yield and *p*-xylene separation rate. Silicalite-1 membrane has shown good performance in *p*-xylene separation, due to its higher diffusion rate compared to its isomers, *m*-xylene and *o*-xylene (Stephane Haag *et al*., 2006). However, silicalite-1 is an aluminum-free analogue of ZSM-5 (Si/Al = ∞) which is catalytically inactive in its pure form. The selective and continuous removal of *p*-xylene from the reaction system could enhance the xylene isomerization toward higher selectivity and yield. Therefore, it has drawn an interest in the synthesis of silicalite-1 membrane with catalytic acid sites.

In order to introduce the acid sites in silicalite-1 membrane, organic-functional groups could be added into the synthesis mixture. Jones *et al.* (1999) reported that the introduction of organic group into the zeolite micropore is difficult due to the large size of organic species, which resulted in a disruption of the crystal structure and multiphase, and thus, crystalline/amorphous mixture is produced. The transformation of organic-functional group present in the amorphous phase to organosulfonic acid group resulted in the formation of acid-functionalized zeolite. The main advantage of this material is the absence of pore blockage in the zeolite crystalline phase and most of the acid sites are located in the amorphous phases of the structure.

However, the synthesis of acid-functionalized silicalite-1 catalytic membrane using organo-functional group is a new task and therefore imposes many challenges. The problems encounters for the synthesis of this new-type membrane are:

- Method for synthesis of membrane and the choice of organo-functional group
- For obtaining well-intergrowth membrane, optimum concentration of the organo-functional group present in the synthesis mixture need to be studied
- Stability of the membrane after functionalization
- The presence of acid sites on the membrane which depends on the amount and type of amorphous species.

After having an appropriate design of acid functionalized silicalite-1 catalytic membrane reactor, the challenge is to test the performance of the membrane in xylene isomerization. By far, the development of acid-functionalized silicalite-1 catalytic membrane reactor for the application of combined xylene isomerization reaction and separation will be an arduous task due to the acid-functionalized silicalite-1 membrane is first synthesized in the present work.

The membrane should possess the ability of xylene isomerization as well as separation of *p*-xylene from the reaction products. In order to optimize *p*-xylene yield and to avoid side reactions other than isomerization, a suitable operating condition such as weight hourly space velocity for isomerization of xylene need to be studied. Another challenge is the selective separation of *p*-xylene after isomerization reaction. High separation factor of *p*-xylene to its isomers should be achieved. By reactive separation of *p*-xylene from the reaction products, it is believed that the conversion of xylene and selectivity of *p*-xylene will be improved.

There is a need for developing a detailed theoretical model that can help in the understanding the performance, potentialities and limitations of the separation of

xylene isomer through silicalite-1 membrane, isomerization reaction as well as combined process of xylene isomerization reaction and separation using acid-functionalized silicalite-1 membrane in a catalytic membrane reactor.

For separation of *p*-xylene from its isomers, the transport mechanism of xylene molecule through membrane is complex; especially for separation based on adsorption and surface diffusion where the adsorption rate is a function of pressure and temperature. The quantification of the adsorption parameters is the basic information that is needed to model the transport mechanism of xylene isomers through silicalite-1 membrane. Although the adsorption of *p*-xylene in silicalite-1 has been studied by various researchers (Pope *et al*., 1986; Richards *et al*., 1988; Choudhary *et al*., 1997), the adsorption data are reported at lower temperature range of 20 ^{o}C – 80 ^{o}C. Most of the adsorption parameters at higher temperature (> 150 ^{o}C) reported in the literature were determined by extrapolation of data obtained at relatively lower temperature (Tarditi *et al*., 2008a). However, as reported by van de Graaf *et al*. (2000), the adsorption parameters such as saturation amount adsorbed on silicalite-1 are a function of temperature and should be determined experimentally. To the best of our knowledge, the adsorption parameters of xylene isomers at higher temperature, i.e. >150 ^{o}C are still not reported in the literature. Besides, the experimental data for the adsorption of *o*-xylene in silicalite-1 membrane are hardly reported in the literature. Therefore, it is important to determine the adsorption parameters for *p*-xylene and *o*-xylene in order to obtain the permeation flux of xylene molecules through silicalite-1 membrane.

A suitable mathematical model (reaction and diffusional transport) that can help in the understanding of the performance of acid-functionalized silicalite-1 membrane in xylene isomerization reaction needs to be derived. Although the reaction scheme of xylene isomerization using acid catalysts has been reported by various researchers, there are still inconsistencies need to be addressed (Li *et al.*, 1992; Iliyas and Al-Khattaf, 2005). Therefore, a suitable reaction scheme that can describe the catalytic activity of the acid-functionalized silicalite-1 membranes need to be figured out. The kinetic parameters of the reaction for the purpose of design and scale up of catalytic membrane reactor need to be determined. It is also crucial to understand the rate controlling steps of the reaction process. The kinetic parameters obtained at different reaction temperature from the reaction scheme model would indentify the rate control factor in the process.

The development of a suitable model of catalytic membrane reactor in order to simulate conversion of xylene at different operating conditions will be extremely important. It would lead to the better understanding of the process and factors responsible for the combined xylene isomerization and reactive separation of *p*-xylene through acid-functionalized silicalite-1 membrane. The data and knowledge generated will be a first step leading to the development of catalytic membrane reactor to be used in the petrochemical industry for the production of *p*-xylene in a single unit. The validity of the model could be verified by comparing the experimental data with the simulated data obtained from the model.

1.6 Objectives

The objectives of the present research are:

1) To synthesize and characterize silicalite-1 and acid-functionalized silicalite-1 membranes.
2) To test the performance of silicalite-1 and acid-functionalized silicalite-1 membranes for the separation of binary and ternary xylene mixture.
3) To develop a mathematical model suitable to describe the separation of xylene isomers through silicalite-1 membrane.
4) To study the performance of acid-functionalized silicalite-1 membranes as catalyst in xylene isomerization reaction and to determine the reaction rate parameters.
5) To propose a suitable mathematical model to represent combined xylene isomerization reaction and permeation of xylene through acid functionalized silicalite-1 membrane in the catalytic membrane reactor.

1.7 Scope of the Study

The scope of the study in the present research is presented in the following section.

1.7.1 Synthesis and Characterization of Silicalite-1 and Acid-functionalized Silicalite-1 Membranes

Silicalite-1 membrane was synthesized using in-situ hydrothermal crystallization method. Two types of acid-functionalized membranes: (1) propylsulfonic acid-functionalized silicalite-1 membrane and (2) arenesulfonic acid-functionalized membrane were synthesized using one-step in-situ hydrothermal

crystallization and subsequent post-synthesis modification. The membranes were characterized using HR-XRD, SEM, TEM, FT-IR, ^{29}Si MAS NMR and ^{13}C CP-MAS solid state NMR, Elemental analysis, TGA, NH_3-TPD, acid-base titration using different ion-exchange agent and nitrogen adsorption-desorption, respectively.

1.7.2 Performance of Silicalite-1 Membrane in the Separation of Binary and Ternary Xylene Mixtures

A vapor permeation test rig was set-up and fabricated for finding the performance of disc type membrane. The test rig was set-up to conduct xylene single-component permeation and separation study for binary and ternary xylene mixture using silicalite-1 membrane at different operating conditions. The rig could be operated as a catalytic membrane reactor system for combined xylene isomerization reaction and separation using acid-functionalized membrane. The operating parameters such as feed composition, feed partial pressure, feed flow rate, temperature and sweep gas flow rate were studied. The performance and optimization of operating process variables (temperature, *p*-xylene feed partial pressure and *p*-xylene feed composition) on the selectivity and flux of the silicalite-1 membrane were studied for the separation of *p*-xylene from binary and ternary xylene mixtures.

1.7.3 Modeling of Xylene Mixture Separation using Silicalite-1 Membrane

The permeation of single component xylene isomer, *p*-xylene and *o*-xylene through silicalite-1 membrane was modeled based on the combination of adsorption and diffusion theory.

1.7.4 Performance of Acid-functionalized Silicalite-1 Membranes in Xylene Isomerization Reaction and Kinetic Parameters Determination

The optimum conditions obtained from DoE approach for binary and ternary xylene mixture separation process was used to evaluate the separation performance of propylsulfonic acid-functionalized silicalite-1 membranes and arenesulfonic acid-functionalized silicalite-1 membranes, respectively. After the separation study, combined *m*-xylene isomerization reaction and separation process using acid-functionalized silicalite-1 membranes was carried out in the membrane reactor. A kinetic model based on time on stream (TOS) was proposed to describe the xylene isomerization reaction using acid-functionalized silicalite-1 membranes at different reaction temperature.

1.7.5 Modeling of Combined Xylene Isomerization Reaction and Separation using Acid-functionalized Silicalite-1 Membrane in the Catalytic Membrane Reactor

The mathematical model is based on the steady state mass balance equations for the membrane and the respective boundary conditions to study the catalytic membrane reactor performance for combined reaction and separation.

The overview research activities flow chart carried out throughout the present study is presented in Figure 1.7.

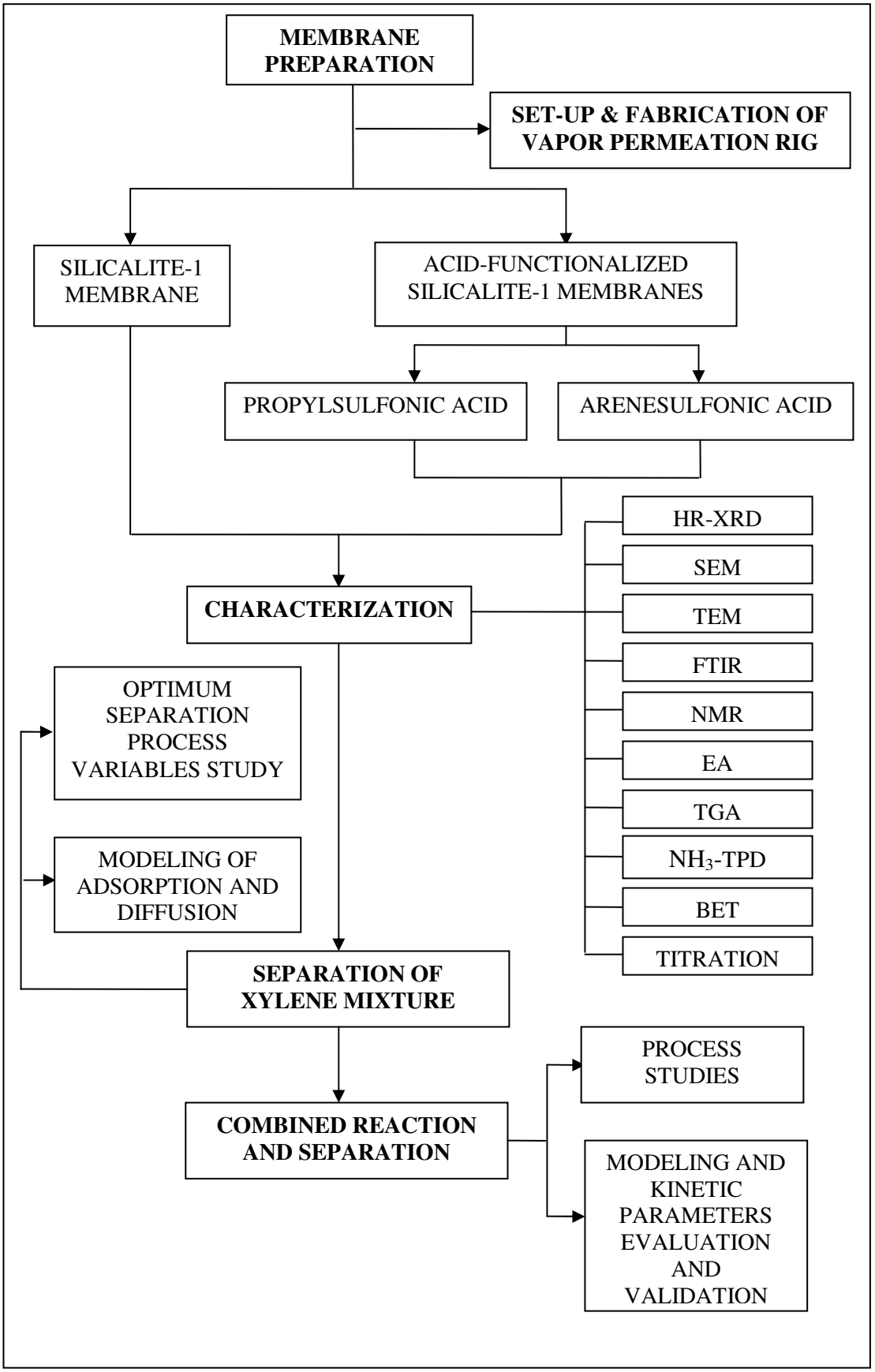

Figure 1.7: Research activities flow chart

1.8 Organization of Thesis

This thesis describes the research work to study the synthesis and characterization of silicailte-1 and acid-functionalized silicalite-1 membranes and their performance in xylene isomer separation and reactive separation of xylene isomers. The fundamental aspects related with transport mechanism of xylene isomers permeation through silicalite-1 were investigated. The isomerization and separation activity in the catalytic membrane reactor using acid-functionalized silicalite-1 membranes was described by a series of mathematical models.

In the chapter 1 (Introduction), a brief introduction about the production of *p*-xylene from the current technologies and the prospects of membrane technologies for *p*-xylene separation are presented. The recent application of zeolite membrane in *p*-xylene separation and the development of acid-functionalized zeolite membrane for combined xylene isomerization reaction and separation are presented. At the end of this chapter, problem statements that provide basis and rationale to justify the research direction to be followed in the current study are included. The objectives of the present study are elaborated in detail together with scope of the study.

Chapter 2 (Literature Review) presents literature review on the synthesis methods for MFI type zeolite membrane which are developed for the last decade. The recent development on acid-functionalized zeolite materials by various researchers is presented. This is followed by the review of characterization techniques used to study the physical and chemical properties of the membrane. The separation of *p*-xylene from binary and ternary xylene mixture using MFI type zeolite membrane reported in the literature are presented subsequently. Beside that,

the background information and a review of experimental data for combined xylene isomerization reaction and separation using catalytic membrane is presented for the purpose of comparison.

Chapter 3 (Modeling and Simulation) presents the process modeling and simulation study. It is divided into three main sections: (i) transport mechanism of xylene permeation and separation through silicalite-1 membrane and (ii) kinetic parameters determination based xylene isomerization reaction scheme and (iii) process modeling for combined xylene isomerization reaction and separation through acid-functionalized silicalite-1 membrane based on mass balance and reaction equations. This chapter presents the theoretical background of the process modeling and solution methodology for the simulation. The assumptions to perform the proposed model are also included in the chapter.

In chapter 4 (Materials and Methods), a detailed description of the experimental work is elaborated. It starts by listing all the materials and chemicals used together with their respective supplier name and purity. The procedure applied for the synthesis of different silicalite-1 and acid-functionalized silicalite-1 membranes and the equipment used during the preparation of membrane are given. The procedure of sample preparation for various characterization methods used in the present study are provided. The set-up of the membrane permeation cell, operating procedure of the vapor permeation test rig, permeation measurement and samples collection and analysis are included. In the following section, the separation process conditions for binary and ternary xylene mixtures were given. The experimental procedure and operating parameters for combined xylene isomerization reaction and

separation in a catalytic membrane reactor is given in this chapter. Lastly, the procedure for products analysis is included.

Chapter 5 (Results and Discussion) includes the results of the experimental data obtained in the present study followed by discussion. This chapter is divided into four sections. The first section presented the characterization of silicalite-1 and acid-functionalized silicalite-1 membranes. This is followed by the performance of silicalite-1 membrane in *p*-xylene separation from binary and ternary xylene mixtures. Design of Experiment (DoE) approach is applied in determination of optimum operating process variables. The third section covers the process studies of combined xylene isomerization reaction and separation in acid-functionalized silicalite-1 catalytic membrane reactor. In the final section, the modeling study for separation and combined reaction and separation processes are presented. The adsorption parameters obtained from separation modeling are applied in the simulation of binary xylene mixture and *p*-/*o*-xylene separation factor. The kinetic parameters obtained from kinetic modeling are applied in the steady state mass balance equations in the membrane, with respective boundary conditions at retentate and permeate sides, to study the catalytic membrane reactor performance in combined xylene reaction and separation. The simulated results are compared with the experimental results.

Chapter 6 (Conclusions and Recommendations) concludes all the major findings obtained in the present study. At last, suggestions and recommendations to improve the present research work as well as the future direction of the current study are presented.

CHAPTER 2

LITERATURE REVIEW

This chapter covers the literature review on:

i. Synthesis methods for zeolite membrane (especially MFI-type zeolite membrane) reported in the recent years.

ii. Different types of chemical and physical techniques for membrane characterization.

iii. Separation results of *p*-xylene from binary and ternary xylene mixture using MFI type zeolite membrane.

iv. The recent developments about acid-functionalized zeolite materials reported by various researchers.

v. The background information of xylene isomerization using zeolite acid catalyst and a review of experimental data for combined xylene isomerization reaction and separation using catalytic membrane reactor.

2.1 Zeolite Membrane Synthesis

Two critical stages are important to be considered during the formation of supported zeolite membrane; (a) nucleation and (b) crystal growth. These two stages are very sensitive to the experimental conditions such as synthesis solution/gel composition, synthesis temperature, synthesis time and type of supports which could be manipulated to control the crystal growth. The most common methods for the synthesis of supported zeolite membranes reported so far are in situ crystallization (Wang *et al*., 2001), secondary (seeding) growth (Nair *et al*., 2001) , vapor phase transport method or dry gel conversion method (Matsukata *et al*.,1993) and microwave-assisted hydrothermal synthesis (Motuzas *et al*.,2006). Figure 2.1