DEVELOPMENT OF CATALYTIC MEMBRANE REACTOR FOR THE PRODUCTION OF ETHYLENE FROM NATURAL GAS BASED ON OXIDATIVE COUPLING OF METHANE TECHNOLOGY

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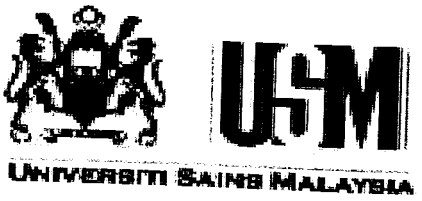
UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
2008



Laporan Akhir Projek Penyelidikan Jangka Pendek

Development of Catalytic Membrane Reactor for the Production of Ethylene from Natural Gas Based on Oxidative Coupling of Methane Technology

by
Prof. Dr. Abdul Rahman Mohamed
Prof. Subhash Bhatia

DITERIMA
20 MAR 2007
UNIT EITD
Universiti Sains Malaysia

UNIVERSITI SAINS MALAYSIA

PEJABAT PENGURUSAN & KREATIVITI PENYELIDIKAN
RESEARCH CREATIVITY AND MANAGEMENT OFFICE [RCMO]

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA *PENDEK*
FINAL REPORT OF SHORT TERM RESEARCH PROJECTS

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1) **Nama Ketua Penyelidik** :
Name of Research Leader :

Ketua Penyelidik *Research Leader*	PTJ *School/Centre*
Prof. Dr. Abdul Rahman Mohamed	School of Chemical Engineering

Nama Penyelidik Bersama
(Jika berkaitan) :
Name/s of Co-Researcher/s
(if applicable)

Penyelidik Bersama *Co-Researcher*	PTJ *School/Centre*
Prof. Subhash Bhatia	School of Chemical Engineering

2) **Tajuk Projek** : Development of Catalytic Membrane Reactor for the Production of Ethylene from Natural Gas Based on Oxidative Coupling of Methane Technology
Title of Project:

3) **Abstrak untuk penyelidikan anda**

(Perlu disediakan di antara 100 – 200 perkataan di dalam **Bahasa Malaysia dan Bahasa Inggeris**. Ini kemudiannya akan dimuatkan ke dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & luar).

Abstract of Research

(Must be prepared in 100 – 200 words in Bahasa Malaysia as well as in English. This abstract will later be included in the Annual Report of the Research and Innovation Section as a means of presenting the project findings of the researcher/s to the university and the outside community)

Abstrak

Malaysia mempunyai banyak simpanan gas asli, di mana metana sebagai komponen utama boleh dipergunakan dan ditukar kepada produk yang lebih bernilai seperti metanol, formaldehid, syngas, bahan api bercecair dan etilena. Penggandingan metana beroksida (OCM) merupakan salah satu cara yang baik untuk penghasilan etilena dari metana. Sistem pemangkin berkomponen-3 telah digunakan untuk kajian tindak balas kimia OCM dalam reaktor bermangkin lapisan terpadat. 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 keputusan eksperimen dengan 43.05% penukaran metana, 70.62% C_{2+} peratusan pemilihan dan 30.40% C_{2+} peratusan penghasilan. Dalam kajian ini, satu reaktor membran bermangkin telah dibangunkan bagi aplikasi dalam tindak balas kimia penggandingan metana beroksida (OCM). 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. 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. Prestasi reaktor bermangkin lapisan terpadat (PBCR), reaktor membran bermangkin (CMR) dan reaktor membran bermangkin lapisan terpadat (PBCMR) telah dibandingkan.

Abstract

Malaysia has abundant reserves of natural gas, in which methane as the main constituent could be utilized and converted into more valuable products such as methanol, formaldehyde, syngas, liquid fuel and ethylene. Oxidative coupling of methane (OCM) is one of the promising routes for the production of ethylene from methane. A 3-components catalyst system (Na-W-Mn/SiO_2) was used to study the OCM reaction in a packed bed catalytic reactor. The predicted optimum condition of temperature 850°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 43.05% methane conversion, 70.62% C_{2+} selectivity and 30.40% C_{2+} yield. In present study, a catalytic membrane reactor was developed for the application in oxidative coupling of methane reaction. The oxygen permeation flux of 0.56cm^3/min.cm^2 with purity of 27.96% was obtained at 850°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°C during the study of OCM reaction. C_{2+} selectivity of 67.5%, methane conversion of 51.55% and C_{2+} yield of 34.73% were obtained at 850°C, CH_4 to O_2 ratio of 3 and sweep gas flow rate at 100cm^3/min in a catalytic membrane reactor. The performances of packed bed catalytic reactor (PBCR), catalytic membrane reactor (CMR) and packed bed catalytic membrane reactor (PBCMR) were compared.

4) Sila sediakan Laporan teknikal lengkap yang menerangkan keseluruhan projek ini. [Sila gunakan kertas berasingan]
Kindly prepare a comprehensive technical report explaining the project (Prepare report separately as attachment)

Senaraikan Kata Kunci yang boleh menggambarkan penyelidikan anda :
List a glosssary that explains or reflects your research:

Bahasa Malaysia	Bahasa Inggeris
Penggandingan metana beroksida (OCM)	*Oxidative Coupling of Methane (OCM)*
Reaktor membran bermangkin	*Catalytic membrane reactor*
Pemangkin berkomponen-3	*3-components catalyst*

5) **Output Dan Faedah Projek**
Output and Benefits of Project

(a) * Penerbitan *(termasuk laporan/kertas seminar)*
Publications (including reports/seminar papers)
(Sila nyatakan jenis, tajuk, pengarang, tahun terbitan dan di mana telah diterbit/dibentangkan).
(Kindly state each type, title, author/editor, publication year and journal/s containing publication)

Conference Paper:

Chua Yen Thien, Abdul Rahman Mohamed and Subhash Bhatia.(2004) Catalytic Membrane Reactor for Oxidative Coupling of Methane – Review and Prospects. *18th Symposium of Malaysian Chemical Engineers (SOMChE 2004),* UTP, 13-14th DEC. 2004.

Journal Paper:

Chua Yen Thien, Abdul Rahman Mohamed and Subhash Bhatia. (2006) Process Optimization of Oxidative Coupling of Methane for Ethylene Production Using Response Surface Methodology. *Journal of Chemical Technology and Biotechnology,* In Press.

(b) **Faedah-Faedah Lain Seperti Perkembangan Produk, Prospek Komersialisasi Dan Pendaftaran Paten atau impak kepada dasar dan masyakarat.**
Other benefits such as product development, product commercialisation/patent registration or impact on source and society

The development of catalytic membrane reactor is a breakthrough in this project and potential to be patented especially on the design and fabrication of the gas-tight and high temperature resistance reactor. It is believed that this technology is favorable to the OCM reaction condition and will catalyze the commerciallization of OCM process in the very near future. Hence, methane could be utilized to alleviate the tight supply of ethylene.

* Sila berikan salinan
* *Kindly provide copies*

(c) **Latihan Gunatenaga Manusia**
Training in Human Resources

i) Pelajar Siswazah : .....1.....
Postgraduate students:
(perincikan nama, ijazah dan status)
(Provide names, degrees and status)
.....
Chua Yen Thien, MSc, Dissertation submitted
.....
.....

ii) Pelajar Prasiswazah : .....
Undergraduate students:
(Nyatakan bilangan)
(Provide number)
.....
.....
.....

iii) Lain-Lain : .....
Others:
.....
.....
.....

6. **Peralatan Yang Telah Dibeli :**
Equipment that has been purchased:

1) Packed bed catalytic reactor with quartz tube liner
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2) Catalytic membrane reactor
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3) Microreactor with controller
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4) Back pressure regulators
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5) Pressure vacuum gauges
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KOMEN JAWATANKUASA PENYELIDIKAN PUSAT PENGAJIAN
Comments of the Research Committees of Schools/Centres

Projek penyelidikan telah dijalankan seperti permohonan asal dengan jayanya.

PROFESOR ABDUL LATIF AHMAD, CEng FIChemE
Dekan
Pusat Pengajian Kejuruteraan Kimia
Kampus Kejuruteraan
Universiti Sains Malaysia, Seri Ampangan
Pulau Pinang.

TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN PUSAT PENGAJIAN
Signature of Chairman
[Research Committee of School/Centre]

15/3/2007
TARIKH
Date

Updated : 16MAC2006

UNIVERSITI SAINS MALAYSIA
SCHOOL OF CHEMICAL ENGINEERING

Final Report

2007

DEVELOPMENT OF CATALYTIC MEMBRANE REACTOR FOR THE PRODUCTION OF ETHYLENE FROM NATURAL GAS BASED ON OXIDATIVE COUPLING OF METHANE TECHNOLOGY

BAHAGIAN PENYELIDIKAN DAN PEMBANGUNAN
CANSELORI
UNIVERSITI SAINS MALAYSIA

Laporan Kemajuan Penyelidikan

Nama Penyelidik/ Penyelaras: Prof. Dr. Abdul Rahman Mohamed

Pusat Pengajian: Pusat Pengajian Kejuruteraan Kimia

Tajuk Projek Penyelidikan: Development of Catalytic Membrane Reactor For the Production of Ethylene from Natural Gas Based on Oxidative Coupling of Methane Technology.

Jumlah Geran Diluluskan: RM 17,600

Geran Tambahan yang Diluluskan: -

Baki yang ada: RM498.90

Tarikh projek bermula dan dijangka siap: 15 Mac 2005 hingga 14 Mac 2007

Lanjutan tempoh yang diluluskan (*sekiranya berkaitan*):
(i)
(ii)
(iii)

Laporan Kemajuan dari segi kerja-kerja yang telah dijalankan:
(*Sila beri Laporan Kemajuan yang terperinci setakat mana yang boleh*)

The development of catalytic membrane reactor for the production of ethylene using natural gas based on oxidative coupling of methane (OCM) has marched to a great advance. The 3-components catalyst system was studied using Design of Experiments (DoE). An oxygen permeable membrane with mixed ionic-electronic conductivity was synthesized to separate oxygen from air, which is cheaper as the reactant in OCM. The catalyst and the membrane were combined to be a catalytic membrane reactor system. The progress of the research was presented and discussed in the sequence as followed:

1) Design and fabrication of catalytic membrane reactor

A catalytic membrane reactor resembles shell and tube heat exchanger was designed for the study in oxidative coupling of methane. Inert materials such as ceramic and quartz were chosen as the reactor casing and tube side of the reactor, respectively, with stainless steel double –flange head as shown in Figure 1 and Figure 2. The membrane tube was sealed to the quartz tubes at both ends with alumina sealant, Ceramabond 569. The development of the catalytic membrane reactor considered the three major prerequisites: 1) A gas-tight reactor system so that the results of analysis would not be affected; 2) Resistant to high temperature without any corrosion of the reactor materials and reaction with the gases; 3) The membrane tube within the reactor could be taken out easily without breaking the membrane tube.

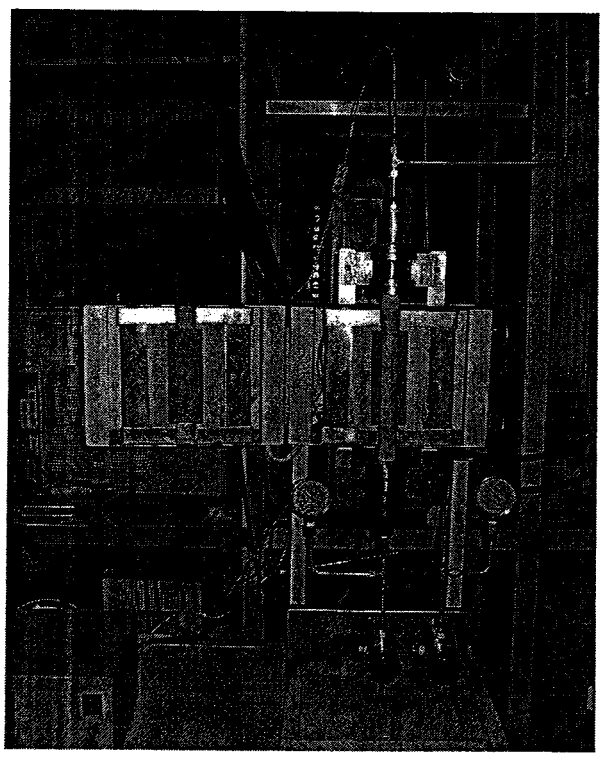

Figure 1 Catalytic membrane reactor and furnace

Leak test was performed prior to the admission of reactant gases into the reactor system. There was proven to have no leaking from the reactant system. However, leaking from the tube side to the shell side of the reactor was difficult to be detected and thus, the relationship of the fluxes of leaked N_2 and O_2 through the pores and cracks of the sealant was defined using the Knudsen diffusion mechanism.

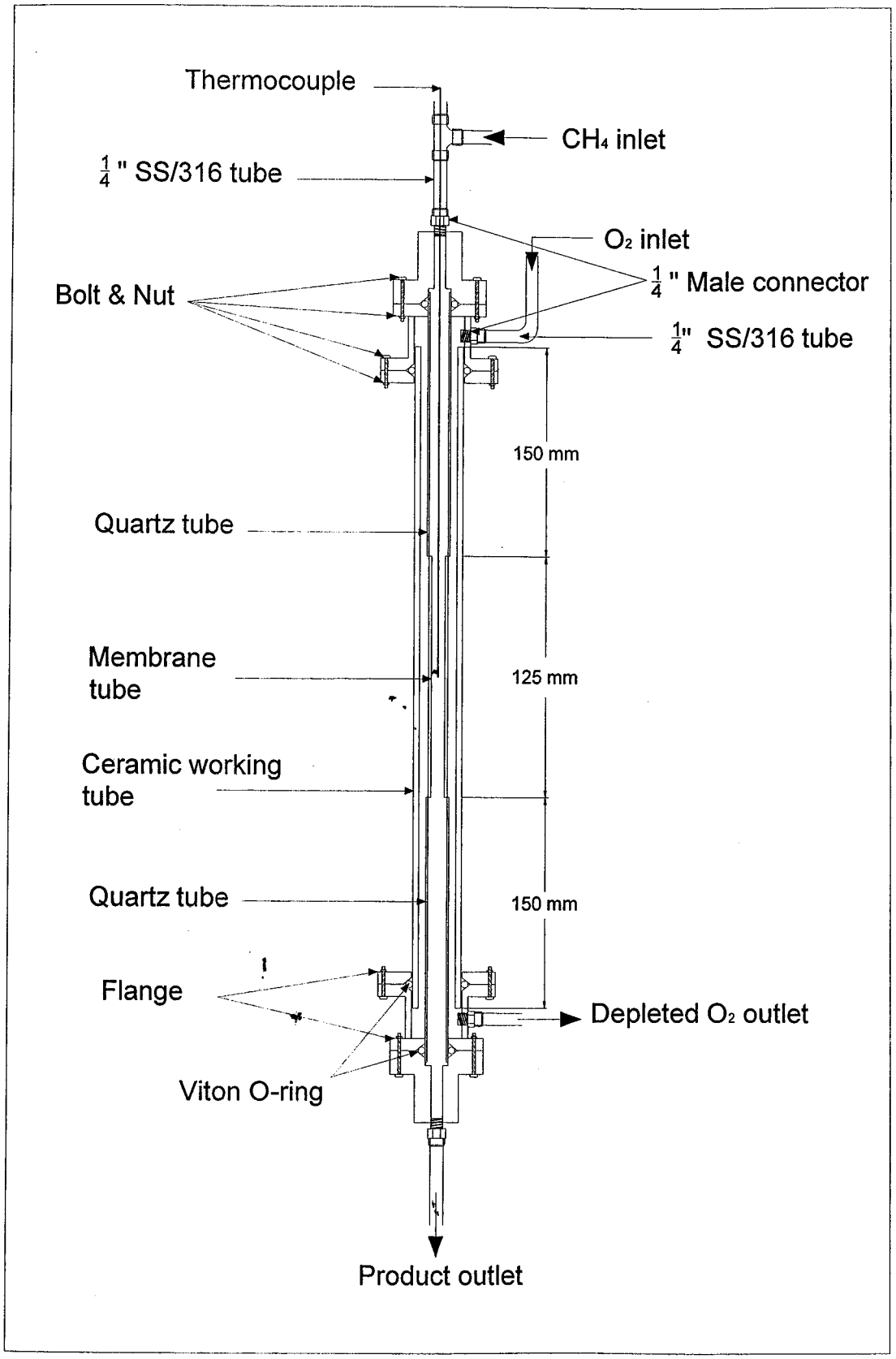

Figure 2 Schematic drawing of catalytic membrane reactor

2) Results and Discussion

2.1) Oxygen permeation test

In order to ensure that the oxygen permeability of the membrane is agreeable, which will facilitate the oxygen distribution and enhance the performance of OCM reaction, oxygen permeation test using the catalytic membrane reactor incorporated with oxygen permeable membrane ($Ba_{0.5}Ce_{0.4}Gd_{0.1}Co_{0.8}Fe_{0.2}O_{3-\delta}$) was studied prior to the OCM reaction study.

The permeation studies were performed at varying temperature (600-900^{0}C) and sweep gas flow rate (30 and 100 cm^3/min). The mixture of O_2 + N_2 resembles the air composition (21% O_2 and 79% N_2) was used as the feed gas to the shell side of the reactor at the flow rate of 150 cm^3/min. The permeation test was based on concentration gradient, and thus, Helium as the sweep gas was fed from the tube side to control the oxygen concentration gradient by "sweeping off" the permeate to the downstream. The permeated oxygen from the total amount of oxygen from the shell side is presented in Figure 3. The percentage of oxygen permeated through the membrane with permeated surface area 32.987 cm^2 was found to increase from 40 to 60% of the total oxygen fed as a function of temperature when helium flow rate was 100cm^3/min. In temperature range of 600 to 900^{0}C, the oxygen permeation flux increased for a factor of 1.3 at helium flow rate 100 cm^3/min. Lu and co-workers (2000) reported a factor of 5 of the oxygen flux increment over a temperature range of 300^{0}C. However, the reported oxygen flux through the $BaCe_{0.8}Gd_{0.2}O_3$ (BCG) dense membrane tube was lower compared to the present study with only oxygen flux 0.10 cm^3/min.cm^2 at temperature 900^{0}C, helium flow rate 108 cm^3/min and air flow rate 78.3 cm^3/min.

Higher helium flow rate provides higher oxygen permeation flux. This is due to an increase of the sweep gas flow rate in the tube side reduces the oxygen partial pressure in the tube side, eventually resulting a greater oxygen partial pressure gradient across the membrane. At temperature 900^{0}C and helium flow rate 30 cm^3/min, the oxygen permeation flux was about 0.215 cm^3/min.cm^2, which is comparable to the reported oxygen flux 0.21 cm^3/min.cm^2 using tubular $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane by Li and co-workers (2000), but almost 4 times higher than the result reported by Lu and co-workers (2000) for the BCG membrane tube (ID 4.6 mm × OD 6 mm × length 11 cm).

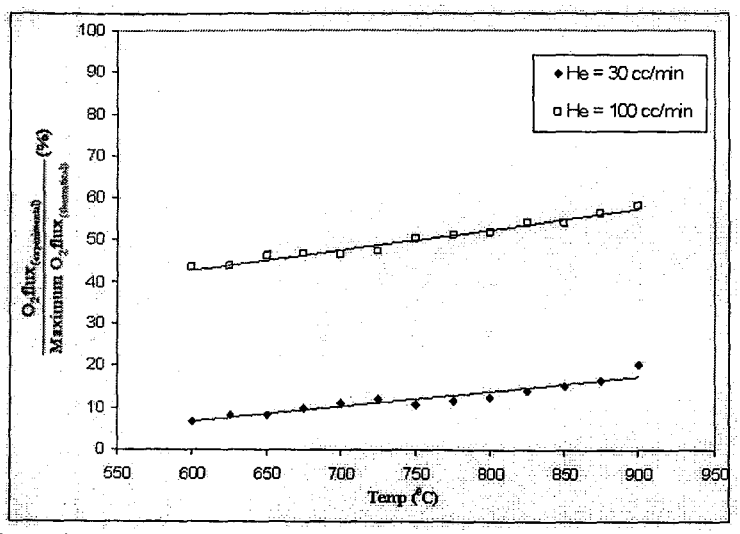

Figure 3 Ratio of experimental oxygen flux to the theoretical oxygen flux in maximum as a function of temperature. Air flow rate = 150 cm^3/min (shell side) and He flow rate (tube side) as given.

2.2) Performance study of catalytic membrane reactor

The performance of catalytic membrane reactor in OCM reaction was studied with varying temperature, methane to oxygen ratio and sweep gas flow rate.

2.2.1) Effect of temperature

Figure 4 shows the results of methane conversion, C_{2+} selectivity, C_{2+} yield and oxygen permeation flux at varying temperature. The air flow rate was maintained at 150 cm^3/min and CH_4/O_2 ratio at 3. The methane conversion was found to increase with respect of temperature (700-900^{0}C) as well as the C_{2+} selectivity and yield. However, the C_{2+} selectivity decreased in lower temperature region, indicates that lower temperature is less conducive to the C_{2+} formation due to the low catalytic activity. In contrast, the oxygen permeation flux obtained was 2.08cm^3/min.cm^2, which was remarkably higher at low temperature (700^{0}C), although the C_{2+} formation was less impressive. It was observed that the oxygen permeation flux dropped intensely at temperature 750^{0}C but started to ascend moderately with the increment of temperature. The rise of oxygen permeation flux after 750^{0}C was mainly influenced by the active OCM reaction as the methane conversion and C_{2+} selectivity increased with respect to temperature. The highest C_{2+} selectivity of 67.5% was obtained at around 800-825^{0}C and started to decline after 900^{0}C.

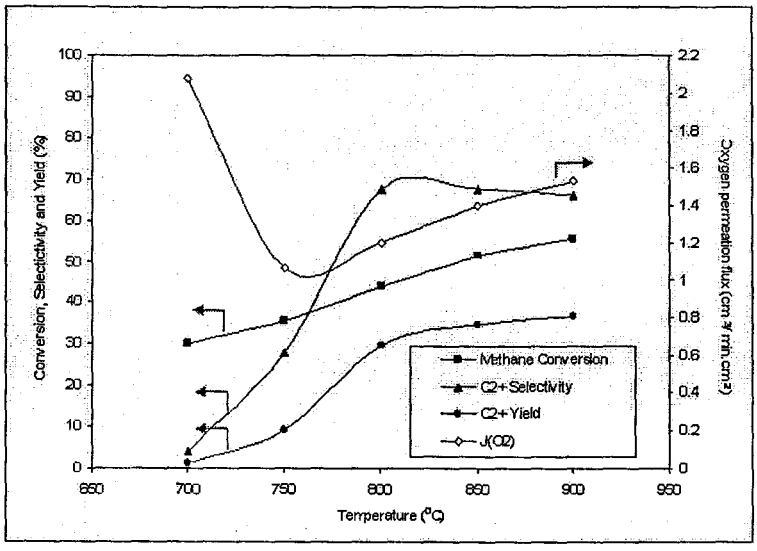

Figure 4 Temperature profile of OCM performance in catalytic membrane reactor with CH_4/O_2 ratio = 3, air flow rate =150 cm^3/min and mixture of 48.6% CH_4 and 51.4% He = 194.5 cm^3/min.

2.2.2) Effect of methane to oxygen ratio

The effect of CH_4/O_2 ratio between the ranges of 0.5-3 to the performance of OCM reactions was presented in Figure 5. Methane conversion, C_{2+} selectivity and C_{2+} yield unanimously increased with the increment of CH_4/O_2 ratio. The oxygen permeation flux was observed reduced with the increment of methane concentration in the tube side. The highest oxygen permeation flux was at 2.6cm^3/min.cm^2 when the CH_4/O_2 ratio was 0.5, but the OCM activity was the lowest at this point. This circumstance was mainly assigned to the recombination of lattice oxygen to gaseous oxygen has predominantly occurred on the membrane surface exposed to OCM reaction. However, one could observe that the high oxygen flux reduced in a sliding pattern at the smaller CH_4/O_2 ratio but almost maintained at 1.5cm^3/min.cm^2 when the CH_4/O_2 ratio was within the range 2-3.

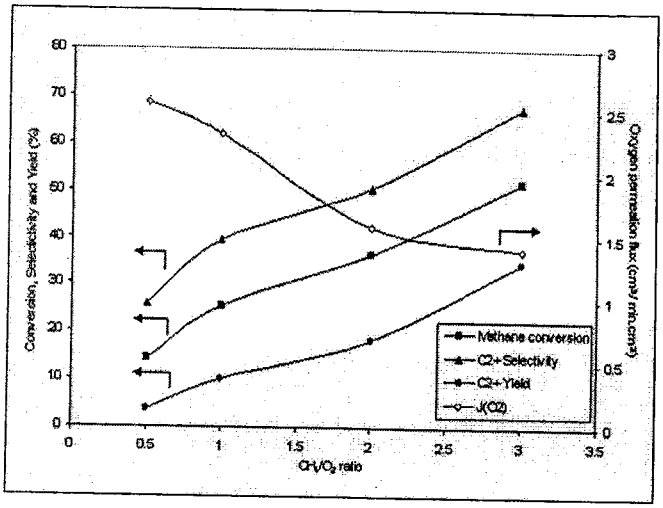

Figure 5 Effect of CH_4/O_2 ratio to the performance of OCM reactions at temperature= 850^0C, air flow rate =150 cm^3/min and He flow rate = 100 cm^3/min.

2.3) Comparison of catalytic membrane reactor and packed bed catalytic membrane reactor in OCM

The performances of catalytic membrane reactor (CMR) and packed bed catalytic membrane reactor (PBCMR) in OCM optimum conditions were studied and compared. The packed bed catalytic membrane reactor has the similar reactor assembly as catalytic membrane reactor, but distinguished with the existence of a catalyst bed weighed 0.4g and packed in the center of the membrane tube as shown in Figure 6.

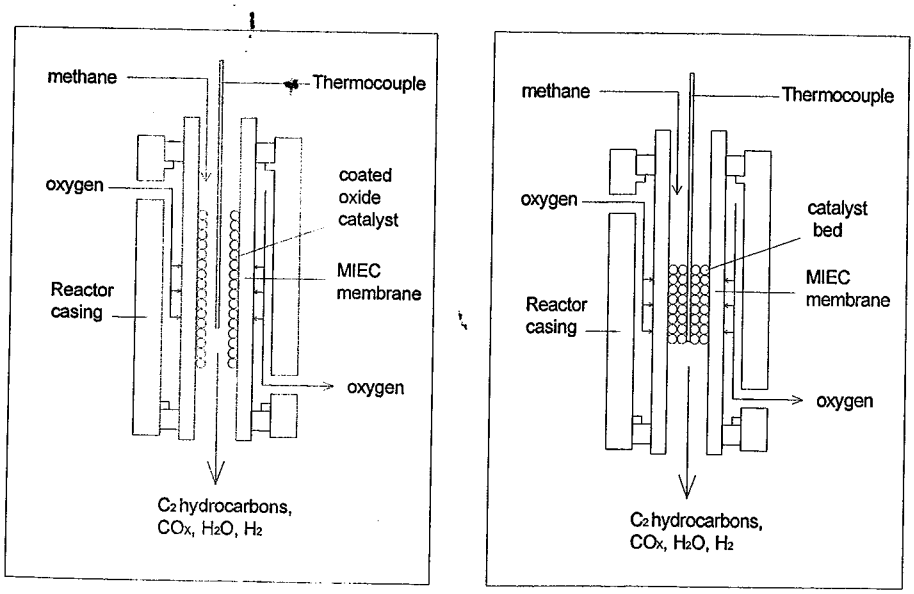

Figure 6 Schematic diagram of (a) Catalytic Membrane Reactor (CMR); (b) Packed Bed Catalytic Membrane Reactor (PBCMR)

Performances of CMR and PBCMR were compared at temperature 850^0C, sweep gas flow rate $100cm^3$/min, air flow rate $150cm^3$/min and CH_4/O_2 ratio of 3 (Table 1). CMR showed its superiority over PBCMR with higher degree of methane conversion and C_{2+} selectivity. The C_{2+} yield obtained from CMR was almost 2.5 times greater with 34.73%. The oxygen permeation fluxes of both reactor types did not differ much.

Table 1 Comparison of CMR and PBCMR performances at T=850^0C, CH_4/O_2 = 3, air flow rate = $150cm^3$/min and He flow rate = $100cm^3$/min.

Reactor type	**Methane Conversion (%)**	**C_{2+} Selectivity (%)**	**C_{2+} Yield (%)**	**J_{O_2} (cm^3/min.cm^2)**
Catalytic membrane reactor (CMR)	51.55	67.37	34.73	1.3973
Packed bed catalytic membrane reactor (PBCMR)	36.35	39.59	14.39	1.2203

3) Conclusions and Suggestions

In present study, catalytic membrane reactor (CMR) performed better than packed bed catalytic reactor (PBCR) and packed bed catalytic membrane reactor (PBCMR) in OCM reaction. However, improvements are needed in the future study especially in tackling the sealant problem of the quartz tube and membrane tube. Leaking of the reactants from the shell side to the tube side of the reactor has influenced the results during OCM reaction. A perfect sealant without defect with highly adhesive was not reported yet in literature and it is still in search. Besides, the membrane should be dense sufficiently to prevent the diffusion of gases from the tube side to the shell side of the reactor. It is suggested that the porous support should be coated with a layer of mesoporous material before the dip-coating of the mixed ionic-electronic conducting membrane.

Apparently, reactor configurations affected the OCM results and it was showed that catalytic membrane reactor has a great prospect in providing a promising C_{2+} yield in OCM reaction. The commercialization of OCM process will be realized in a very short future.

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Lu, Y., Dixon, A.G., Moser, W.R., Ma, Y.H. and Balachandran, U. (2000). Oxygen-permeable Dense Membrane Reactor for the Oxidative Coupling of Methane. *Journal of Membrane Science, 170*, 27-34.

LIST OF PUBLICATIONS

Conference paper:

Chua Yen Thien, Abdul Rahman Mohamed and Subhash Bhatia. (2004). Catalytic Membrane Reactor for Oxidative Coupling of Methane – Review and Prospects. *18th Symposium of Malaysian Chemical Engineers (SOMChE 2004),* UTP, 13-14th Dec. 2004.

Journal paper:

Chua Yen Thien, Abdul Rahman Mohamed and Subhash Bhatia. (2006). Process Optimization of Oxidative Coupling of Methane for Ethylene Production using Response Surface Methodology. *Journal of Chemical Technology and Biotechnology*, In Press.

TANDATANGAN PENGERUSI

JAWATANKUASA PENYELIDIKAN

PUSAT PENGAJIAN

SOMChE 2004

December 13-14, 2004

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Proceedings: Volume I

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Universiti Teknologi PETRONAS

and

Institut Jurutera Kimia Malaysia

CATALYTIC MEMBRANE REACTOR FOR OXIDATIVE COUPLING OF METHANE – REVIEW AND PROSPECTS

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ABSTRACT

The rising price of crude oil recently has spurred the researchers in searching for better alternatives intensively for the benefits of global economics. Natural gas in abundant deposits however is potentially to be converted to more valuable fuels and chemicals that may help in mitigating the triggered bearish sentiment in the crude market and as a demulcent for the oil tightness. Oxidative coupling of methane (OCM) is one of the promising routes in utilizing the low cost natural gas to the production of ethylene, which may provide a cost-effective way to convert natural gas to olefins compared to the conventional thermal cracking of ethane. The limitation of the low yield of ethylene product (< 30%) by using OCM has diminished the industrial interest. It is undoubtedly that the future and ongoing developments in ethylene technology will take their momentum from both market forces and technological advances. This overview is attempted to discuss some of the developments and outstanding opportunities in the emerging area of catalytic membrane reactor and the development of catalyst in order to overcome this problem. Recent developments of OCM will be presented, converging to the special emphasis in catalytic membrane reactor, which shows its good prospects to be implemented and commercialized industrially. The utilization of natural gas by using OCM is a promising route since the preferred route to ethylene will be the one based on the cheapest raw material, minimum energy consumption and low investment.

Keywords: OCM, Catalytic membrane reactor, Ethylene, Oxygen Permeable Membrane.

1 INTRODUCTION

The oil crisis since 1970s has spurred and provoked the scientists and researchers to other alternatives in reducing the oil dependence globally. At this critical stage, the closest path to overcome the demand of oil is by using the abundant hydrocarbon resource, i.e. natural gas, which is mainly used as clean-burning fuels and production of chemicals. The estimated world natural gas reserves is 1.735×10^{14} m^3, which is almost 6 times greater than the crude oil reserves over the world and it is widespread over the world (Energy Information Administration, 2002). The abundance of natural gas reserves is not the only reason that shifts the attentions of researchers, but also the special characteristics of natural gas as the cleanest, safest, and most useful of all energy sources. Comparatively, the low cost natural gas is more beneficial as cheaper raw material that may reduce the cost of production, thus will diminish the inflation and meet the demand of global market. Methane, as the main constituent of natural gas, can be converted into more valuable chemicals such as methanol, formaldehyde, syngas and ethylene. Ethylene as the vital chemical building block in producing products such as polyethylene, ethylene oxide, ethanol, and styrene, has a major portion in the global market. Most of the ethylene is made by the thermal cracking of any naphthenic or paraffinic hydrocarbon heavier than methane; the amount of ethylene and by-products formed will depend upon molecular weight of feed. Today, ethane from natural gas is another alternative that promises a cheaper feedstock in the production of ethylene. Since the percentage of ethane in natural

gas is small as compared to methane, thus oxidative coupling of methane devices a more attractive and enduring path on the edge of oil crisis.

Oxidative coupling of methane (abbreviated as OCM) is one of the highly viable means of process in the production of ethylene from methane. The promising result of this process is first reported by Keller and Bhasin at 1982, and thence a myriad of research works have been studied extensively varied from type of catalysts, reactor configurations and operating processes. However, the limitation of the low yield of ethylene product (< 30%) by using OCM has diminished the industrial interest and many research works are hitherto been developed and improved to meet the interest threshold. This overview is the introduction of the oxidative coupling of methane in general basis, further emphasizing to the development of catalyst and the prospects of catalytic membrane reactor in OCM for the purpose of industrial commercialization.

2 OXIDATIVE COUPLING OF METHANE

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 in presence of oxygen 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).

2.1 CATALYSTS IN OCM

The study of catalyst performance, its active sites, catalytic activity/selectivity, stability, reproducibility, preparation method and properties in OCM have been extensively reported. Several catalysts were elaborated and found to be effective in this complex heterogeneous-homogeneous process and some recent studies are presented in Table 1. Parameters of metal oxides, such as basicity, band gap, and electrical conductivity are some 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, 1995a). Catalyst Li/MgO has been widely studied (Lunsford et al., 1995a) due to its appreciable 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.

TABLE 1. Methane Conversion, Yield and Selectivity of C_2 Product for Several Catalysts

References	Reaction Temperature (K)	Catalyst	Results (%)		
			C_2 yield	C_2 selectivity	CH_4 conversion
Lunsford et al. (1998)	1123	- $Mn/Na_2WO_4/SiO_2$ - $Mn/Na_2WO_4/MgO$	10.7 8.8	79.4 86.4	13.5 10.2
Hong et al. (2001)	1023	- $CaCl_2$-promoted Ca_2PO_4Cl	22	59	39
Lee et al. (2002)	923	- O_2-pretreated $Ni_3(SbTe_3)_2$	11	79	25
Ji et al. (2003)	1073	- Na_2WO_4-Mn/SiO_2	19.6	66.4	29.5
Chou et al. (2003)	1053	- SnO_2 modified 5% Na_2WO_4-2% Mn_2O_3/SiO_2	24.1	73.1	33
Dedov et al. (2003)	1123	- La-Ce/MgO	16.1	72.4	22.3

Several papers were addressed to the rare earth oxides supported on basic materials or promoted with alkaline oxides as catalysts for the OCM (Dedov et al., 2000; Yu et al., 1998). The productivity of these systems may be attributed either to the catalyst basicity or availability of the activity sites as oxygen vacancies and/or other defects important for

oxygen activation. A considerable research work has been conducted by Dedov and co-workers, 2003 on various components, such as CeO_2, Tb_4O_7, La_2O_3, Y_2O_3, Tm_2O_3, Sm_2O_3, Yb_2O_3, Eu_2O_3, La-Nd, La-Pr-Nd, La-Ce, La-Ce/MgO and the mixture of components. The best result is shown by using Ceria-lanthana supported on MgO, in which the addition of Ce to La furnishes detectable enhancement of the catalyst efficiency in C_{2+} production. The chloride-containing oxides constituted effective catalysts for OCM that enhance both the conversion and selectivity. $CaCl_2$-promoted calcium chlorophosphate is one of the chloride-containing catalysts that exhibited good catalytic performance, where the presence of $CaCl_2$ yielded high ethylene selectivity (Hong et al., 2001).

Other efforts have been emphasized on the Na-W-Mn/SiO_2 catalyst system, which had been one of the most effective catalysts reported (Palermo et al., 1998; Lunsford et al., 1998a; Ji et al, 2003; Chou et al., 2003). Palermo and co-workers reported that the full trimetallic formulation Mn/Na_2WO_4/SiO_2 calcined at 750^{0}C can generate an excellent catalyst in terms of high C_2 selectivity (80%) at high conversion (33%) at reaction temperature 1123K and total flow rate 18 ml/min. The structural, catalytic, and spectroscopic results indicated that Na plays a dual role both as a structural and chemical promoter, the phase transition from the amorphous silica to α-cristobalite is a critically important requirement for the production of effective catalyst (Palermo et al., 1998). The characterization of this catalyst has led to the conclusion that tetrahedral WO_4 surface species with one W=O and three W-O-Si surface bonds as the OCM active site, with manganese oxide enhancing the exchange between gaseous and lattice oxygen (Wu et al., 1995). Many studies have been done on this catalyst by Lunsford and co-workers and they compared the catalytic behaviors of $NaWO_4$-Mn/SiO_2, Na_2WO_4-Mn/MgO and Na_2WO_4/MgO, which are suggested that Na-O-Mn species are the most probable active sites (Lunsford, 1995b & 1998b).

2.2 DEVELOPMENT OF CATALYTIC MEMBRANE REACTOR IN OCM

An appropriate system of catalysts may enhance OCM performance as mentioned in previous section. These results are quite interesting, but still fall short of the commercial viability threshold, typically producing yields lower than 30%. It is reported that dissociation of oxygen is a necessary requirement for the generation of methyl radicals and the subsequent coupling of methyl radicals to ethane and ethylene. Membrane is suggested as the best alternative in this role of reactant distribution. Thus, researchers have prompted in developing membrane reactor in improving the production of ethylene in OCM.

Various types of membrane reactor have been proposed such as inert membrane, catalytic membrane, composite membrane, porous membrane and dense membrane, which are classified according to their characteristics in selectivities and permeability. Both of these characteristics are determined by the interaction between the membrane and the permeating molecules which gives rise to the different transport mechanisms. Inert membrane reactor is differentiated from catalytic membrane reactor, the former has catalyst packed in the inner tube of membrane, or apart from the membrane structure; whereas the latter has catalyst doped or coated on the surface wall of the membrane, which behave as both the reactant distributor and reaction site. When the separation and reaction processes are combined into a single unit, the membrane, besides providing the separation function, also often results in enhanced selectivity and/or yield.

2.2.1 Development of Oxygen Permeable Membrane

The traditional meaning of the term *membrane* is associated to the concept of a permeable or semi-permeable phase, often in the form of thin film, made from a variety of materials such as inorganic solids and polymers, which is capable of imposing certain restrictions on the permeation flux of some substances. Thus, in *selective permeation* membranes only certain molecules meet the permeation requirements, and the membrane acts as a barrier to block the other substances (Coronas & Santamaria, 1999). A solid-state electrochemical reactor using stabilized zirconias (principally YSZ) has been applied in OCM studies (Lapena-Rey and Middleton, 2003). The limited electronic conductivity of YSZ needs the usage of external voltage (typically between 0.1 and 1 volt), which imposes an electrical current through the membrane. A considerable C_{2+} selectivity of 86% but low C_{2+} yield

4% was obtained. The application of electrochemical reactor in OCM is an interesting discovery but it is not applicable in industry due to the need of external voltage over the membrane. In recent years, some research efforts have been directed toward searching for ionic conducting membrane, which will enhance the oxygen permeation flux in membrane reactor as given in Table 2.

TABLE 2. Oxygen Permeability of Different Membrane from Literature

References	Reactor	Membrane	O_2 permeation flux
Xu, N. et al. (1999)	Quartz tube	ZrO_2-doped $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ membrane disk	1.3 ml/min cm^2 at 1223K
Wang et al. (2002)	Quartz tube	$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ tubular membrane	1.12 ml/cm^2 min at 1143K
Yang, N. et al. (2003)	Quartz tube	$La_2Ni_{0.8}Fe_{0.2}O_{4+\delta}$ membrane disk	> 1 ml/min cm^2 at 750K
Tan et al. (2004)	Quartz tube	Ag doped $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) membrane disk	3 ml/min cm^2 at 1250K
Deng et al. (2004)	Alumina tube	$SrGe_{0.1}Co_{0.8}Fe_{0.1}O_{3-\delta}$ membrane disk	1.24 ml/min cm^2 at 1173K
Li et al. (2004)	Alumina tube	ZrO_2 and iso-molar excess BaO doped $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane disk	1.69 ml/cm^2 min at 1250K
Akin & Lin (2004)	- quartz shell - mullite support tube	Fluorite-structured $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) -mixed conducting tubular membrane	0.041-0.92 ml/min cm^2 at 1203K

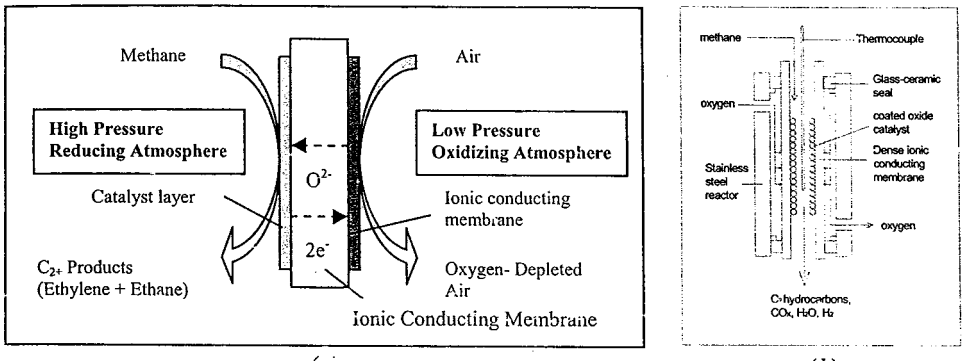
Ionic conducting dense membranes are used for molecular scale separations involving gaseous mixture, such as oxygen separation. These membranes made of ceramic and consist of solid oxides (ZrO_2, Y_2O_3, Bi_2O_3) as well as of solutions of mixed oxides (perovskites, brownmillerites, etc.), which act as solid electrolytes allowing the transport of oxygen (Marcano and Tsotsis, 2002). Ceramic membranes have the advantages of being chemically inert ad stable at high temperatures, conditions under which polymer membranes fail. Separation through dense ceramic membrane is governed by a solution-diffusion mechanism (Baker, 2004), which the driving force is oxygen partial pressure gradient across the membrane.

A noteworthy application of oxygen permeable membrane is using air as the reactant to separate oxygen that may permeate through the membrane and further catalyzed to react with methane (Dixon et al., 2000). Wang and co-workers, 2002 have successfully separated oxygen at permeation flux 1.12ml/min.cm^2 from air at flow rate 150ml/min and temperature 875^{0}C by using $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane. The oxidative reaction by using air as an economical oxygen source is highly potential in demonstrating a cost reduction process (Xu & Thomson, 1997; Zeng & Lin, 2000). Due to the mixed electron and oxygen ion conducting properties, these membranes are permeable to oxygen at elevated temperature without the need of outside electrical circuitry for electron transportation, which is necessary in traditional oxygen pumps (Shao et al., 2000). Perovskite-type (ABO_3) ceramic membrane is one of the highly ionic and electronic conductivity membranes that exhibit the highest oxygen permeability.

Two of most widely studied membranes, $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ are addressed individually by exchanging of the mixture composition (Xu & Thomson, 1997; Diethelm and Van herle, 2004), or by doping/addition of metal ions to improve the structure stability and oxygen permeability (Xu, N. et al., 1999; Wang et al., 2002; Yang, L. et al., 2003; Yang, N. et al., 2003; Tan et al., 2004; Deng et al., 2004; Li et al., 2004). Akin and Lin have proposed the fluorite-structured $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) membrane by considering the effect of reaction side condition in OCM, where the oxygen permeation depends strongly on the oxidation reaction rate and reactant flow (Akin & Lin, 2004). However, oxygen permeation flux reported for most of these membranes are still lower than the industrially targeted values, which are 5-10 ml/min cm^2 at temperature range 973-1223K (Lin, 2001). Other considerations of membrane synthesis have to be taken into account for the application in OCM, especially in preventing the permeation of methane through the membrane to the air feed side. This is an arduous task due to the slight difference of kinetic diameter between methane (3.8Å) and oxygen (3.46Å).

2.2.2 New Emerging Application of Catalytic Membrane Reactor in OCM

An innovation in recent years has been to develop processes with reduced overall environmental impact and towards greater economic. 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 functioned 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 (a) and 1 (b). Figure 1(*b*) shows the catalytic membrane reactor, which resembles the shell and tube configuration by using ionic conducting membrane tube 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.



(*a*) (*b*)

FIGURE 1. (*a*) Oxygen separations and chemical reaction on membrane surface and (*b*) schematic diagram of catalytic membrane reactor for the production of ethylene.

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. 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/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.

2.2.3 Recent Problems and Challenges of Oxidative Coupling of Methane

Recently, there is a great incentive in developing packed bed membrane reactor (PBMR) and catalytic membrane reactor (CMR) for oxidative coupling methane and numbers of research papers have been published as presented (Nozaki et al, 1992; Santamaria et al., 1994; Coronas et al., 1997; Lu et al., 2000; Xu & Thomson, 1997; Dixon et al, 2000; Zeng & Lin, 2000). However, their implementation in industry is still lack of interest due to the low production; for these are just preliminary discovery and further improvement are needed. Some researchers have proposed studies on the modified porous ceramic membrane by coating catalyst on a porous alumina tube (Nozaki et al, 1992); or packed catalyst inside the membrane tube (Coronas et al., 1997); or treating the membrane tube with $La(NO_3)_3$ aqueous solution for thermal stabilization with packed of catalyst within the membrane tube, also called as packed bed membrane reactor (Lu et al., 2000). These works were found to be ineffective in terms of ethylene yield and selectivity because porous membrane is poor in controlling oxygen permselectivity, and the permeability of methane to the air side might occur. In addition, the reactant stream in a packed-bed catalytic membrane reactor bypassing the catalyst packed in the reaction side may occur if there is insufficient pressure drop across the membrane. This discovery has encouraged other researchers in searching for better membrane reactor design, such as the replacement of porous membrane tube by ionic-conducting perovskite-type oxide membrane (Xu & Thomson, 1997; Dixon et al, 2000) and dense fluorite-structured membrane (Zeng & Lin,

2000; Akin & Lin, 2004), where the membranes have both oxygen permeable membrane and catalytic behavior for methyl couple reaction as presented in Table 3.

Table 3 Reported results of CMR performance in OCM

Type of CMR	Temp. of Reaction (K)	Oxygen Permeation Flux (ml/cm^2min)	CH_4 conversion (%)	C_{2+} selectivity (%)	C_{2+} yield (%)	References
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ disk membrane	1098	0.35	4.1	26.46	1.08	Xu &Thomson (1997)
$BaCe_{0.8}Gd_{0.2}O_3$ Tubular membrane	1053	0.04	26	62	16	Dixon et al., (2000)
$Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ tubular membrane	1203	0.1	15	69	10.4	Akin & Lin (2004)

These have a remarkable potential though the technological gap is still exist in achieving the industrial practice. The main challenge is the fabrication of ionic conducting membrane, where solid state reaction/isostatic pressing method (easier method) was mostly used by researchers, which is not applicable in industry. Suggestions that the membrane used should be easily provided in market, which has a uniform distribution of pore size and the modification can be done by coating the desired ionic conducting material and catalyst on the membrane. Sol gel method is one of the methods for dip coating the ionic conducting material and catalyst on the membrane (Yang, N. et al, 2003; Shaula et al., 2003). The membrane reactor studies reported further enlightened possible application opportunities but also strengthened the consciousness that the problems relating to limited thermodynamic stability and poor dimensional stability of membrane, and to accomplish the requirements for industrial commercialization.

3 CONCLUSION

The rising price of crude oil up to US$ 48 per barrel has indirectly soars the ethylene prices especially from those naphtha-based ethylene producers. Oxidative coupling of methane by using catalytic membrane reactor is one of the promising routes. The most favorable catalysts are Li/MgO and Mn-Na_2WO_4/SiO_2, which presented the highest C_{2+} product selectivity and yields. By integrating the high permselective, thermally stability mixed ionic/electronic conducting membrane and coated with catalyst, it is anticipated that OCM will be successfully to be industrial commercialized and bring more benefits to the global market.

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Process optimization of oxidative coupling of methane for ethylene production using response surface methodology

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Abstract: The statistical design of experiments (DoE) was used in the process study of oxidative coupling of methane (OCM) over Na–W–Mn/SiO_2 catalyst. A set of factors with a certain range was screened using factorial design with respect to three responses: methane conversion, C_{2+} products selectivity and ethylene/ethane ratio. The variances were analyzed and the interaction effects of the process parameters were evaluated. With the understanding of the process, the optimization of the process was further studied using response surface methodology coupled with central composite design (CCD). The optimum conditions were obtained as reaction temperature = 850 °C, gas hourly space velocity = 23 947 $cm^3 g^{-1} h^{-1}$, catalyst pretreatment period = 2 h, dilution ratio = 0.2 and CH_4/O_2 ratio = 7. 40.55% of methane conversion and 79.51% of C_{2+} product selectivity were obtained under these optimum conditions. Experimental runs under optimum conditions were repeated and compared with the simulated values obtained from the model. There was good agreement between the experimental and simulated values.
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Keywords: oxidative coupling of methane (OCM); design of experiment (DoE); interaction effects; optimization; Na–W–Mn/SiO_2 catalyst; ethylene

INTRODUCTION

The oxidative coupling of methane (OCM) has been widely studied since the 1980s and it was hitherto believed that this process had the potential and capability of overcoming the hurdle of economic constraints of low yield of ethylene (<30%), which greatly reduced industrial interest. Thus, a great deal of effort has been devoted to improving ethylene production in OCM by developing highly active and selective catalysts and modifying the reactor configuration (packed bed reactor, fluidized bed reactor, membrane reactor, microwave and RF (radio frequency) plasma reactor, etc.). This single-step direct conversion of methane to ethylene has proved effective over a wide range of metal oxide catalysts. The ethylene yield, however, was restricted by the heterogeneous and homogeneous reaction of complete oxidation to carbon oxide in both the catalyst surface and the gas phase. Most of the reported studies on OCM focused on the investigation of the intrinsic reaction between reactant and catalyst surface over a myriad of metal loadings.[1–5] There are several variables involved in the OCM process. Our previous work has simulated the plug flow reactor performance in OCM using La_2O_3/CaO catalyst.[6] A list of parameters were studied based on the 'one-factor at a time' approach but the results implied that there is a need to search for optimum process conditions for the production of ethylene. Furthermore, the effect of interaction between factors was neglected during the modeling, leading to the possible misinterpretation of factors operating in the process study of OCM. In continuation of the previous work of elucidating the influence of each factor under plug flow reactor conditions, design of experiments (DoE) was employed in the current study using a trimetallic catalyst system, Na–W–Mn/SiO_2, one of the most studied three-component catalysts.[7–12] Na–W–Mn/SiO_2 demonstrated a promising result with 20% of methane conversion and 80% C_{2+} selectivity at a ratio of 7.4 and is stable for up to 97 h of reaction time.[7] This catalyst was studied over a range of parameters: operating temperature 775–850 °C, gas hourly space velocity (GHSV) 18 500–165 000 $cm^3 g^{-1} h^{-1}$ and CH_4/O_2 ratio 3–7.5 under different conditions.[8–12] So far, there is no reported work on the optimization study in OCM using this three-component catalyst but the catalyst morphology, basicity and electrical properties presented in the literature provide a better insight into the catalyst development.

The understanding of reaction mechanisms involved and the effects of factors in the OCM process are

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definitely important to the further development of this technology, and thus the present study is focused on the process of OCM by determining the optimum process parameters in maximizing C_{2+} yield using DoE coupled with response surface methodology (RSM). DoE provides a better understanding of the relationship of the factors and responses that govern the performance of the three-component catalyst in the OCM process. Consideration of the interaction effect of process parameters may merit a more accurate prediction in optimization studies.

EXPERIMENTAL

Catalyst preparation

5 wt% Na_2WO_4–2 wt% Mn/SiO_2 catalysts were prepared using two different methods: incipient wetness impregnation[11] and mixture slurry,[13] respectively. Synthesis of catalyst using the incipient wetness impregnation method was carried out by impregnating the silica gel support (Davisil, 636, 35–60 ME; Sigma-Aldrich, St Louis, MO, USA) with aqueous solutions in appropriate concentrations of $Mn(NO_3)_2$ (AR, Merck, Rahway, NJ, USA), evaporated to dryness and dried in air at 130 °C. The material was cooled to 25 °C, followed by introduction of aqueous solution with the appropriate concentration of Na_2WO_4 (AR, Merck). The resulted mixture was well mixed and evaporated to dryness. The catalyst was dried in air at 130 °C for 8 h, followed by calcination at 850 °C for 8 h. It was then pelletized, crushed and sieved to 40/60 mesh. In the mixture slurry method, silica sol (30–50 wt%, Sigma-Aldrich) was used as the silica precursor, which was added with an appropriate amount of $Mn(NO_3)_2$ and Na_2WO_4. After stirring the mixture at 80 °C for 5 h until homogeneous, the mixture was dried overnight at 100 °C and calcined at 850 °C for 8 h as with the previous method and the resulting powder was crushed and sieved to 40/60 mesh.

Characterization

X-ray diffraction patterns of the fresh and used catalysts were conducted on a Philips (Almelo, The Netherlands) PW 1820 system with Cu Kα monochromatic radiation at 2θ values of 10–90° with a step of 0.10°/5 s at room temperature.

Catalytic activity test

The catalytic activity test was conducted in a single-pass plug flow reactor consisting of a stainless steel casing with and without a quartz tube liner (i.d. 10 mm). 0.4 g of catalyst was packed and retained in the quartz tube liner by quartz wool above and below the catalyst bed. The remaining space of the reactor below the catalyst bed was filled with quartz wool to reduce the free volume and to minimize further reaction of the desired product in the post-catalytic volume.[11] A K-type thermocouple was attached to the outside wall of the reactor to monitor the furnace, and the temperature along the catalyst bed inside the reactor was measured by another thermocouple and monitored using the temperature controller, so that the exothermicity of the reaction could be detected easily by observing the temperature difference between the furnace and the catalyst bed. Reactant gases CH_4 (99.92%), oxygen (99.8%) and nitrogen (99.999%) were co-fed into the reactor without further purification. Methane flow rate was regulated by an MKS (Wilmington, MA, USA) mass flow controller (Model 246c), whereas mass flow controllers (Brooks 5890; Emerson Process Management, Hatfield, PA, USA) were used to regulate nitrogen and oxygen gas flow rates. A cold trap was placed at the outlet of the reactor to separate any condensed water vapor from the reaction product. Figure 1 shows a schematic diagram of the experimental set-up used in the present study. The volume shrinkage of the outlet flow caused by condensation of water vapor was considered in the calculation. The reaction products were analyzed using an online gas chromatograph HP 6890 (Hewlett-Packard, Waldbronn, Germany) equipped with a flame ionization detector, using a Poropak Q column (Hewlett–Packard) for the separation of CH_4, C_2H_4, C_2H_6 and C_3H_8, and a thermal conductivity detector, using a 0.5 nm molecular sieve column for the separation of H_2, O_2, CO_2, N_2 and CO. Blank runs in the quartz tube with the quartz wool showed negligible conversion under the reaction conditions. The methane conversion and C_{2+} products (ethylene + ethane) selectivity are defined as follows:

$$\text{Methane conversion: } X_{CH_4}(\%) = \frac{\text{moles of } CH_4 \text{ converted}}{\text{moles of } CH_4 \text{ in feed}} \times 100 \quad (1)$$

$$\text{Selectivity of } C_{2+} \text{ product: } S_{C_{2+}}(\%) = \frac{\sum(n \times \text{moles of } C_n \text{ in products})}{\text{moles of } CH_4 \text{ converted to all products}} \times 100 \quad (2)$$

$$\text{Yield of } C_{2+} \text{ product: } Y_{C_{2+}}(\%) = \text{methane conversion} \times C_{2+} \text{ selectivity} \quad (3)$$

where n is 2.

RESULTS AND DISCUSSION

Characterization

The crystalline phases of fresh and used catalyst are shown as X-ray diffraction (XRD) patterns in Fig. 2. After calcination at 850 °C, the silica support was transformed from an amorphous phase to α-cristobalite phase.[8] It was reflected significantly with the existence of crystalline phases of $Na_2W_2O_7$, Na_2WO_4, Mn_2O_3 and α-cristobalite on the fresh catalyst (Fig. 2a). Both the crystalline phases of $Na_2W_2O_7$ and Na_2WO_4 inferred that Na has a higher affinity to combine with WO_4 than Mn.[9] The used

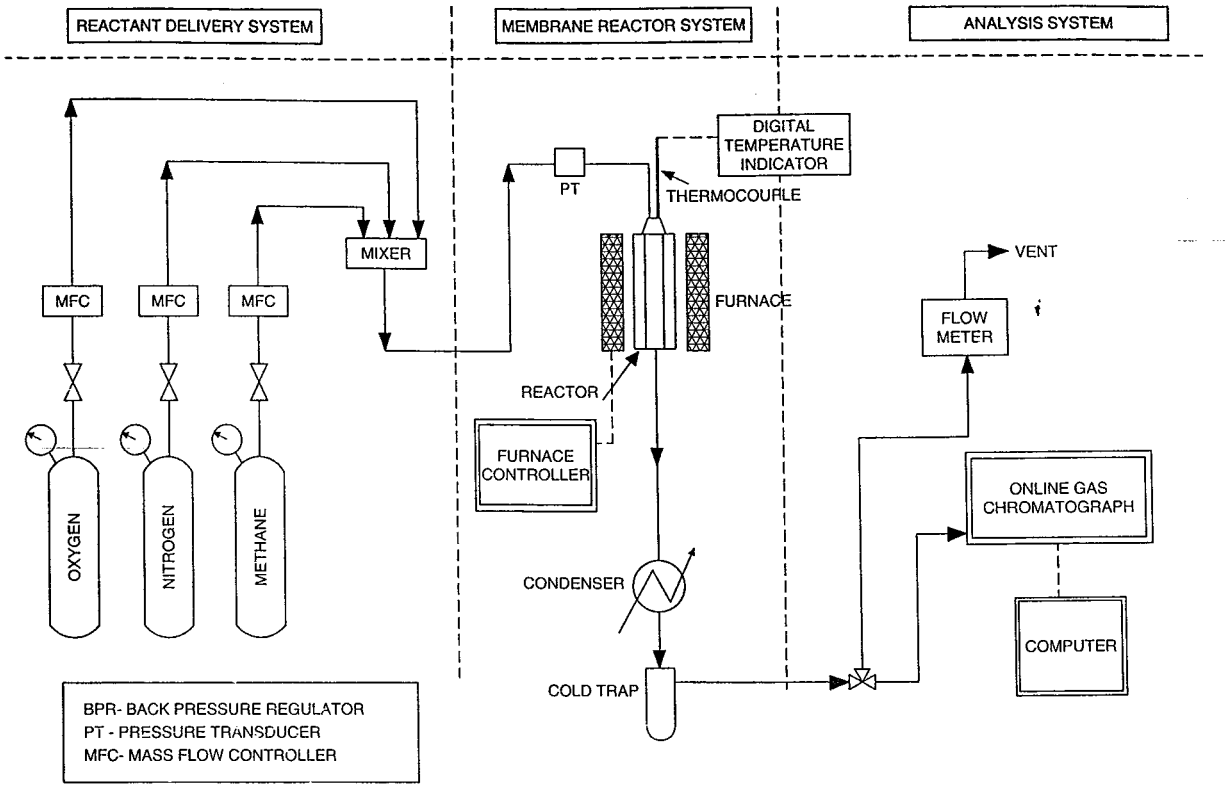

Figure 1. Experimental set-up of OCM test rig.

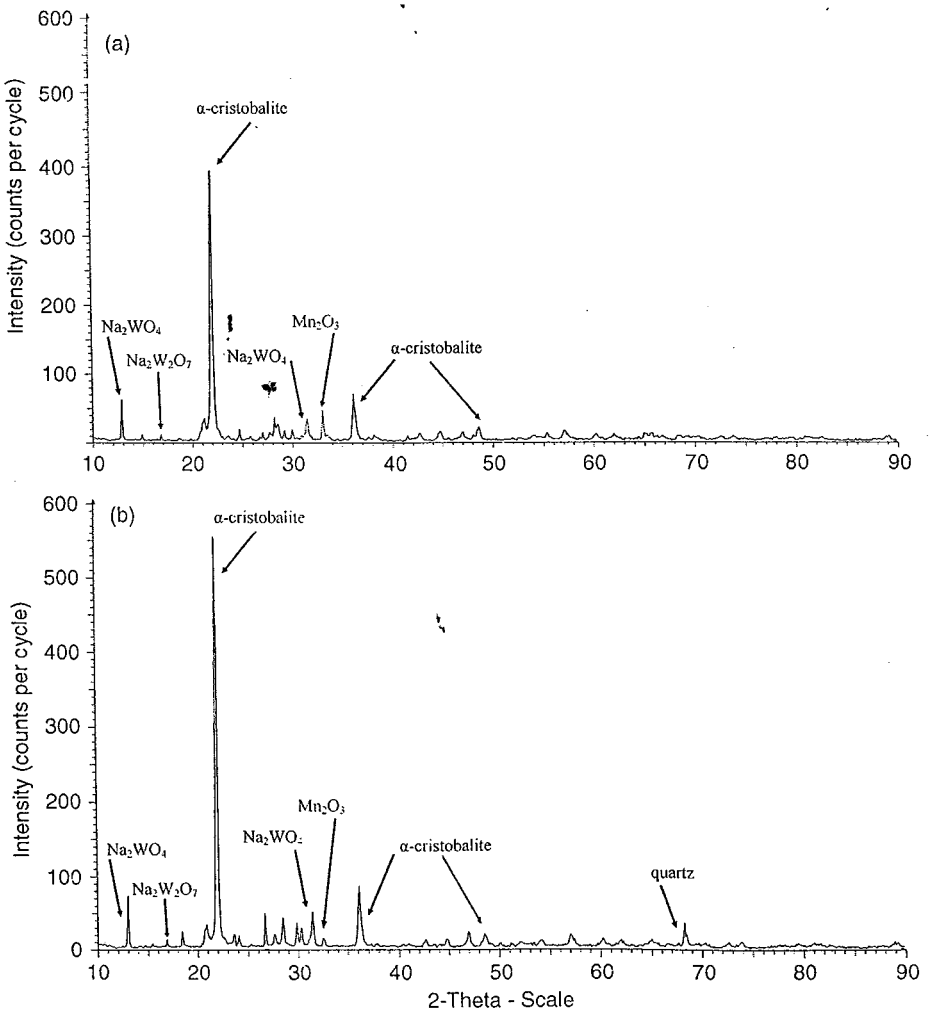

Figure 2. X-ray diffraction pattern of (a) fresh and (b) used Na–W–Mn/SiO_2 catalyst.

catalyst, which was tested in OCM reaction for 5 h, did not show any substantial differences in the XRD patterns compared to the fresh catalyst (Fig. 2b). The crystalline phase of quartz, however, was exhibited in the used catalyst, which is due to the exothermicity of the high-temperature reaction (an increment of >30 °C from the operating temperature) resulting in the quartz phase appearing in the used catalyst.[13] Therefore, it could be concluded that there was a strong interaction between sodium (Na), tungsten (W) and manganese (Mn) with the silica support, in which the phase transition of amorphous silica to α-cristobalite is crucial to the high performance of catalyst in the OCM reaction, and which will occur only after the catalyst is doped with Na, W and Mn.

Catalyst activity

In the preliminary study of the OCM process two types of reactor were used and the performance of the Na–W–Mn/SiO_2 catalyst in terms of catalytic activity was determined. The plug flow reactor without quartz liner gave low selectivity and therefore lower yield of C_{2+} product as compared to the reactor with quartz liner. The best performance in the stainless steel reactor was 24.2% of methane conversion, 37.4% selectivity of C_{2+} product and 9.05% of C_{2+} yield at 780 °C, 9000 $cm^3 g^{-1} h^{-1}$ of GHSV without dilution and a CH_4/O_2 ratio of 4. A large amount of coke formation was observed due to the reaction of the stainless steel and the reactant gases at high temperature. It is important that an inert material of construction be used for the reactor in the OCM process. In the present study, a quartz liner was used in the stainless steel casing in order to avoid contact of reactant gases with the stainless steel. It was observed that there was no coke formation during reaction in the quartz reactor. Mass balance for the carbon atom based on the composition and flow rate of inlet and outlet gases was better than 5%. A series of experimental runs was conducted over the Na–W–Mn/SiO_2 catalyst.

Process studies

Several relevant factors were screened and analyzed using factorial design and ANOVA, respectively, prior to optimization of the process. The range of parameters involved was decided based on the reported studies in the literature.[8,14] In order to collect as much pertinent information on the process as possible, five independent variables were selected for study with the three responses: (a) methane conversion, (b) selectivity of C_{2+} product and (c) ethylene/ethane ratio, as presented in Table 1. The relationships between the variables and responses were obtained using regression analysis of Design Expert (Stat-Ease, Minneapolis, MN, USA) 6.0.6 software. Interactions between the process factors and the effect of each factor on the responses were also evaluated.

Table 1. Independent variable range at low and high level

Factors	Unit	Factor code	Low level (−1)	High level (+1)
Temperature	°C	A	750	850
GHSV	$cm^3 g^{-1} h^{-1}$	B	18 000	35 000
Pretreatment time	h	C	0	2
Dilution ratio	–	D	0.2	0.5
CH_4/O_2 ratio	–	E	3	7

A full factorial design required a total run of 32 experiments. Since some of the combinations of effect terms were aliased, a single-replicate two-level half-fraction factorial design with 16 runs of experiment was conducted in a random manner. The design matrix and response data obtained are presented in Table 2. The yield of C_{2+} was not included as the response in this factorial design, as it could be obtained from the multiplication of methane conversion and C_{2+} selectivity. A reproducibility test was performed at a selected condition as shown in Table 2, runs 16–18. Three of the responses are acceptably reproducible but the data for C_{2+} selectivity deviate most, with a standard deviation of 1.3343.

Conversion of methane

The ANOVA for methane conversion was obtained and the two-level factorial model in terms of coded factors is represented as follows:

$$\begin{aligned} CH_4 \text{ conversion } (\%) &= 35.24 + 1.24A - 3.44B \\ &+ 2.69C - 3.42D + 2.30E + 5.16AB \\ &- 0.96AC + 1.69AD + 0.23AE - 4.23BC \\ &+ 2.53BE - 2.89ABE + 7.06ACD \end{aligned} \quad (4)$$

The ANOVA of this model (Eqn (4)) with a 'Prob >F' value of 0.1748 (greater than 0.05) implied that the model was not significant relative to the pure error. The value of 'Prob >F' of all the selected terms in Eqn (4) was found to be insignificant to methane conversion, though the model terms AB, BC and ACD have greater effects over the model, with contributions of 18.05%, 17.37% and 24.17%, respectively. Thus, it could be concluded that the process parameters (operating temperature, GHSV, catalyst pretreatment period, dilution ratio and CH_4/O_2 ratio) did not have much effect on the methane conversion over the range of the present experimental study.

A simulated model should be in agreement with the experimental result and this was normally derived with a high value of R^2. The methane conversion predicted from the model (Eqn (4)) was in agreement with the experimental values, with an R^2 value of 0.9709. As mentioned previously, the effects of each process parameter on the methane conversion were insignificant but, interestingly, it was found that there were interaction effects between the process parameters, which masked the effects of the main factors on the methane conversion. The interaction is

Table 2. Experiment matrix of $2^{(5-1)}$ fractional–factorial design

	Factors					Responses		
Run	A	B	C	D	E	CH_4 Conversion (%)	C_{2+} Selectivity (%)	C_2H_4/C_2H_6 ratio
1	850	35000	2	0.5	7	40.43	62.09	1.64
2	850	35000	0	0.2	7	54.45	52.72	2.07
3	750	35000	2	0.5	7	19.96	34.38	0.44
4	750	18000	0	0.2	3	35.96	13.90	1.28
5	850	18000	0	0.2	3	31.93	8.31	1.20
6	750	35000	2	0.2	3	30.98	57.18	1.09
7	750	18000	0	0.5	7	34.77	55.11	0.86
8	850	18000	2	0.5	3	45.94	30.76	3.25
9	850	18000	0	0.5	7	24.34	47.68	1.76
10	750	35000	0	0.2	3	15.08	25.05	1.47
11	750	18000	2	0.5	3	41.83	2.79	1.76
12	850	35000	2	0.2	3	29.66	45.48	2.37
13	850	18000	2	0.5	7	47.46	29.70	2.12
14	750	18000	2	0.5	7	33.48	37.55	0.71
15	850	35000	0	0.2	3	45.86	13.87	1.20
Repeated runs for reproducibility test								
16	750	35000	0	0.2	7	31.68	63.75	0.79
17	750	35000	0	0.2	7	32.61	65.75	0.79
18	750	35000	0	0.2	7	31.63	66.28	0.80
Mean[a]						31.9733	65.26	0.7933
SD[a]						0.5519	1.3343	0.0058

[a] Calculated statistic for reproducibility checking of repeated experiments (run 25 to run 30).

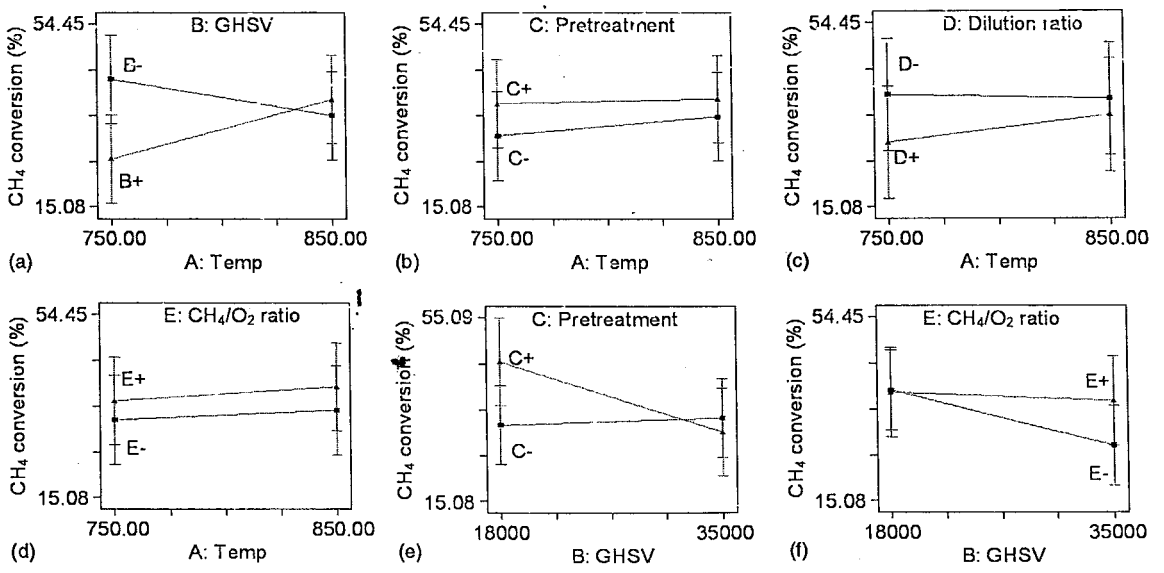

Figure 3. Interaction plots of effect of factor variables on methane conversion: (a) AB; (b) AC; (c) AD; (d) AE; (e) BC; (f) BE.

commonly defined when the difference in response between the levels of one factor is not the same at all levels of the other factors.[19] The interaction effects of the process parameters on the performance of CH_4 conversion were evaluated from the model and are shown in Fig. 3. The low level of each factor was indicated by a '−' sign whereas the high level was indicated by '+'. Methane conversion increased at lower operating temperature and lower GHSV but decreased at higher temperatures (Fig. 3a). It is advisable to operate at a higher GHSV if the operating temperature is higher. The lower GHSV provided higher methane conversion if the catalyst was pretreated for 2 h, but conversion dropped at the higher value if there was a greater value of GHSV (Fig. 3e). There was no significant difference in the methane conversion if the catalyst was not pretreated in spite of the temperature change. Figure 3(f) shows the possibility of interaction between factors GHSV and CH_4/O_2 ratio if a wider range of GHSV is used. It was suggested that the methane conversion might be increased if more methane were introduced into the reaction zone accompanied by high GHSV. There

Table 3. ANOVA table of C_{2+} selectivity

Source	Sum of squares	d.f.	Mean square	*F*-value	Prob >*F*[a]
Model	5805.62	12	483.80	418.79	0.0002
A	0.051	1	0.051	0.044	0.8476
B	263.70	1	263.70	228.26	0.0006
C	99.40	1	99.40	86.05	0.0027
D	84.92	1	84.92	73.50	0.0033
E	1547.07	1	1547.07	1339.16	<0.0001
AB	145.04	1	145.04	125.55	0.0015
AD	653.41	1	653.41	565.60	0.0002
AE	206.51	1	206.51	178.75	0.0009
BC	1232.06	1	1232.06	1066.49	<0.0001
BD	1066.35	1	1066.35	923.05	<0.0001
BE	240.35	1	240.35	208.05	0.0007
ABE	372.68	1	372.68	322.60	0.0004
Residual	3.47	3	1.16		
Corr. total	5809.08	15			

[a] Values of Prob $F < 0.05$ are significant under 95% level of confidence.

was no interaction between factors AC, AD and AE as displayed in Fig. 3(b), (c) and (d), respectively.

Selectivity of C_{2+} product

A better understanding of the factors' effect on the OCM process could be acquired by evaluating the ANOVA of the C_{2+} product's selectivity (Table 3), which is represented by the following equation with coded factors:

$$C_{2+}\text{ selectivity (\%)} = 28.11 + 0.056A + 5.74B + 3.52C - 4.61D + 13.91E + 3.69AB + 9.04AD - 4.40AE + 12.41BC - 16.33BD + 5.48BE + 4.83ABE \quad (5)$$

The model of C_{2+} selectivity was significant with a model *F*-value of 418.79 and temperature was the only factor that was insignificant. In this case, model terms B, D, E and BD contributed 17.83%, 11.91%, 26.63% and 16.20%, respectively, and emerged as the major effects on C_{2+} selectivity. However, the interaction term of the factors were all significant to the model and thus the main factors' effects were less meaningful.

The predicted and experimental C_{2+} selectivity from Eqn (5) was compared with the R^2 value of 0.9994. C_{2+} selectivity increased at a higher dilution ratio with the increment of operating temperature and this can be well comprehended by referring to Fig. 4. At a lower dilution ratio, a better selectivity will be obtained at lower temperatures (Fig. 4b). At higher temperatures methane conversion increased but C_{2+} selectivity decreased, which may be attributed to the thermal cracking of methane, ethane and ethylene or further conversion of methyl and ethyl radicals to CO_x product. Therefore, more diluent should be introduced into the reaction zone to 'sweep off' the intermediate product (ethylene and ethane) and, at the same time, avoiding contact of gaseous oxygen with the C_{2+} product. In order to maximize C_{2+} selectivity, it was important to examine the role of diluent to the GHSV of the process. During consideration of the relationship between diluent and space velocity, which were indicated by the dilution ratio and GHSV, respectively, it was observed that C_{2+} selectivity increased dramatically as GHSV doubled at lower dilution ratio (Fig. 4e). At higher GHSV, the C_{2+} selectivity reduced if more diluent was fed into the reaction zone, which diluted the reactant and shortened the contact time, in consequence alleviating the coupling of methyl radicals to ethane and ethylene products. Thus, a higher dilution ratio should be accompanied by a lower GHSV to provide better C_{2+} selectivity. When the GHSV was at a low level, C_{2+} selectivity was better for the catalyst without pretreatment, and vice versa (Fig. 4d). Consequently, it could be concluded that the C_{2+} selectivity increased with the increment of GHSV at a lower dilution

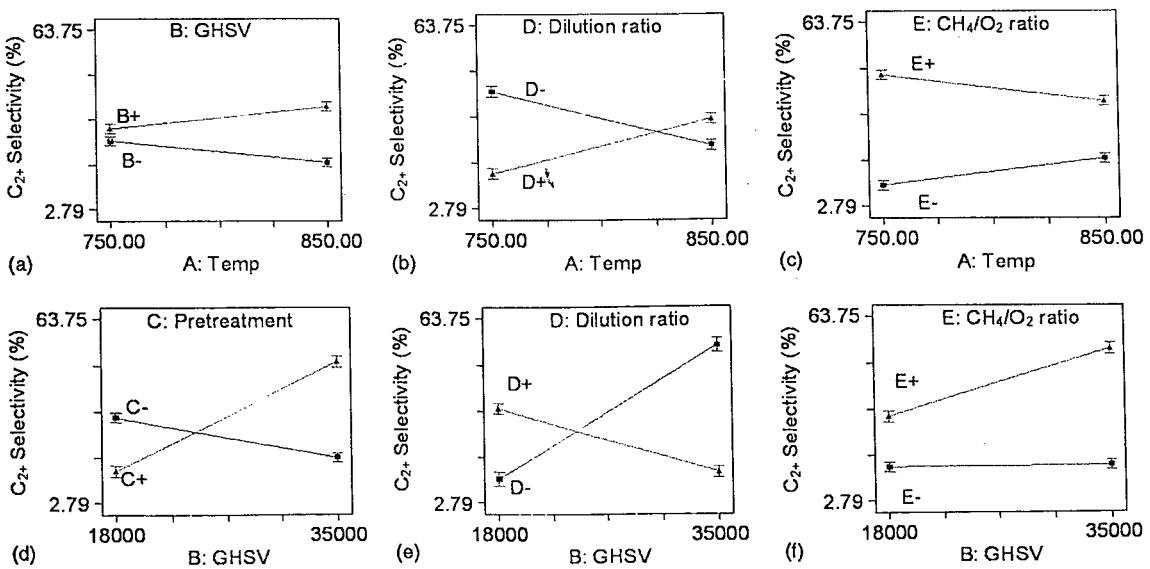

Figure 4. Interaction plots of effect of factor variables on C_{2+} selectivity: (a) AB; (b) AD; (c) AE; (d) BC; (e) BD; (f) BE.

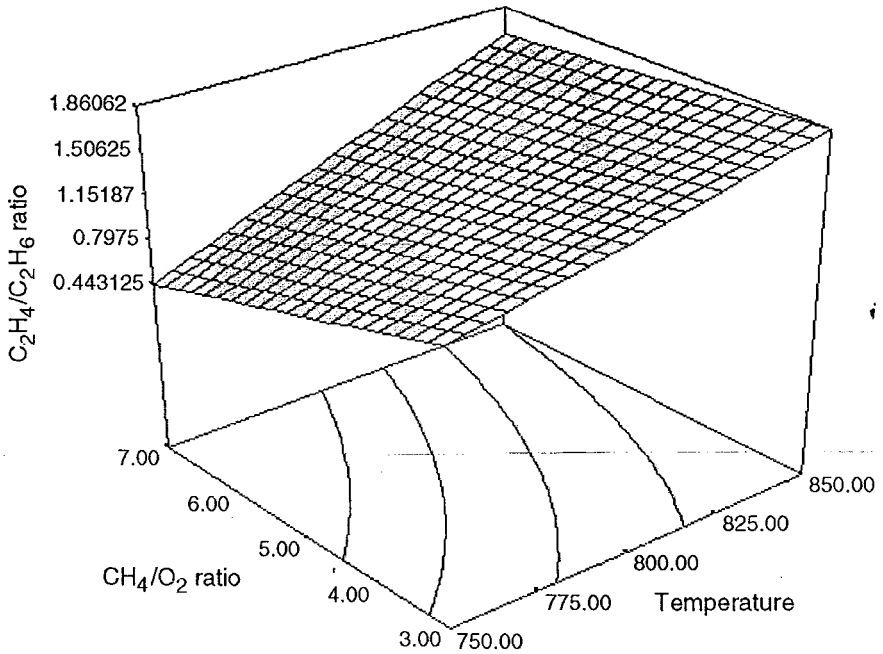

Figure 5. Effect of reaction temperature and CH_4/O_2 ratio on C_2H_4/C_2H_6 ratio.

ratio by using the pretreated catalyst. Under such circumstances, the effect of temperature over this particular range was insignificant and therefore could be neglected. An interaction between factors *A* and *B* might be observed if a wider range of parameters were selected. It can be concluded that interactions between factors *AB*, *AE* and *BE* were not significant in this study (Fig. 4a, c and f).

C_2H_4/C_2H_6 ratio

The effect of the parameters on the C_2H_4/C_2H_6 ratio was scrutinized to find the conditions that favored the formation of ethylene. There was a notable increment of the C_2H_4/C_2H_6 ratio as the operating temperature increased (Fig. 5), and this was in line with the observation reported by Rane *et al.*[15] They proposed that the conversion of ethane to ethylene is due to the decomposition of more ethyl radicals and/or thermal cracking of ethane molecules at a higher temperature. The C_2H_4/C_2H_6 ratio increased dramatically with the increment of temperature almost four times regardless of the effect of CH_4/O_2 ratio. In other words, the interaction between temperature and CH_4/O_2 ratio to C_2H_4/C_2H_6 ratio was negligible. The C_2H_4/C_2H_6 ratio slightly decreased as the CH_4/O_2 ratio increased from 3 to 7. This discrepancy could be explained by postulating that the existence of oxygen in a greater amount was initially encouraging the redox mechanism on the catalyst surface, and was eventually followed in the gas phase reaction of hydrogen abstraction from methane, ethane, methyl and ethyl radicals to ethylene.

There was an interaction effect between the dilution ratio and GHSV to the C_2H_4/C_2H_6 ratio, as depicted in Fig. 6. C_2H_4/C_2H_6 ratio increased with the increment of dilution ratio at lower GHSV, which demonstrated that a dilution ratio of 0.5 has more diluent and this may dilute the mixture of gases in enhancing the conversion of ethane to ethylene, while carrying the desired product away from the reaction zone and shortening the contact time of ethylene and oxygen. However, it was also favorable to the C_2H_4/C_2H_6 ratio if higher GHSV accompanied by less diluent was introduced into the reaction system.

Optimization of OCM process

Subsequently, the model was analyzed and refined to discard factors having an insignificant effect in the overall process. Since the ANOVA of methane conversion exhibited an insignificant model, the factor screening process was dominated by the ANOVA of C_{2+} selectivity in deciding the factors to be eliminated. Therefore, the process variable of temperature variation at 750–850 °C was removed from the model due to the insignificant effect on both methane conversion and C_{2+} selectivity model. Further experiments were conducted at a fixed operating temperature of 850 °C because the C_2H_4/C_2H_6 ratio was greater at higher temperature. The process study was then taken further, to the optimization study, using response surface methodology[16–19] coupled with central composite design. There were 30 runs in total and the upper and lower levels of the factors were identical to those in Table 2, except for the temperature factor, and the responses are presented in Table 4. Design Expert 6.0.6 software was used to simulate and predict the optimum conditions based on the experimental data in Table 4. Six runs were repeated at operating temperature 850 °C, GHSV 26 500 $cm^3\ g^{-1}\ h^{-1}$, catalyst pretreated for 1 h, dilution ratio of 0.35 and CH_4/O_2 ratio of 5. The standard deviations of CH_4 conversion, C_{2+} selectivity, C_2H_4/C_2H_6 ratio and C_{2+} yield were 3.2033, 5.16046, 1.58 and 0.1951, respectively.

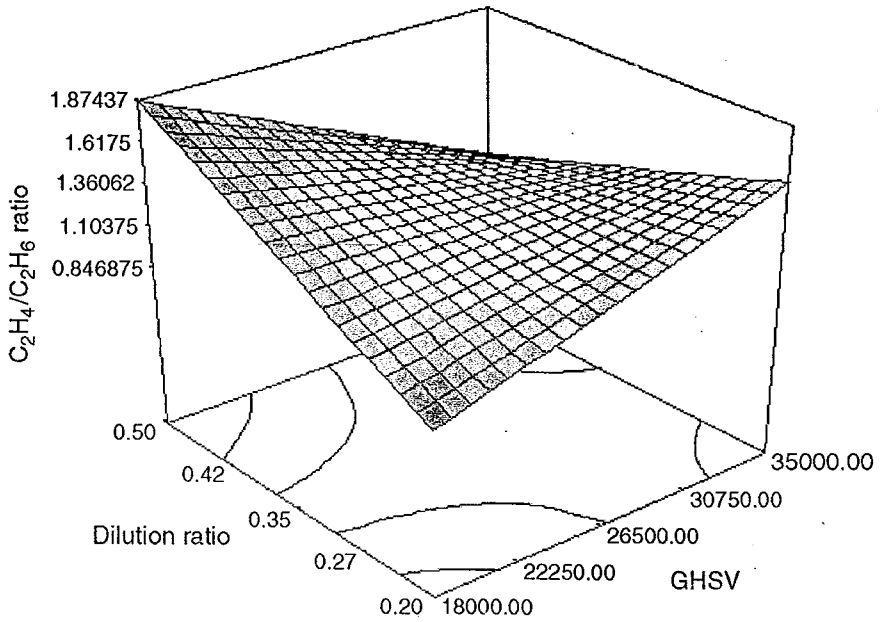

Figure 6. Effect of GHSV and dilution ratio on C_2H_4/C_2H_6 ratio.

Table 4. Experiment matrix of 2^4 full factorial with central composite design

	Factors				Responses			
Run	GHSV ($cm^3\ g^{-1}\ h^{-1}$)	Pretreat time (h)	Dilution ratio	CH_4/O_2 ratio	CH_4 Conversion (%)	C_{2+} selectivity (%)	C_{2+} yield (%)	C_2H_4/C_2H_6 ratio
1	35 000	0	0.2	7	54.45	52.72	28.71	2.07
2	35 000	2	0.5	7	38.54	59.29	22.85	1.64
3	35 000	2	0.2	3	43.99	47.09	20.71	2.37
4	18 000	2	0.2	7	42.01	77.12	32.40	1.53
5	18 000	2	0.5	7	48.11	31.61	15.21	2.12
6	18 000	0	0.2	3	32.78	9.02	2.96	1.20
7	18 000	0	0.5	3	43.62	25.85	11.28	2.76
8	18 000	0	0.2	7	25.61	57.13	14.63	1.15
9	18 000	0	0.5	7	42.49	62.15	26.41	1.76
10	18 000	2	0.2	3	44.63	51.44	22.96	2.72
11	35 000	0	0.2	3	46.54	14.97	6.97	1.25
12	18 000	2	0.5	3	36.12	32.72	11.82	3.25
13	35 000	0	0.5	7	35.40	70.73	25.04	1.15
14	35 000	2	0.5	3	49.37	30.80	15.21	2.13
15	35 000	2	0.2	7	43.18	73.75	31.85	1.32
16	35 000	0	0.5	3	46.78	65.71	30.74	2.07
17	26 500	1	0.5	5	30.66	61.72	18.92	1.39
18	18 000	1	0.35	5	37.42	65.42	24.48	1.93
19	26 500	2	0.35	5	41.83	65.50	27.40	1.30
20	35 000	1	0.35	5	37.96	58.66	22.27	1.48
21	26 500	0	0.35	5	20.74	60.58	12.56	1.20
22	26 500	1	0.35	7	36.66	73.56	26.97	1.20
23	26 500	1	0.35	3	46.84	51.10	23.94	1.63
24	26 500	1	0.2	5	41.78	61.76	25.80	1.49
25	26 500	1	0.35	5	25.60	67.98	17.40	1.99
26	26 500	1	0.35	5	27.94	71.82	20.07	1.68
27	26 500	1	0.35	5	33.10	56.92	18.84	1.85
28	26 500	1	0.35	5	27.01	69.27	18.71	1.42
29	26 500	1	0.35	5	25.61	67.42	17.27	1.75
30	26 500	1	0.35	5	23.91	64.94	15.53	1.63
Mean[a]					27.195	66.3917	17.97	1.72
Standard deviation[a]					3.2033	5.16046	1.58	0.1951

[a] Calculated statistic for the reproducibility checking of the repeated experiments (run 25 to run 30).

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Selectivity is less reproducible compared to the other responses.

All the factors included within the specified range and with the aim of maximizing methane conversion and C_{2+} selectivity were the main concern in determining the optimum conditions. Several sets of combination were predicted as the optimum conditions and listed according to their order of desirability. Optimum conditions with higher C_{2+} selectivity and a reasonable desirability were eventually chosen. The predicted optimum conditions with desirability 0.864 was GHSV of 23 947 $cm^3 g^{-1} h^{-1}$, catalyst pretreatment period of 2 h, dilution ratio 0.2, CH_4/O_2 ratio 7, giving 40.55% methane conversion and 79.51% C_{2+} selectivity, which corresponded to 32.24% of C_{2+} yield and a C_2H_4/C_2H_6 ratio of 1.45. Since the C_{2+} yield was affected by the methane conversion and C_{2+} selectivity, optimization was concentrated in maximizing the C_{2+} yield. The model of C_{2+} yield was represented by a two-level factorial equation as follows:

$$C_{2+}\text{ yield }(\%) = 20.63 + 2.34A + 2.28B - 0.53C + 4.30D - 1.75AB + 0.87AC - 0.30AD - 5.19BC - 0.70BD - 2.09CD \quad (6)$$

where A is the GHSV, B is the time of catalyst pretreatment, C is the dilution ratio and D is the CH_4/O_2 ratio.

Figure 7 shows the effect of GHSV and catalyst pretreatment period on C_{2+} selectivity. It was found that the pretreated catalyst was beneficial in giving higher selectivity over a GHSV range of 20 000–26 500 $cm^3 g^{-1} h^{-1}$. The optimum value of the C_{2+} yield under the optimum conditions is shown

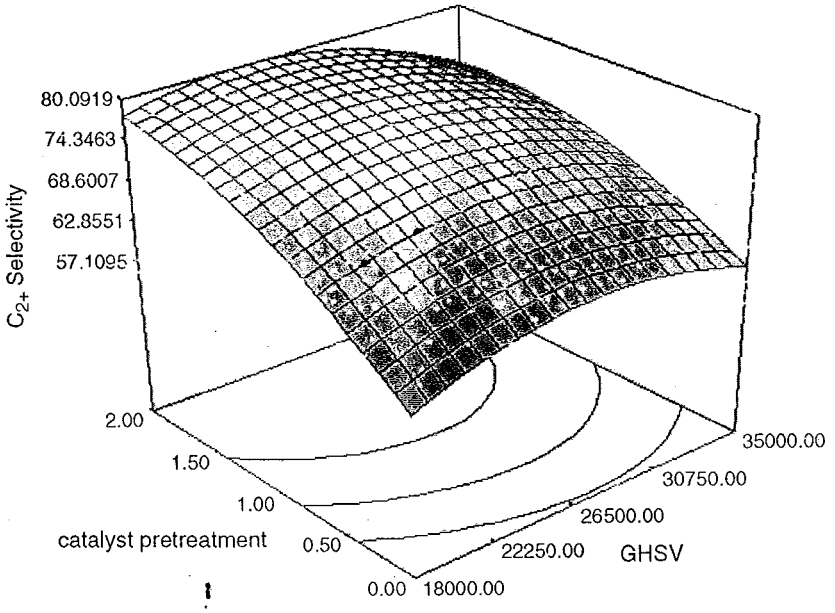

Figure 7. Effect of GHSV and catalyst pretreatment period on C_{2+} selectivity.

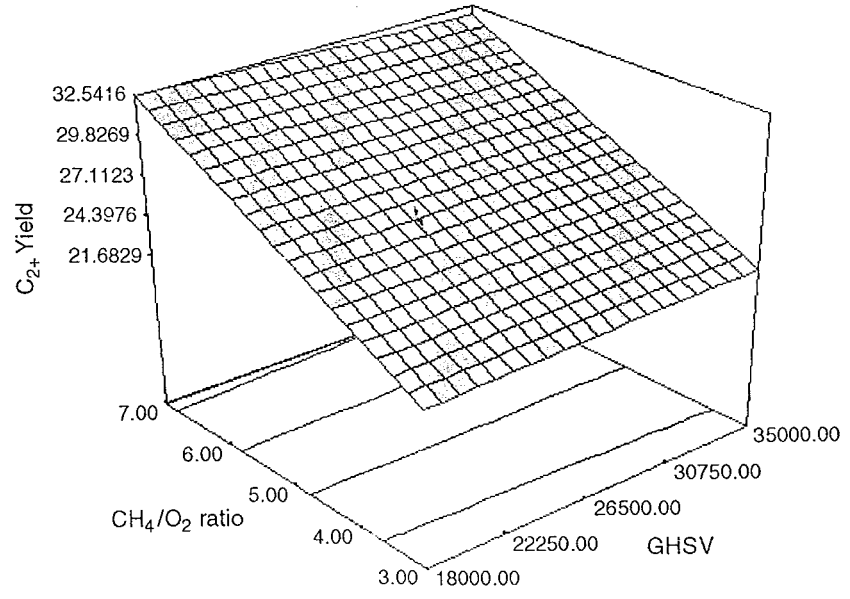

Figure 8. Effect of GHSV and CH_4/O_2 ratio on C_{2+} yield.

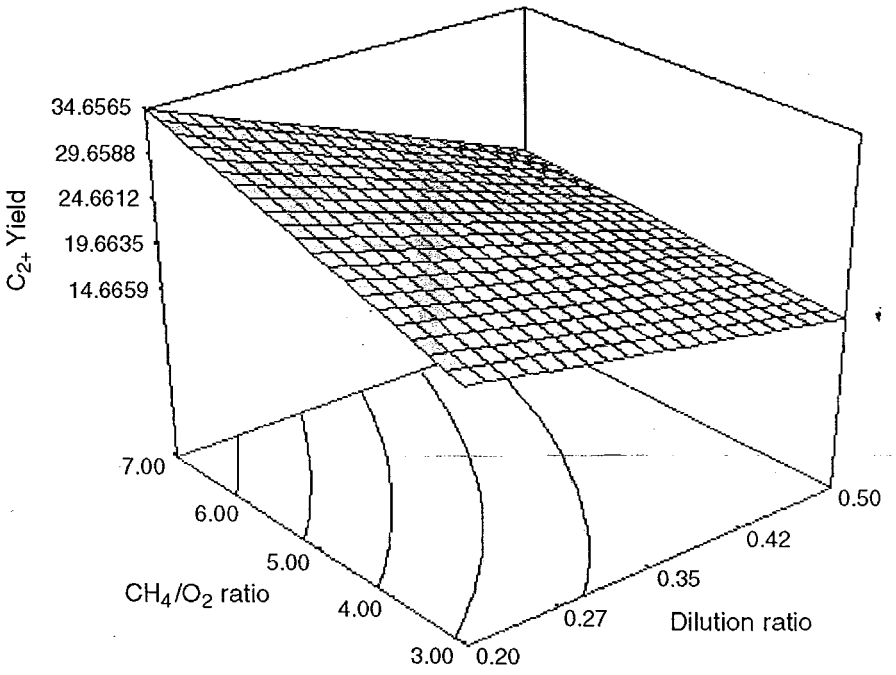

Figure 9. Effect of dilution ratio and CH_4/O_2 ratio on C_{2+} yield.

Table 5. Reproducibility test under optimum condition over Na–W–Mn/SiO_2 catalyst prepared by different methods

	CH_4 conversion (%)			C_{2+} selectivity (%)			C_{2+} yield (%)		
Run	X_{CH_4} (exp)	X_{CH_4} (DoE)	ΔError (%)	$S_{C_{2+}}$ (exp)	$S_{C_{2+}}$ (DoE)	ΔError (%)	$Y_{C_{2+}}$ (exp)	$Y_{C_{2+}}$ (DoE)	ΔError (%)
1[a]	43.50	40.55	6.78	65.99	79.51	20.49	28.71	32.24	12.30
2[a]	43.05	40.55	5.81	70.62	79.51	12.59	30.40	32.24	6.05
3[a]	42.29	40.55	4.11	70.80	79.51	12.30	29.94	32.24	7.68
4[b]	42.14	40.55	3.77	77.45	79.51	2.66	32.64	32.24	1.23
5[b]	44.88	40.55	9.65	69.68	79.51	14.11	31.27	32.24	3.10
Mean error			6.02			12.43			6.07
Standard deviation (σ)			2.37			6.39			4.29

[a] Catalyst prepared by incipient wetness impregnation method.
[b] Catalyst prepared by mixture slurry method.

in Figs 8 and 9, respectively, displaying the interaction effect of GHSV, dilution ratio and CH_4/O_2 ratio to C_{2+} yield.

Experiments were carried out under the simulated optimum conditions to obtain methane conversion and C_{2+} selectivity. Table 5 presents the experimental results under the optimum conditions with the calculated error expressed as a percentage. Methane conversion was in agreement with the simulated and experimental values, with a mean error of 6.02%. C_{2+} selectivity, however, deviated from the simulated value with a mean error of 12.43%. The experimental C_{2+} selectivity had a lower value compared to the simulated value of 79.51%. This could be due to the uncontrollable situation inside the packed bed catalyst during the reaction. The fast reaction of methane and intermediate products (ethane and ethylene) with oxygen to make carbon oxide may reduce the C_{2+} selectivity. Thus the direct contact of methane and oxygen should be inhibited during the OCM reaction. Another catalyst sample prepared using the mixture slurry method was also tested by conducting experiments under the optimum conditions. The experimental values are compared with the simulated values obtained from the proposed model in Table 5. The performance of catalyst prepared by the impregnation method or mixture slurry method was almost identical in regard to methane conversion, but catalyst prepared by the mixture slurry method gave a higher C_{2+} selectivity and C_2H_4/C_2H_6 ratio.

CONCLUSION

The study of interaction effects of parameters on methane conversion, C_{2+} selectivity and C_2H_4/C_2H_6 ratio is important in understanding the OCM process. The five process variables were screened using a half-fractional factorial design and four influential factors were identified at the particular range. The OCM process was optimized using a central composite design in order to obtain maximum C_{2+} yield

under the optimum conditions by considering the effects of interaction between process variables on methane conversion and C_{2+} selectivity. The predicted optimum conditions with desirability 0.864 were GHSV of 23 947 $cm^3 g^{-1} h^{-1}$, catalyst pretreatment period of 2 h, dilution ratio 0.2 and CH_4/O_2 ratio 7, resulting in 40.55% methane conversion and 79.51% C_{2+} selectivity, with 32.24% of C_{2+} yield and a C_2H_4/C_2H_6 ratio of 1.45. A catalyst prepared by the mixture slurry method was found to provide higher C_{2+} selectivity compared to that prepared by the impregnation method. The Na–W–Mn/SiO_2 catalyst prepared by the mixture slurry method gave 42.14% methane conversion, 77.45% C_{2+} selectivity and 32.64% C_{2+} yield under optimum conditions. In conclusion, the predicted value under optimum conditions was similar to the experimental result before applying DoE, indicating that other approaches in reactor configuration such as catalytic membrane reactor should be considered, which has the superiority of providing higher C_{2+} selectivity than the conventional packed bed reactor.

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TEMPOH BERAKHIR 31 JANUARI 2007

304.PJKIMIA.6035137

DEV OF CATALYTIC MEMBRANE REACTOR FOR PRODUCTION OF ETHYLENE FROM NATURAL GAS

JUMLAH GERAN :-

Tempoh Projek:15/03/2005 - 14/03/2007

NO PROJEK :-

PANEL :- J/PENDEK

PENAJA :-

Vot		Peruntukan (a)	Perbelanjaan sehingga 31/12/2006 (b)	Tanggungan semasa 2007 (c)	Perbelanjaan Semasa 2007 (d)	Jumlah Perbelanjaan 2007 (c + d)	Jumlah Perbelanjaan Terkumpul (b+c+d)	Baki Peruntukan Semasa 2007 (a-(b+c+d)
11000	GAJI KAKITANGAN AWAM	900.00	0.00	0.00	0.00	0.00	0.00	900.00
21000	PERBELANJAAN PERJALANAN DAN SARAHI	700.00	0.00	0.00	0.00	0.00	0.00	700.00
23000	PERHUBUNGAN DAN UTILITI	300.00	2.80	0.00	0.00	0.00	2.80	297.20
24000	SEWAAN	400.00	0.00	0.00	0.00	0.00	0.00	400.00
27000	BEKALAN DAN ALAT PAKAI HABIS	10,100.00	9,648.30	0.00	250.00	250.00	9,898.30	201.70
29000	PERKHIDMATAN IKTISAS & HOSPITALITI	5,000.00	6,825.00	375.00	0.00	375.00	7,200.00	(2,200.00)
26000	BAHAN MENTAH & BAHAN UNTUK PENYELE	200.00	0.00	0.00	0.00	0.00	0.00	200.00
		17,600.00	16,476.10	375.00	250.00	625.00	17,101.10	498.90
	Jumlah Besar	17,600.00	16,476.10	375.00	250.00	625.00	17,101.10	498.90