DEVELOPMENT OF A CATALYTIC MEMBRANE REACTOR FOR THE PRODUCTION OF ETHYLENE USING OXIDATIVE COUPLING OF METHANE (OCM)

by

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LIST OF NOMENCLATURE

Symbol	Description	Unit
A	Factor code in DoE	-
A_i	Chromatogram area of component *i*	Pa.s or uV.s
A_{surf}	Membrane surface area	cm^2
B	Factor code in DoE	-
C	Factor code in DoE	-
C_i	Molar concentration	mol %
C_n	Molar concentration of nitrogen at the sweep gas	mol %
C_0	Molar concentration of oxygen at the sweep gas	mol %
C_{total}	Total molar concentration	mol %
D	Factor code in DoE	-
E	Factor code in DoE	-
E_a	Activation energy	kJ/mol
F_i	molar flow rate of reactant *i*	mol/s
$F_{i,in}$	Inlet molar flow rate of reactant *i*	mol/s
$F_{i,out}$	Molar flow rate of unreacted species *i*	mol/s
$F_{j,out}$	Molar flow rate of product *j*	mol/s
F_S	Sweep gas flow rate	cm^3/min
GHSV	Gas hourly space velocity	$cm^3/g.hr$
$J_{N_2}^{leak}$	Flux of leaked N_2 through pores and cracks	$cm^3/min.cm^2$
J_{O_2}	Oxygen permeation flux	$cm^3/min.cm^2$
$J_{O_2}^{leak}$	Flux of leaked O_2 through pores and cracks	$cm^3/min.cm^2$
n_C	number of carbon atom	-
S_j	Selectivity of product *j*	%
S_f	Sensitivity factor	mol/pA.s or mol/uV.s
R	Ratio of total outlet flow rate to total inlet flow rate	-
R^2	A measure of the amount of variation around the mean explained by the model.	-
t	Student *t*-test factor	-
T	Temperature	^0C or K
V_i	Total inlet flow rate	cm^3/min
V_0	Total outlet flow rate	cm^3/min

$\bar{\chi}$	mean value	-
X_i	Conversion of reactant *i*	%
Y_j	Yield of product *j*	%
+	High level	
-	Low level	

Greek letters

α	Level of significance

Subscripts

i	reactant species
j	product species
s	adsorbed species

LIST OF ABBREVIATIONS

Symbol	Description
ANOVA	Analysis of variance
A.R.	Analysis reagent
BPR	Back pressure regulator
C_2	Ethylene and ethane
C_{2+}	Ethylene, ethane and propylene
CCD	Central composite design
$CH_3^{\cdot}$	Methyl radical
CL	Confidence level
CMR	Catalytic membrane reactor
CNMR	Catalytic non-permselective membrane reactor
CO_x	Carbon oxides
Cor total	Totals of all information corrected for the mean
DF	Degrees of freedom for the model
DoE	Design of experiments
e	electron
EDTA	Ethylene diamine tetraacetic acid
EDX	Energy dispersive X-ray spectroscopy
F-value	Test for comparing model variance with residual (error) variance
FBR	Fluidized-bed reactor
FBCMR	Fluidized-bed catalytic membrane reactor
FBMR	Fluidized-bed membrane reactor
FID	Flame ionization detector
GC	Gas chromatograph
$h^{\cdot}$	electron holes

HR-XRD	High resolution X-ray diffraction
ID	Inner diameter
MFC	Mass flow controller
MIEC	Mixed ionic-electronic conducting
N	Number of experimental run
OCM	Oxidative coupling of methane
OD	Outer diameter
O_O^x, O^{2-}	Lattice oxygen
O_2 (g)	gaseous oxygen
O_2 (s)	surface adsorbed oxygen
Prob >F	Probability of seeing the observed F value if the null hypothesis is true (there is no factor effect)
PBCR	Packed bed catalytic reactor
PBCMR	Packed bed catalytic membrane reactor
PBMR	Packed bed membrane reactor
PG	Pressure gauge
PTFE	Polytetrafluoroethylene
PVG	Pressure and vacuum gauge
RSM	Response surface methodology
SS	Stainless steel
SEM	Scanning electron microscopy
Std. Dev.	Standard deviation
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TGA	Temperature gravimetric analysis
$V_O^{\cdot\cdot}$	Oxygen vacancy
XRD	X-ray diffraction

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PEMBANGUNAN REAKTOR MEMBRAN BERMANGKIN BAGI PENGHASILAN GAS ETILENA SECARA PENGGANDINGAN METANA BEROKSIDA (OCM)

ABSTRAK

Satu reaktor membran bermangkin berbentuk penukar haba kelompang dan tiub berintegrasi dengan tiub membran seramik telah dibangunkan bagi aplikasi dalam tindak balas kimia penggandingan metana beroksida (OCM). Sistem pemangkin berkomponen-3 telah digunakan untuk kajian tindak balas kimia OCM dalam reaktor bermangkin lapisan terpadat. Kesan-kesan pelbagai parameter operasi telah dikaji dengan menggunakan cara rekabentuk eksperimen. Kesan interaksi bagi setiap parameter telah didapatkan dan metodologi permukaan sambutan bergabungkan dengan rekabentuk komposit tengah digunakan untuk menentukan keadaan optimum. Jangkaan keadaan optimum pada suhu 850°C, halaju gas ruang berjam pada 23,947sm^3/g.jam, tempoh prarawatan mangkin selama 2 jam, nisbah CH_4 ke O_2 sebanyak 7 dan nisbah pencairan 0.2 memberikan 40.55% penukaran metana, 79.51% C_{2+} peratusan pemilihan dan 32.24% C_{2+} peratusan penghasilan. Keputusan eksperimen dengan 43.05% penukaran metana, 70.62% C_{2+} peratusan pemilihan dan 30.40% C_{2+} peratusan penghasilan diperoleh pada keadaan optimum.

Rekabentuk reaktor membran bermangkin melibatkan dua langkah: 1) Penyalutan seramik tiub membran komersil (OD 10mm, ID 7mm, panjang 12.5sm) dengan bahan campuran ionik-elektronik berkonduksi (MIEC) pada permukaan luaran dengan teknik sol-gel. 2) Penyalutan permukaan dalaman tiub dengan mangkin berkomponen-3 menggunakan cara salut-celup campuran buburan. Ujian kemeresapan oksigen dijalankan sebelum kajian tindak balas OCM dengan mengubahkan suhu dan kadar aliran gas sapu. Fluks kemeresapan oksigen sebanyak 0.56 $sm^3/min.sm^2$ dengan ketulenan 27.96% diperolehi pada suhu 850 °C. Penambahan metana ke bahagian tiub reaktor membran bermangkin meningkatkan

nilai fluks oksigen ke 1.3973 $sm^3/min.sm^2$ pada 850 °C semasa kajian tindak balas OCM. Aktiviti bermangkin bagi lapisan bersalutan mangkin dikajikan bagi penukaran metana dan penghasilan C_{2+}. Peratusan pemilihan C_{2+} 67.5%, penukaran metana 51.55% dan peratusan penghasilan C_{2+} 34.73% telah diperolehi pada suhu 850 °C, nisbah CH_4 kepada O_2 dengan nilai 3 dan kadar aliran gas sapu $100sm^3/min$ dalam reaktor membran bermangkin. Permukaan membran telah dicirikan dengan kaedah-kaedah XRD, TEM, SEM, EDX sebelum dan selepas tindak balas kimia.

Reaktor membran bermangkin lapisan terpadat (satu lapisan mangkin terpadat dalam tiub membran) dijalankan pada keadaan optimum yang sama seperti reaktor mangkin lapisan terpadat untuk kajian kesan penaburan oksigen semasa tindak balas OCM. Prestasi reaktor bermangkin lapisan terpadat (PBCR), reaktor membran bermangkin (CMR) dan reaktor membran bermangkin lapisan terpadat (PBCMR) telah dibandingkan. Reaktor membran bermangkin lapisan terpadat tidak sebaik reaktor bermangkin lapisan terpadat kerana pemirauan gas dari zon bermangkin di PBCMR. Reaktor membran bermangkin menunjukkan prestasi terbaik antara ketiga-tiga reaktor dari segi peratusan penghasilan C_{2+} sebanyak 34.73% dan berpotensi untuk penghasilan etilena secara tindak balas OCM.

DEVELOPMENT OF A CATALYTIC MEMBRANE REACTOR FOR THE PRODUCTION OF ETHYLENE USING OXIDATIVE COUPLING OF METHANE (OCM)

ABSTRACT

A catalytic membrane reactor resembles shell and tube heat exchanger integrated with a tubular ceramic membrane was developed for the application in oxidative coupling of methane (OCM) reaction. A 3-components catalyst system (Na-W-Mn/SiO_2) was used to study the OCM reaction in a packed bed catalytic reactor. The effects of various operating parameters were studied using design of experiments method. The interaction effects of each parameter were obtained and response surface methodology coupled with central composite design was applied in determining the optimum condition. The predicted optimum condition of temperature 850^{0}C, gas hourly space velocity at 23,947cm^3/g.hr, catalyst pretreatment period of 2 hrs, CH_4 to O_2 ratio 7 and dilution ratio 0.2 gave 40.55% methane conversion, 79.51% C_{2+} selectivity and 32.24% C_{2+} yield. The experimental value of with 43.05% methane conversion, 70.62% C_{2+} selectivity and 30.40% C_{2+} yield was obtained at an optimum condition.

The design of catalytic membrane reactor involved two steps process: 1) Coating of the commercial ceramic membrane tube (OD 10mm, ID 7mm, length 12.5cm) with mixed ionic-electronic conducting (MIEC) materials on the outer surface using sol-gel technique, 2) Coating the inner surface of the tube with 3-components catalyst using mixture slurry dip-coating method. Oxygen permeation test was performed prior to the study of OCM reaction with varying temperature and sweep gas flow rate. The oxygen permeation flux of 0.56cm^3/min.cm^2 with purity of 27.96% was obtained at 850^{0}C. The introduction of methane to the tube side of the catalytic membrane reactor increased the oxygen flux value to 1.3973cm^3/min.cm^2 at 850^{0}C during the study of OCM reaction. The catalytic activity of the coated catalyst layer was studied for methane conversion and C_{2+} yield. The C_{2+} selectivity of 67.5%, methane

conversion of 51.55% and C_{2+} yield of 34.73% were obtained at 850^{0}C, CH_4 to O_2 ratio of 3 and sweep gas flow rate at 100cm^3/min in a catalytic membrane reactor. The membrane surface was characterized using XRD, TEM, SEM and EDX before and after reaction.

Packed bed catalytic membrane reactor (a catalyst bed packed within the membrane tube) was also studied under same optimum condition as packed bed catalytic reactor to study the effect of oxygen distribution during the OCM reaction. The performances of packed bed catalytic reactor (PBCR), catalytic membrane reactor (CMR) and packed bed catalytic membrane reactor (PBCMR) were compared. The packed bed catalytic membrane reactor did not perform better than the packed bed catalytic reactor due to gas bypassing the catalytic zone in PBCMR. The catalytic membrane reactor performed the best among the three reactors in terms of C_{2+} yield of 34.73% and has potential for the production of ethylene using OCM reaction.

CHAPTER ONE

INTRODUCTION

The oil price has leapt abruptly to another zenith since 1970's and this has become a critical issue that harassing and staggering the global economy. Apparently, the oil deficiency is one of the reasons contributing to the price rising of global oil. The widespread usage of oil in industry and transportation inducing the imbalance of oil supply-demand over the global scale, in consequence the tendency of oil dependence has deepened and the global oil markets are confronting with the predicament of supply constraints on crude oil. Researchers have been searching for alternatives in substituting the non-renewable oil but the finding and the course of research are time consuming, and it is impossible to completely replace the oil, which has a wide coverage of usage, instantaneously. Natural gas, the near of kin of crude oil; in a massive deposit, providing a closest pathway in alleviating and soothing the oil tightness. Methane, as the main constituent of natural gas, can be converted into more valuable chemicals such as methanol, formaldehyde, syngas, liquid fuel and ethylene.

1.1 PRODUCTION OF ETHYLENE USING NATURAL GAS

Ethylene is one of the largest tonnage petrochemical, with demand over 90 million tonne per year worldwide (Online Library, 2003a; Online Library, 2003b). Ethylene is the raw material in the manufacture of number of chemicals, such as plastic, fiber and other organic chemicals that are eventually to the industries of packaging, transportation, construction, medical ware and a myriad of consumer market. Ethylene is produced primarily from steam cracking (thermal pyrolysis) of hydrocarbons ranging from natural gas (ethane, propane and butane) to petroleum liquids (naphtha, kerosene and gas oil); followed by separation of the fractions. Ethylene is also recovered from

the refinery-off gas streams as well as from ethanol dehydration (Online Library, 2004). These processes, however, are highly endothermic, energy intensive and low in ethylene selectivity, which depends strongly on the choice of feedstock.

Due to the increasing demand of ethylene over the global market and the rising price of ethylene feedstock, researchers have devoted considerable effort over the past 30 years in finding economic process route for the production of ethylene and hitherto few alternatives have been reported (Picciotti, 1997). Oxidative coupling of methane (abbreviated as OCM) is one of the promising routes for the production of ethylene by fully utilizing the abundance reserves methane, which is the main constituent of natural gas and the special characteristic of natural gas as the cleanest, safest, and most useful of all energy sources as the low cost feedstock, a more economic and enduring path for the production of ethylene on the edge of oil crisis.

1.2 OXIDATIVE COUPLING OF METHANE (OCM)

1.2.1 Definition

Oxidative coupling of methane is a single-step conversion and highly exothermic reaction. It is a process for the formation of ethylene by coupling two methyl radicals after the abstraction of a hydrogen atom from each methane molecule, respectively. However, the selectivity of ethylene is always diminished due to the formation of carbon oxides directly from the combustion of methane and C_{2+} products with the presence of oxygen, which acts as an oxidizing agent of catalyst.

1.2.2 Reaction scheme of OCM process

In the early stage of the study in OCM process, the details of mechanism involved in OCM was once a hotly discussed issue due to the complexity of reactions

between reactants in gas phase reactions and heterogeneous reactions over bulk and surface catalyst. Generally, methane is a predominant reactant in the presence of oxidant (e.g. oxygen, nitrous oxide or carbon dioxide) in gas phase. The reaction scheme for the OCM reaction is generally depicted as network shown in Figure 1.1, in which carbon oxide has the great tendency to be the final product. Most of the carbon oxide was formed during the direct thermal cracking of methane (path 5), which is a parallel reaction with the coupling of methyl radicals to become ethane (path 1); and part of it from the consecutive reaction of combustion of ethane and ethylene to carbon oxide (path 2 and 4). Therefore, it is essential to control the selectivity of ethylene by inhibiting the occurrence of undesired reaction path (path 2, 4 and 5, respectively).

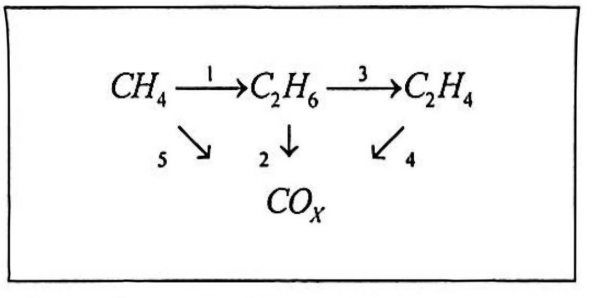

Figure 1.1 General reaction scheme for the oxidative coupling of CH_4 to C_2H_6 and C_2H_4. (Roos et al., 1989)

1.2.3 Interactions of molecular oxygen with metal oxides

There are a wide variety of catalysts being used in the study of OCM process, varying from the pure basic oxides to transition metal oxides (Lunsford, 1995). The role of catalyst is primarily to facilitate the abstraction of one hydrogen from methane. The oxygen species on the catalyst surface, either in the form of surface lattice oxygen (e.g. O^{2-}) or adsorbed oxygen (e.g. O_2^-, O_2^{2-} and O^-), provide a reaction site to interact with methane and form methyl radical. However, some methane or intermediate hydrocarbon species will react with gas phase oxygen to complete oxidation to carbon

oxide. Thus, OCM catalyst should be capable to suppress the occurrence of complete oxidation to the formation of carbon oxide product as well.

After the initial reaction of methane and the metal oxide of catalyst, the gas phase oxygen will adsorb on the surface of metal oxides by the following steps: coordination, electron transfer, dissociation and incorporation into the oxide lattice to form activated oxygen species (Ito et al., 1985).

$$O_2(g) \rightleftharpoons O_2(s) \overset{e}{\rightleftharpoons} O_2^-(s) \overset{e}{\rightleftharpoons} O_2^{2-}(s) \rightleftharpoons 2O^-(s) \overset{2e}{\rightleftharpoons} 2O^{2-}(s) \qquad (1.A)$$

Metal oxide acts as reducing agent while the adsorbed oxygen is oxidizing agent in the course of this reaction. The chemisorption of oxygen to the metal oxides varies depending on the type of conductivity (e.g. *n*-, *p*- type and ionic conductivity).

1.3 CATALYTIC MEMBRANE REACTOR (CMR)

1.3.1 Basic concepts of membrane separation processes

The concept of membrane-based separation was first introduced at the early 18th century and believed to be beneficial over most of the conventional separation processes (distillation, adsorption, absorption, etc.) in reduction of capital investment and energy savings (Hsieh, 1996). A membrane is a thin film with permeable or semi-permeable phase that acts as a barrier for the separation of chemical substances. The basic membrane separation process is illustrated in Figure 1.2; where the species retained in the fluid stream are called as retentate while the species passing through the membrane are termed as permeate. There are two important parameters in describing the membrane performance, which are permeability and permselectivity. Permeability is usually defined as the flux of the flow through the membrane with respect to the membrane thickness and driving force; whereas the permselectivity is the ability of the membrane to separate the permeate from the retentate.

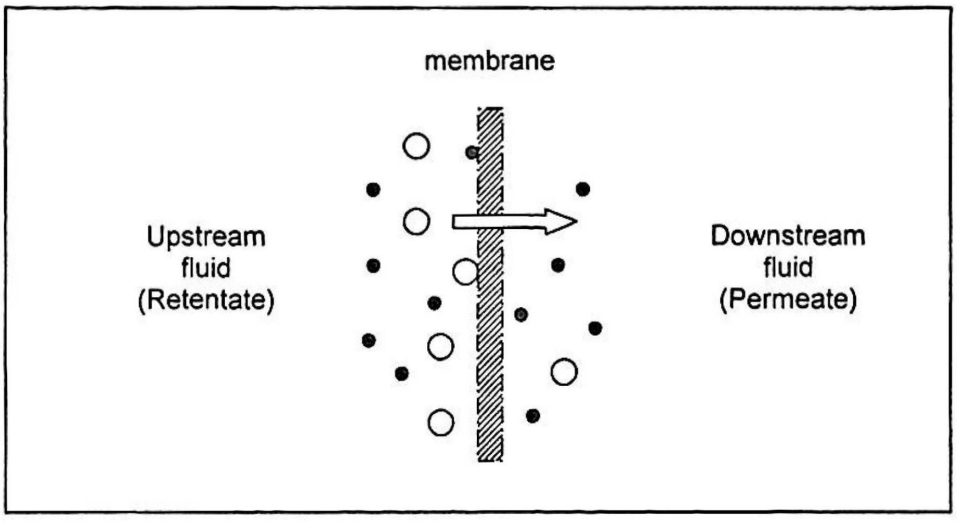

Figure 1.2 Schematic diagram of the basic membrane separation principle

Membrane could be synthesized by a variety of materials ranging from inorganic to polymer substances, which must possess the ability in separating the mixture of fluid in its particular application. The membrane separation processes are generally classified into filtration (micro-, ultra-, nano-), dialysis, electrodialysis, reverse osmosis, pervaporation and gas separation (Baker, 2004). The usage of both polymer and ceramic membrane are determined by their applications. Most of the polymer-made membranes are commercially available in the industry (mostly for the biotechnological and water purification applications), which are relatively cheap and well-developed; but poor in mechanical strength, low resistance to harsh environment, high pressure drops and high temperature. The introduction of inorganic membrane, either metallic (e.g. stainless steel, bronze and silver) or ceramic (e.g. alumina, silica, zirconia, mullite, titania and magnesia), provided another breakthrough in the membrane development, which has overcome the problems in the usage of polymeric membrane. These membranes are applicable for high temperature (200 – >900^{0}C) processes such as gas separation and reactive-based processes in chemical, petrochemical and pharmaceutical industries.

In the separation process, the transport mechanism is determined by the nature of the membrane, in which the driving force (e.g. pressure gradient, concentration gradient, electrical potential, temperature, etc.) across the membrane is highly

dependent to the type of membrane. The classification of membrane type and its character associated with the particular transport processes was epitomized and classified as in Table 1.1.

Table 1.1 Types and properties of membranes (Baker, 2004)

Type of membrane	*Description*
Isotropic membranes (Symmetric membranes) Macroporous membranes	- Average pore diameters larger than 50nm - Molecular, Knudsen diffusion and convective flow as the transport mechanisms
Mesoporous membranes	- Average pore diameters in the intermediate range between 2 and 50 nm - Molecular, Knudsen diffusion and convective flow as the transport mechanisms
Microporous membranes	- Pore diameters smaller than 2 nm - Separation of solutes in molecular, pore-flow and Knudsen diffusion depending upon the solutes in the fluid mixture
Nonporous, dense membranes	- Transport of solutes by driving force of a pressure, concentration or electrical potential gradient - Separation of components in a mixture is determined by their diffusivity and solubility in the membrane material
Electrically charged membranes	- Consist of pore walls carrying charged ions - Separation is determined by exclusion of ions of the same charge as the fixed ions of the membrane structure, rather than by the pore size
Anisotropic membrane (Asymmetric membrane)	- Consists of an extremely thin surface layer supported on a much thicker, porous substructure - Separation properties and permeation rates based on the surface layer.

Most of the ceramic membranes are asymmetric type with the composite system; a macroporous layer as the support providing the mechanical strength and a microporous layer or dense membrane coated above the support for the separation purposes (some composite system consists of intermediate mesoporous layer as support to the top layer). The microporous layer should be as thin as possible to enhance the permeation flux.

The inorganic membrane has better thermal resistance than polymer membrane, but sintering or phase transformation take place at elevated temperature that might alter the microporous structures of inorganic membranes. For alumina membrane, the metastable phases of gamma alumina, one of the poorly crystalline transition alumina, subject to phase transition at temperature beyond 700^{0}C to δ, delta- (between 700^{0}C and 800^{0}C) to θ, theta (between 900 and 1,000^{0}C) and eventually to alpha phase alumina (between 1,000 and 1,100^{0}C). The membrane pore diameter increased dramatically from 4.8nm (gamma-alumina) to about 78nm (alpha-alumina) during the phase transition process (Hsieh, 1996).

1.3.2 Oxygen permeable membrane

The early application of membrane reactor in OCM was initiated by using porous inert membrane reactor in which the membrane served as the oxygen distributor. There was a breakthrough in the development of membrane reactor as other efforts in introducing the electrochemical reactor, which is capable to permeate oxygen through a dense membrane with external voltage provided (typically between 0.1 and 1 volt). The operation of the electrochemical membrane reactor resembles a fuel cell with the external voltage imposes an electrical current over the membrane. The oxygen flow rate is controllable over the membrane by changing the polarity and the magnitude of the voltage drop across the membrane (Ma et al., 1998). However, the need of external voltage implying the addition of the operating cost, and suggesting that it was not applicable in industry.

This intriguing discovery has sparked the membrane reactor technology to another attempt of introducing dense ionic conducting membrane, which is permselectivity to oxygen without the supply of external voltage. Ionic conducting dense membranes are used for molecular scale separations involving gaseous mixture, such as oxygen separation. These membranes made of ceramic and consist of solid

oxides (ZrO_2, Y_2O_3, Bi_2O_3) as well as of solutions of mixed oxides (perovskites, brownmillerites, etc.), which act as solid electrolytes allowing the transport of oxygen (Marcano & Tsotsis, 2002). Ceramic membranes have the advantages of being chemically inert and stable at high temperatures, conditions under which polymer membranes fail. Separation through dense ceramic membrane is governed by a solution-diffusion mechanism (Baker, 2004), where the driving force is oxygen partial pressure gradient across the membrane. The high temperature in OCM is favorable to this membrane type in enhancing the ionic conductivity of the solid oxide within the membrane, and hence oxygen is attracted to the membrane and permeated through the membrane.

1.3.3 Membrane formation by sol-gel method

A sol-gel process is a wet chemical route used to synthesize ceramics, and generally, involving the transition (gelation) of a system from a colloidal suspension of a solid particles or clusters in a liquid "sol" into a dual phase material of a solid skeleton filled with a solvent "gel" phase. A *colloid* is a suspension in which the dispersed phase is so small (~1-1000nm) that gravitational forces are negligible and interactions are dominated by short-range forces, such as van der Waals attraction, coulombic and steric forces. A *sol* is a stable colloidal suspension of solid particles within a liquid, whereas a *gel* is a porous 3-dimensionally interconnected solid network that expands in a stable fashion throughout a liquid medium and is only limited by the size of the container (Brinker & Scherer, 1990; Pierre, 1998).

Sol-gel process is a wide studied technology and highly applicable in the fabrication of glass and ceramic materials into various forms: ultra-fine powders, thin film coatings, microporous inorganic membranes, aerogel, ceramic fibers, monolithic ceramic and glasses. It is advantageous over the conventional ceramic preparation method because the initial step chemical process in sol-gel is always carried out at low

temperature, which is essential for the kinetic control of various chemical reactions. Furthermore, the nucleation and growth of the primary colloidal particles can be controlled. There is a wide scope of procedures in sol-gel process with a selected precursor as the starting compound for the preparation of a colloid consist of a metal or metalloid element surrounded by various ligands, such as metal alkoxides and metallic salts. The sol is formed when the precursor in a mixture of solvent and acid or base solution was subjected to a series of hydrolysis and condensation (further to polymerization) (Pierre, 1998). A variety of ceramic materials could be formed by different routes (coating, gelling, precipitating and spinning) as depicted in Figure 1.3. In present study, sol-gel process will be implemented for the preparation of oxygen permeable membrane by coating the xerogel film on an alumina support as will be discussed in detail in Section 3.4.

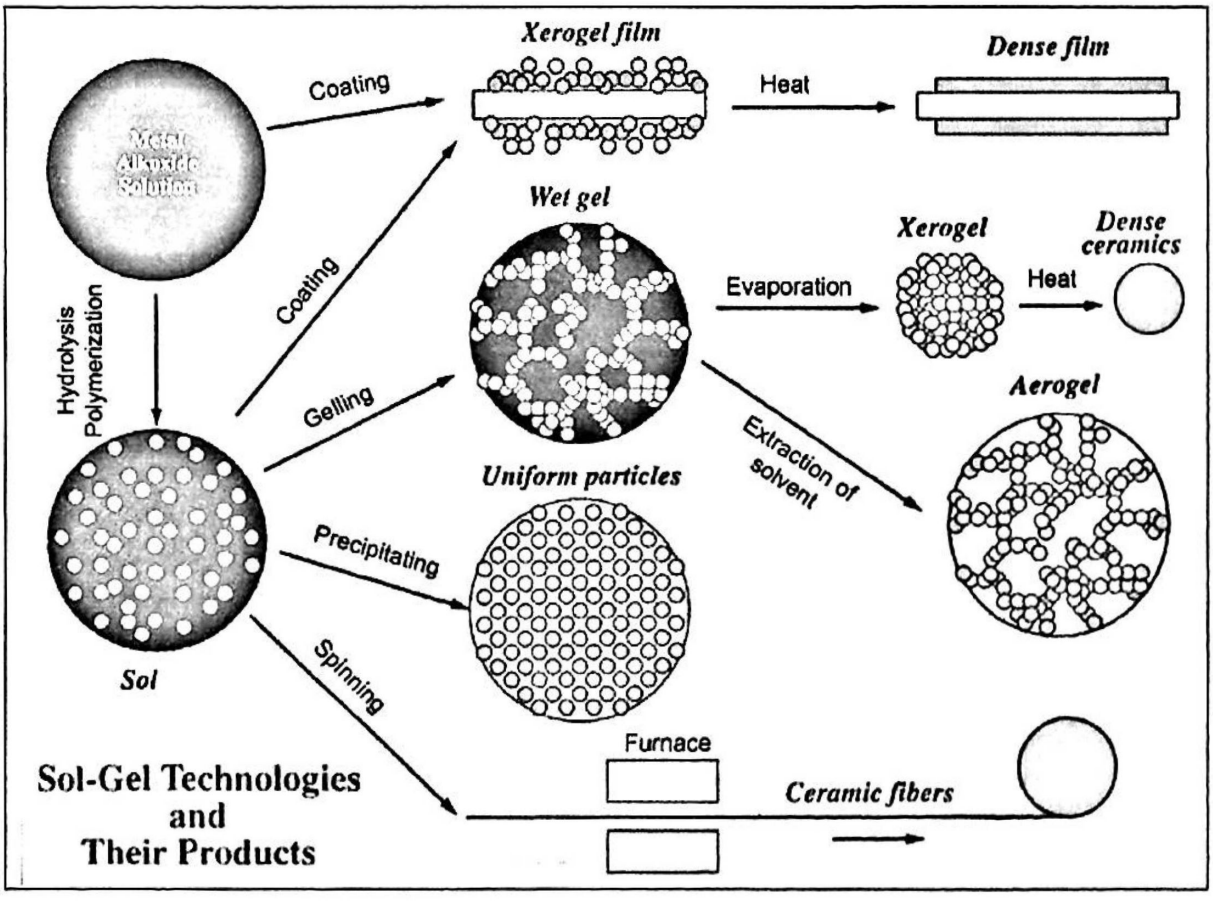

Figure 1.3 Simplified chart of sol-gel process. (Chemat Technology Inc., 1998)

1.3.4 Synergistic effects of separation and reaction

The technology of membrane-based reactive process is combining two discrete processes, separation and reaction in a single unit, which results into a membrane reactor. The conventional packed bed reactor has limitation of the reaction equilibrium. In packed bed reactor the reactants are premixed and brought into contact with the reaction products, inducing the uncontrollable reaction between products and intermediate or reactant to the undesirable one. The synergistic effect of separation and reaction occur simultaneously within a single unit is particularly apparent for reactions limited by thermodynamic equilibrium considerations, for example, the catalytic hydrocarbon dehydrogenation or esterification reactions (Marcano & Tsotsis, 2002).

The membrane functions as the separator of the desired product from the mixture stream, encouraging the reaction to proceed on the right side of reaction and producing more products; in other words, shifting the equilibrium of the reaction "to the right" (according to Le Chatelier's Principle) for higher conversion. Meanwhile, this will enhance the selectivity and yield of the product by preventing the further conversion of desired product to the undesired one for certain reactions. Some of the porous inert membrane, however, used as the distributor of the reactants in order to elongate the reaction site along the membrane, providing more reaction site but mitigating the hot spot of reaction zone as compared to the catalyst bed in the packed bed reactor.

There are variety of reactor configurations in the classification of membrane reactors as listed in Table 1.2 according to the design and application of membrane reactor to the particular reaction. The membrane in catalytic membrane reactor (CMR) has both the functions as separator and catalyst, which is normally prepared by materials that possessed the ability to separate the desired substance and simultaneously providing the reactive site. Catalytic non-permselective membrane reactor (CNMR) employs the membrane with catalytic property but only distribute the

reactant for the enhancement of yield and selectivity of the product. Currently, the mostly used reactor configuration in research study is packed bed membrane reactor (PBMR) with the catalyst packed in the membrane tube. The membrane might separate the desired product from the mixture products at the downstream, or simply to distribute the reactant for the purpose of increasing reaction site, which acts as separator or reactant distributor, respectively. However, the former type of membrane should only be applicable under certain conditions; in which the molecular size of the desired product greatly differs from other components in the mixture, or the membrane has the affinity to absorb the desired product such as the catalytic behavior, or called as packed bed catalytic membrane reactor (PBCMR).

Table 1.2 Classification of membrane reactors (Marcano & Tsotsis, 2002)

Acronym	Description	Features
CMR	Catalytic membrane reactor	- A membrane with intrinsically catalytic layer or a membrane prepared by catalytic material. - Both separation and reaction occur at the membrane surface.
CNMR	Catalytic non-permselective membrane reactor	- A membrane providing catalyst site but could not separate certain substances as CMR, mostly acts as reactant distributor than separator.
PBMR	Packed-bed membrane reactor	- Catalyst packed either in the interior or exterior the membrane volume. - Membrane acts as reactant distributor
PBCMR	Packed-bed catalytic membrane reactor	- Catalyst packed either in the interior or the exterior of the membrane volume. - Membrane prepared by catalytic material and functions to separate certain substances
FBMR	Fluidized-bed membrane reactor	- Similar as PBMR but catalyst was not packed. - Has better temperature control than PBMR especially for exothermic process
FBCMR	Fluidized-bed catalytic membrane reactor	- Similar as FBMR but membrane with catalytic properties.

1.3.5 Application of CMR in OCM

An innovation in recent years has been aroused to develop processes with reduced overall environmental impact and towards greater economics. The development of catalytic membrane reactor has sparked the revolution of technology, which create a synergistic combination involving chemical reaction sequence with a membrane-based chemical separation. In OCM, catalytic membrane reactor is used as the combined unit for methane coupling reaction and oxygen separation synergy on either side of the membrane wall as schematically illustrated in Figure 1.4.

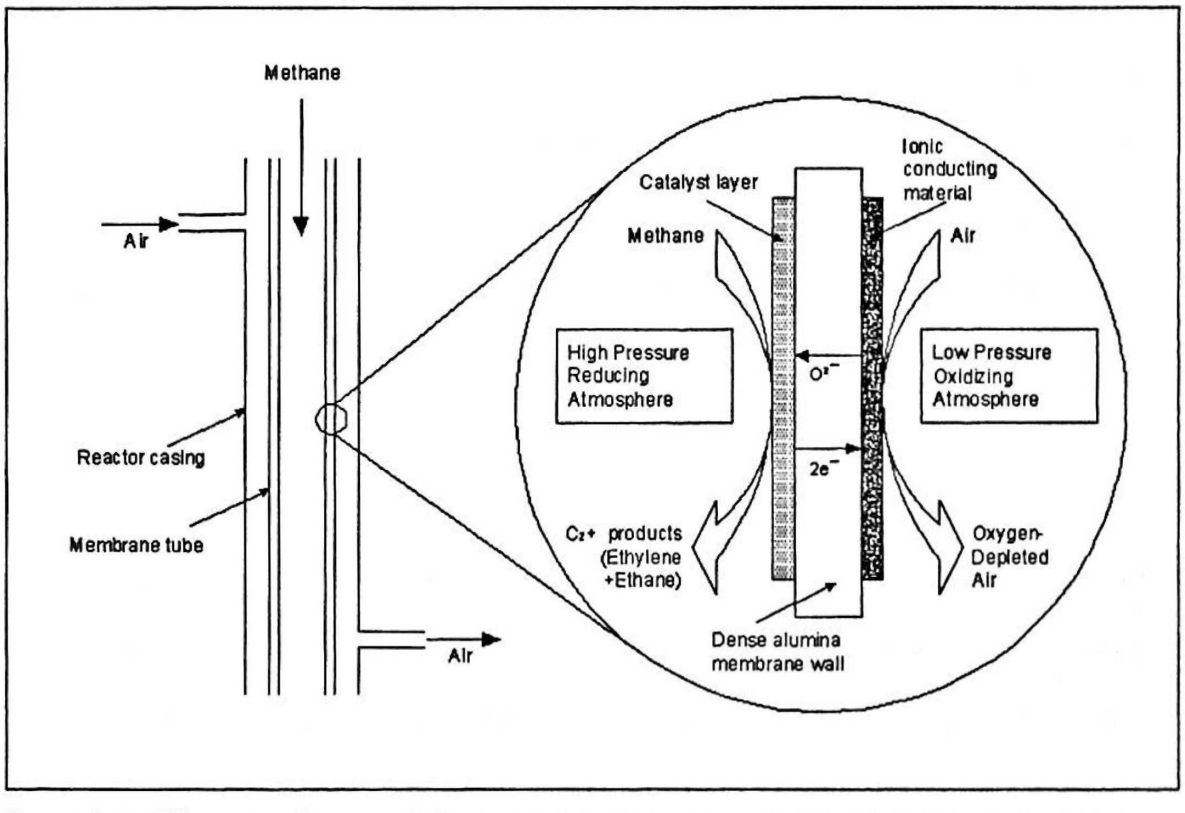

Figure 1.4 Diagram of synergistic oxygen separation and chemical reaction on the membrane surface (Sammells et al., 2000)

The catalytic membrane reactor resembles the shell and tube configuration by using ionic conducting membrane tube in which the air is fed at the shell side and oxygen is separated by permeating through the membrane into the tube side; at the same time methane at the tube side is activated by the oxygen active species, O^{2-} and

may couple to form C_{2+} products. At high temperature with the presence of oxygen partial pressure gradient across the membrane, oxygen molecules in the high oxygen pressure side adsorb on the membrane surface and dissociate into oxygen ions, which then migrate through the bulk via the oxygen vacancies (or by the interstice oxygen mechanism) to the surface of the opposite membrane side, where the oxygen ions recombine with electron holes to form oxygen molecules. Electrons migrate through the membrane in a direction opposite to the oxygen ions to keep local electrical neutrality (Shao et al., 2001a).

Catalytic membrane reactor shows a further intriguing application: the reaction site is extended along the membrane inner wall, thus reaction is faster with higher selectivity and yield, at the same time reducing the hot spot as exist in catalyst packed-bed reactor. The application of catalytic membrane reactor is favored in OCM process due to the fast reaction rate, and the utmost point is, to avoid the direct contact of gas phase oxygen and methane by feeding them in different chambers, shell side and tube side, respectively, in order to inhibit the complete oxidation of C_{2+} product to carbon oxide.

Catalytic membrane reactor has the potential to advance the process industry by enhancing selectivity and yield, reducing energy consumption, improving operation safety, and miniaturizing the reactor system. The prospects of catalytic membrane reactor with mixed ionic and electronic conducting membrane for oxidative coupling of methane seem good as to render the technology economically competitive. However, performance has to be improved relative to present day state-of-art.

1.4 PROBLEM STATEMENT

The commercialization path of OCM process requires the reaction performance with the single-pass methane conversion at 35-37%, 85-88% C_2 selectivity and 30% or higher of C_{2+} selectivity. The research reported in literature so far are facing the problems of achieving the required C_{2+} selectivity, which was mainly attributed to the complete oxidation of methane and C_{2+} products to carbon oxide in gas phase reaction. The present work is to develop a catalytically active membrane reactor system, for which it shows its superiority over packed bed reactor as reported from literature.

Prior to the study on the catalytic membrane reactor, the OCM reaction was studied over a 3-components catalyst, Na-W-Mn/SiO_2. This trimetallic oxides system was reported to be highly effective in achieving almost 80% of C_{2+} selectivity with better stability. However, the optimum condition in OCM reaction using this catalyst have not been determined yet and thus, process study over the 3-components catalyst was done using the design of experiments. Furthermore, the deactivation of these catalyst systems has to be tackled in order to prolong the stability periods of the catalyst during the OCM reaction.

By far, the development of catalytic membrane reactor for the application of OCM is still an arduous task due to the high operating temperature, the risks of membrane fouling and the problem of mechanical strength. An appropriate material for the fabrication of the reactor casing could be ceramic or quartz that can withstand the high operating temperature and inert to the reactant during OCM process. A design of highly impervious system, with the gas-tight and resistance to high temperature (800-1000^{0}C) material is required to reach the objectives in yielding the maximum performance in OCM process.

After having an appropriate design of catalytic membrane reactor, the coming challenge is to synthesis a dense and highly oxygen permselective membrane. The mixed ionic-electronic conducting (MIEC) membrane was deposited on a porous support. In order to obtain high oxygen permeation flux, the membrane must be dense and in a thin film form. The problem that should be overcome is how to develop a dense layer on top of the support without the conflict of mismatch between the membrane and support, also without the impairment of the porosity of the support. The membrane should possess the ability of separate oxygen from air and providing two chambers, the shell and tube side of the reactor for air flow and methane gas, respectively. This is to avoid the methane gas and products to permeate to the shell side. Another challenge is the synthesis of mixed ionic-electronic conducting membrane on the outer surface of the membrane tube and the 3-components catalytic layer on the inner surface.

Though the concept of catalytic membrane reactor is being extensively done by other researchers, it is still failed to attract the industrial interest due to the low C_{2+} achieved. The low C_{2+} yield is believed due to the disk-shaped catalytic membrane, which the reaction zone was limited on the surface of the membrane disk. It is believed that catalytic membrane in tubular type will overcome this problem and highly potential to the commercialization of methane oxidative coupling.

1.5 OBJECTIVES

The main objective in this work is to study the oxidative coupling of methane (OCM) process over a 3-components catalyst, further to be employed in catalytic membrane reactor in purpose of achieving a higher yield of ethylene. The objectives of this project are:

1) To prepare and characterize a 3-components catalyst system in order to obtain the optimum process condition in a packed bed catalytic reactor using design of experiments (DoE).
2) To develop and characterize a mixed ionic and electronic conducting membrane for separation oxygen from air.
3) To study the oxygen permeability of the mixed ionic-electronic conducting membrane at different temperatures.
4) To design and fabricate a catalytic membrane reactor for the study of OCM reaction using 3-components catalyst film.
5) To compare the performance of packed-bed catalytic reactor, packed bed catalytic membrane reactor and catalytic membrane reactor for OCM reaction.

Figure 1.5 shows the flow diagram of the activities in achieving the objectives of the present study.

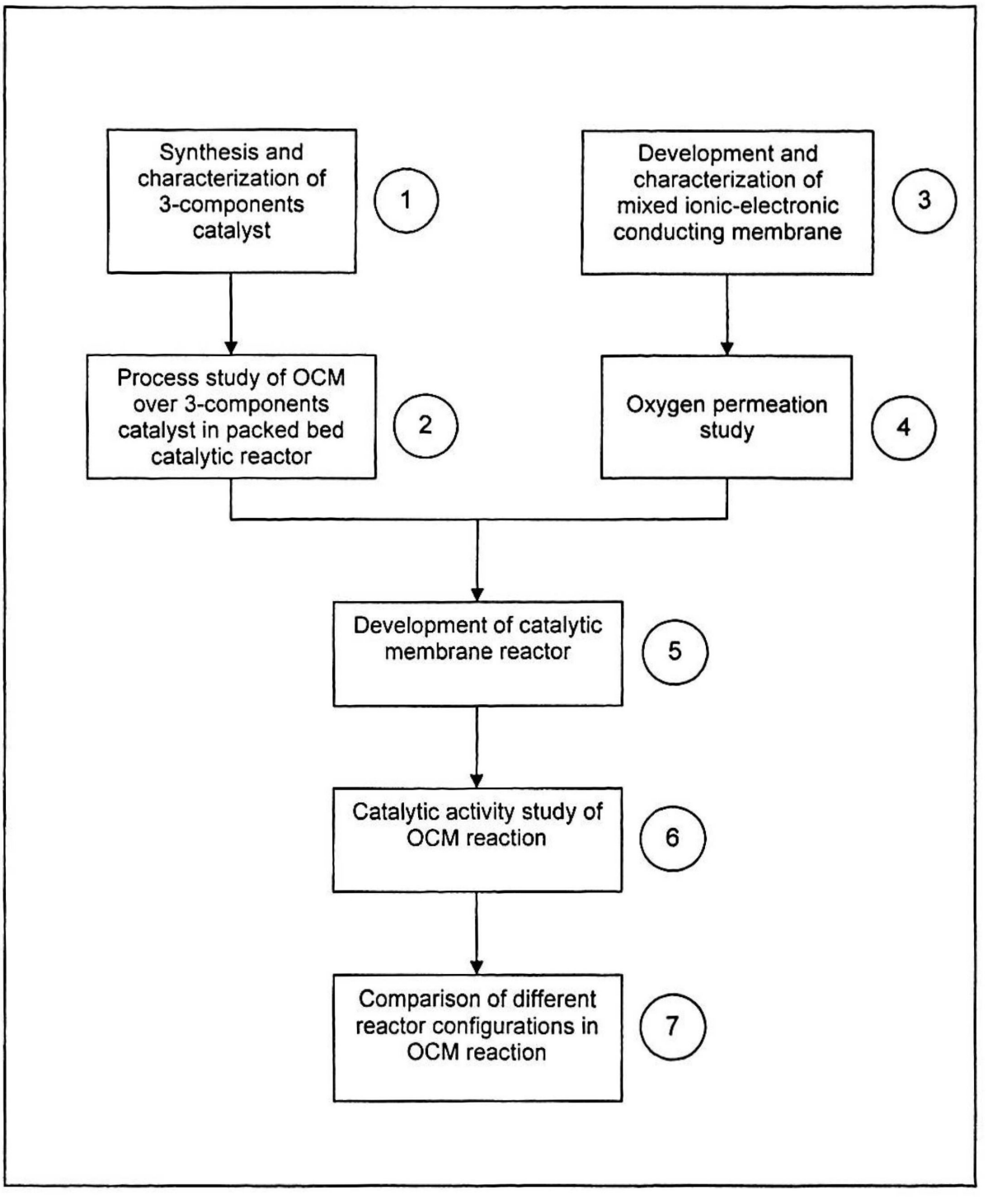

Figure 1.5 Activities flow diagram in achieving the objectives of the present research

1.6 SCOPE OF THE WORK

The research work was divided into two stages, (a) study of 3-components catalyst performance in OCM process in a packed bed quartz reactor and (b) development of catalytic membrane reactor. The first stage was conducted using a 3-components catalyst, which was a combination of trimetallic oxides system selected based on the studies reported in the literature. The performance of these catalysts prepared by different methods such as incipient wetness impregnation and mixture slurry method were studied and compared using a packed-bed catalytic reactor. A variation of parameters such as operating temperature, GHSV, period of catalyst pretreatment, dilution ratio and CH_4 to O_2 ratio were studied to evaluate the methane conversion, C_{2+} selectivity and C_{2+} yield by using Design of Experiments (DoE). The factors were initially screened by a factorial design, and optimization of the process was done using response surface methodology (RSM) coupled with central composite design (CCD).

The second stage of the research covered the development of a mixed ionic and electronic conducting (MIEC) material. The commercial alumina membrane tube was used and modified to be more stable and resistance to high temperature operation by doping lanthanum on the surface of the alumina membrane tube. A combination of metals and rare earth alkaline materials were used to form a perovskite type MIEC material prepared by sol-gel method and the membrane was prepared by dip-coating the MIEC material at the outer surface of the alumina membrane tube. Perovskite-type dense ceramic membrane in tubular form is applied due to the ionic conducting characteristic for the affinity towards oxygen; at the same time possess catalytic activity for the oxidative coupling of methane.

The membrane reactor was designed and fabricated by using materials that are inert to the OCM process and capable to sustain high operating temperature. The design of reactor resembles like a shell and tube reactor, in which methane was fed into the tube side; oxygen was passed through the shell side and permeated through the membrane into the tube side. Before the study of OCM reaction, the membrane reactor was first tested for the oxygen permeation by feeding oxygen and nitrogen to the shell side without introducing methane. The phase structure, surface morphology and surface composition of the membrane were characterized in order to understand the characteristic of the membrane.

After the oxygen permeation test, the 3-components catalyst layer was coated along the inner surface of the membrane support and was tested by passing methane from the tube side. The study of reactor performance is evaluated in terms of the oxygen permeability flux, methane conversion, C_{2+} (ethane + ethylene + propylene) selectivity and yield. The results were compared to the performance of the conventional packed bed catalytic reactor and packed bed catalytic membrane reactor.

The aim of this project was to develop a catalytic membrane reactor for the OCM process, which is believed to have the capability to overcome the low yield of C_{2+} product. In the present study, the commercial-type alumina tube was used rather than synthesizing it in consideration of the future work in industry by any possibility of the commercialization of OCM process.

1.7 ORGANIZATION OF THE THESIS

This thesis comprises six chapters. Chapter 1 presents the current production of ethylene in industry and the potential of natural gas as the low cost material. An introduction of oxidative coupling of methane process is given in brief. The emphasis was cast on the usage of the catalytic membrane reactor in this process by illuminating the current problem statement. The objectives of this research work are also covered in this chapter as well. The scope of the present study highlights the research work done in order to meet all the objectives.

Chapter 2 summarizes the research published in the literature including the study of catalyst performance, type of oxygen permeable membrane, the design of catalytic membrane reactor and its performance in OCM process. The trend of the research in this field has been covered, starting from the broad study of catalyst performance in the early 1980s to the reactor configuration.

Chapter 3 addresses the preparation methods for the 3-components catalyst, synthesizing of MIEC membrane and the description of the reactor system. The development of the catalytic membrane reactor was also stated. The experiments were carried out using different reactor configurations, (a) packed bed catalytic reactor (PBCR), (b) catalytic membrane reactor (CMR) and (c) packed bed catalytic membrane reactor. The experimental procedure followed for different kind of studies is also presented.

Chapter 4 presents the results of OCM reaction in packed bed catalytic reactor and catalytic membrane reactor. The process was studied and analyzed using the Design of Experiment (DoE) and the optimum condition was predicted using Response Surface Methodology (RSM) coupled with Central Composite Design (CCD).

Characterization of the 3-components catalyst was also carried out by several methods of analysis. The oxygen permeation test of the MIEC membrane was conducted to separate oxygen from air. The performance of catalytic membrane reactor with the 3-components catalyst film was also tested in OCM reaction. A packed bed catalytic membrane reactor, with a catalyst bed packed within the membrane tube was used to study the effect of oxygen distribution under the optimum condition. The performance of catalytic membrane reactor and packed bed catalytic membrane reactor was compared with the conventional packed bed catalytic reactor. The phase structure, surface composition and surface morphology of the membrane were discussed in this chapter as well.

The overall outcome obtained in the present study are summarized and concluded in Chapter 5. Suggestions on some further improvements of the research work that could be done in future are raised up in order to bring the continuity of progress and development of OCM research work in USM.

CHAPTER TWO

LITERATURE REVIEW

The production of ethylene from the utilization of natural gas is a promising route as compared to the conventional ethane thermal cracking and naphtha steam cracking processes. Oxidative coupling of methane is an exothermic process involves the catalytic conversion of methane to ethane, which is further converted in situ into ethylene, and other sequential reactions produce small amounts of higher hydrocarbons (often reported as C_{2+} products) in presence of oxygen. A number of researches on OCM have been conducted intensively in order to obtain higher C_{2+} yield (>30%) as required for industrial interest. Attempts have been endeavored in the study of reactor configurations, types of catalysts, ionic conductive membrane development and its characterization, reaction mechanism, oxygen permeation flux in the membrane reactor, and optimization of the operating conditions.

2.1 REACTION MECHANISMS

The mechanism of oxidative coupling of methane requires the knowledge of an unusual type of oxidation catalysis, which encompass both the surface and gas phase free-radical chemistry. Oxygen as a co-reactant acts as an oxidant in activating methane to methyl radical. There is a general consensus that methyl radicals combine or couple to form ethane, which can be oxidatively or thermally dehydrogenated to ethylene (Lane & Wolf, 1988) or may enter into chain branching reactions that ultimately result in the formation of CO_x (Lunsford, 1995). Lane and Wolf (1988) have investigated the mechanism of OCM in the absence of catalysts by co-feeding methane and oxygen, where the products were C_2H_6, C_2H_4, C_3H_8, C_3H_6, CO (main product), CO_2,

H_2, H_2O and traces of HCHO, C_4 and C_5 hydrocarbons under varying operating conditions as follows:

Primary mode of initiation:	$CH_4 + O_2(g) \rightarrow CH_3\cdot + HO_2\cdot$	*(2.1)*
Ethane formation by methyl radical termination:	$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$	*(2.2)*
Ethylene Formation	$C_2H_6 \rightarrow C_2H_4 + H_2$	*(2.3)*
Secondary combustion:	$C_2H_6 + 3O_2(g) \rightarrow CO.CO_2 + 3H_2O$	*(2.4)*
	$C_2H_4 + 2.5O_2(g) \rightarrow CO.CO_2 + 2H_2O$	*(2.5)*
	$CO + O_2(g) \rightarrow CO_2$	*(2.6)*
Termination reactions:	$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$	*(2.7)*
	$H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2$	*(2.8)*

Where $O_2(g)$ is denoted as gas phase molecular oxygen.

In presence of catalyst, Roos and co-workers (1989) reported that the formation of active sites on the surface of Li/MgO catalyst, may involve the decomposition of surface lithium carbonate in the presence of gas-phase oxygen, which is possibly by the adsorption of oxygen on the site resulting from the loss of CO_2. Assumption is made that the process is reversible; CO_2 will re-adsorb on the surface and poisoning the catalyst by forming the inactive surface carbonate. Ito and co-workers (1985) however proposed the heterogeneous reaction model based on the original scheme in a more detail way by separating the oxide ion vacancy and adsorbed oxygen species.

$$CH_4 + O_s^- \rightarrow CH_3\cdot + OH_s^- \qquad (2.9)$$

$$2\ OH_s^- \rightarrow H_2O + O_s^{2-} + V_O^{\cdot\cdot} \qquad (2.10)$$

$$O_s^{2-} + V_O^{\cdot\cdot} + \frac{1}{2} O_2 \Leftrightarrow 2\ O_s^- \qquad (2.11)$$

The symbol $V_O^{\cdot\cdot}$ denotes an oxide ion vacancy, and subscript 's' is an adsorbed species. Reaction (2.1) is quite similar to reaction (2.9), but the latter shows the

adsorbed oxygen species at the active site in the presence of catalyst and this gives better understanding of the reaction mechanism. The active species of oxygen (the adsorbed oxygen) encourages the formation of methyl radical in reaction (2.9). The formation of ethane and ethylene in the presence of catalyst is similar with reaction (2.2) and (2.3). In practice, the formation of undesirable product CO_2 retarded the production of ethylene to a great extent. The reaction paths (2.4) and (2.5) lead the combustion of hydrocarbons that produces CO_2, which is influenced by the reaction temperature.

2.2 CATALYSTS PERFORMANCE IN OCM

The study of catalyst performance, its active sites, morphology, catalytic activity/selectivity, stability, reproducibility, preparation method and properties in OCM have been extensively reported (Lunsford et al., 1998; Hong & Yoon, 2001; Takenaka et al., 2001; Lee et al., 2002; Chou et al., 2003; Dedov et la., 2003; Ji et al., 2003; Rane et al., 2006). Several catalysts were elaborated and found to be effective in this complex heterogeneous-homogeneous process and the recent studies are presented in Table 2.1. Parameters of metal oxides, such as basicity, band gap, and electrical conductivity are some of the important parameters in affecting the catalyst performance. The more effective catalysts are divided into five groups: a) highly basic pure oxides, of which the early members of the lanthanide oxide series (excluding CeO_2) are the best; b) Group IA or IIA ions supported on basic oxides (for example, Li/MgO, Ba/MgO and Sr/La_2O_3); c) monophasic oxides; d) a few transition metal oxides that contain Group IA ions; and e) any of these materials that are promoted with chloride ions (Lunsford, 1995). In the early 1980s, catalyst Li/MgO has been widely studied (Lunsford, 1995) due to its impressive catalytic activity in OCM. Improvement in the methane conversion, C_{2+} products yield and selectivity can be achieved by doping other components such as Ce, La, Sn, Ti and B (Nagaoka et al., 1999), which are believed, to improve the catalyst activity and stability. Takenaka and co-workers (2001) studied the catalyst performance