

## MESOPOROUS INORGANIC MEMBRANE REACTOR FOR OXIDATIVE COUPLING OF METHANE

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### ABSTRACT

Mesoporous inorganic membrane has been developed and characterized for oxidative coupling of methane reactions. In this research,  $\gamma$ -alumina membrane was modified with Lanthanum. The membrane has shown thermal stability in prolonged exposure to high temperature application of 600-900°C. The results were confirmed by TGA and OCM experimentations. TGA results showed only 2-3% loss from initial weight that is mainly due to evaporation of water and release of the nitrate compound. The membrane was also found stable for at least a month of operation while the catalyst was being regenerated to regain its activity. The SEM cross-sections show successful deposition of Lanthanum in spite of its non-uniform deposition layer and cracks formation.

### 1. INTRODUCTION

The applications of inorganic membrane reactors have become one of the most active researches by looking from an increasing number of publications over the last few years. The fact that many researchers are involved in this area, somehow show that inorganic membrane reactor poses numerous potentials as an alternative to the conventional reactors. As a starting point, polymer membrane has been accepted largely in the natural gas purification and air separation. Development of inorganic membrane however, is slower than polymer membrane. So far, inorganic membrane is only used in food and drinking processing industries<sup>(1)</sup>. The fact that polymer membrane cannot stand high temperature leaves the window open for utilization of inorganic membrane, particularly ceramic membrane for high temperature applications. As an example, considerable efforts have been made to study perovskite type ceramic membrane for air separation and conversion of methane to synthetic gas at high temperature. These are reflected by the involvement of two major corporations, Air Products and BP-Amoco in these areas<sup>(2)</sup>. Oxidative coupling of methane (OCM) reaction requires operating temperature as high as 600-900°C even though it operates at ambient pressure. At such high temperature, only inorganic membrane

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can be used for the reactions. However, there are challenges that have to be met before inorganic membrane can be commercially used in such operation.

Oxidative coupling of methane (OCM) is one of the selected projects designed for the development of cost effective chemical conversion of methane to more valuable and easily transportable chemicals and fuels. Up till now, yield of OCM has never reached beyond 30%, which is the benchmark for commercialization. The latest development in OCM shows membrane reactor has become the central attention for the operation. The most significant potential of membrane in OCM process is its ability to increase the selectivity of the products by controlling the addition of reactant. In this case, oxygen is distributed along the membrane reactor length. It is a vital step because the presence of excessive oxygen was often deleterious to ethylene-ethane ( $C_2$ ) selectivity. Gas-phase oxygen often triggers deep oxidation of intermediate and desired product species to yield undesired CO and  $CO_2$  ( $CO_x$ ). It is true for most catalysts used in OCM, where the apparent reaction order for oxygen in deep oxidation is higher than coupling reaction<sup>(3)</sup>. Therefore, it is essential to keep low oxygen concentration in order to favor for the desired reaction paths and thus improving the selectivity at a given conversion level. In addition to higher selectivity of  $C_2$  hydrocarbons, the distributed oxygen also would mitigate the thermal hot spots for the highly exothermic OCM reactions. Therefore, it allows the reactor to operate such that higher methane conversion can be achieved at higher overall oxygen to methane ratio than that of co-feed reactor. In the latter reactor, oxygen to methane ratio is bounded by the explosion limit. This explosion limit is decreased or even eliminated with the use of membrane reactor.

The main focus of this paper is the development of mesoporous inorganic membrane reactor based on  $\gamma$ -alumina by certain modifications in the laboratory for its use in OCM operation. Therefore, detailed characterization of the membrane and its stability test under prolong exposure to heat are the central topics discussed in this paper. Some experimental results based on this membrane reactor filled with fixed bed of oxide catalyst (called fixed bed membrane reactor, FBMR) for OCM process is also presented at the end of the paper.

## 1.1 Inorganic membrane selection

There are two major types of inorganic membrane that are constantly being used in OCM research, mainly dense and porous. Dense inorganic membranes are membranes made of polycrystalline ceramic or metal, which allows certain gas species to permeate through its crystal lattice<sup>(2)</sup>. Porous inorganic membrane in the other hand consists of several classifications based on the pore size of the membrane. Mesoporous inorganic membrane, also the main focus of this paper is defined as porous membrane with a pore diameter between 2 to 100 nm. The other two classes, microporous and macro porous inorganic membranes are membranes with pore sizes of  $<2$  nm and  $>100$  nm, respectively<sup>(1,2)</sup>.

What makes dense and porous membranes apart is the different transport mechanism through these membranes. While dense membrane allows only transportation of one species (eg.  $O_2$ ) by ion conducting and molecular sieve, (to name a few transport mechanisms), porous membrane

is nonselective. It allows  $O_2$  transport faster than the other species by means of Knudsen diffusion, laminar and surface transport mechanisms through the pore network<sup>(3)</sup>. The aim here is mainly to increase permeation flux of oxygen, which is low in dense membrane. Lanthanum cobaltite based dense membrane for example, has oxygen permeation flux lower than industrially targeted values ( $3.7 \times 10^{-2}$  -  $7.4 \times 10^{-2}$  mol/m<sup>2</sup>s) (Lin, 2001). However, the latest development in dense membrane was more promising with  $C_2$  yield achieved as high as 17%<sup>4</sup>. Moreover, some of the dense membrane showed structural instability in reducing environment, which caused phase change/segregation and ion reduction<sup>(2)</sup>.

The idea of a porous membrane reactor was based on process selection to formation of hydrocarbons vs. nonselective formation of methane to  $CO_x$ . Here, the delivery of oxygen is by bulk instead of solid state ionic diffusion as in dense membrane, thus allowing smooth distribution of oxygen feed that is mainly governed by pressure differential. In fact, low partial pressure in the reaction site has been found to promote the formation of  $C_2$  hydrocarbons<sup>(5)</sup>. A number of reports utilizing porous ceramic membranes over OCM reactions have shown improvement in  $C_2$  selectivity and  $C_2$  yield<sup>(5, 6, 7)</sup>. In a research utilizing macroporous alumina membrane stabilized with Lanthanum has shown significant increase of  $C_2$  selectivity in comparison to fixed bed reactor with highest  $C_2$  yield achieved at 27.5%<sup>8</sup>.

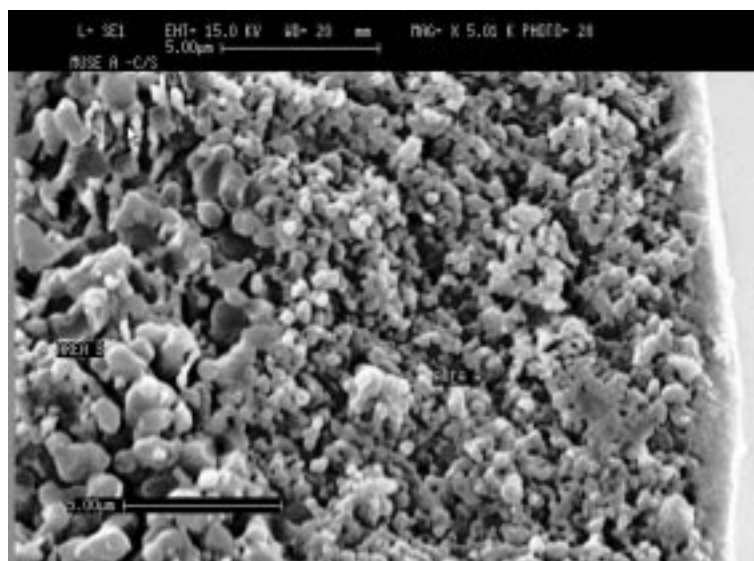
According to Lafarga and co-workers<sup>(3)</sup>, the term thermal stability when applied to ceramic membranes usually refers to their ability to withstand prolonged exposure to high temperatures, without a major change in their morphological properties. The stability of the membrane structure and texture-related properties such as surface area and pore characteristics are critical to obtain good membrane performance. The consequence of long exposure to harsh environment may result in cracks. This results in the development of preferential permeation paths or back-permeation that bypassing contact of the reactants with catalysts. While the loss of surface area can probably be tolerated in fixed bed membrane reactor, degradation of other characteristics such as increase in pore radius and development of cracks results in significant decrease in performance of the membrane.

The practical utilization of alumina membrane at high temperature depends on, among others, thermal and hydro-thermal stability of the membrane. Alumina type membrane such as  $\gamma$ -alumina changes its phase structure with increasing temperature from 700°C ultimately to the most stable  $\alpha$ -alumina at around 1200°C. There is also a tremendous increase in pore size as  $\gamma$ -alumina changes to  $\alpha$ -alumina<sup>(10)</sup>. Therefore, since OCM is operated at such a high temperature, some modifications are in order before the membrane can be used to suppress the phase changes at high temperature (900-1100°C) from  $\gamma$ - to  $\alpha$ -alumina. Lin and co-workers<sup>(11)</sup> reported that thermal and hydro-thermal stability of  $\gamma$ -alumina can be improved by doping with Lanthanum oxide on the grain surface of the membrane. Therefore, addition of lanthanum either in alumina sol or in the calcined alumina could stabilize the pore structure of the  $\gamma$ -alumina. Not only that, the presence of lanthanum oxide and lanthanum aluminate in the membrane could improve the reactions because of their good catalytic properties for OCM process<sup>(8)</sup>. Lafarga and co-workers<sup>(3)</sup> deposited silica inside the pore structure of  $\alpha$ -alumina membrane with the aim to partially block the pores of the original membrane tube.

## 2. EXPERIMENTAL

### 2.1 Membrane preparation

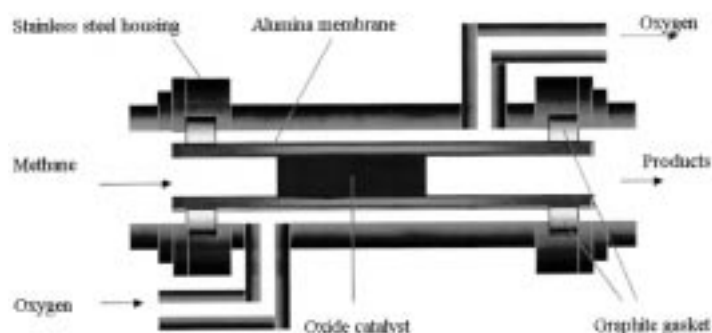
$\gamma$ -alumina membrane tube (ID=7 mm, OD=10 mm) was supplied by SCT, US Filter Corporation. Figure 1 shows a SEM picture of a cross section of a fresh  $\gamma$ -alumina membrane tube. The top layer of the membrane, which is in the inner side of the tube comprises of  $\gamma$ -alumina with the thickness of about 3  $\mu\text{m}$  and pore size of 5 nm. The outer layers are  $\alpha$ -alumina. Due to the long storage, the membrane tube was first cleaned with de-ionized water and dried overnight prior to the modification with lanthanum oxide. Dip coating method was used for the coating of membrane with salt solution. The coating of membrane with 50% aqueous  $\text{La}(\text{NO}_3)_3$  prepared by mixing  $\text{HNO}_3$  and  $\text{La}_2\text{O}_3$  was carried out by immersing the inner side of the tube into  $\text{La}(\text{NO}_3)_3$  solution. The membrane tube was then calcined at 400°C overnight. The immersion and calcination steps were repeated several times before its final calcination at 900°C for 50 hours. In order to define the permeation area, it was necessary to coat the membrane tube with an impervious layer of enamel. To achieve this, both ends of the membrane tube were coated with aqueous solution of titanium oxide repeatedly<sup>(3)</sup>. The tube was then calcined at 800°C for 6 hours. The impervious coating over both ends of the membrane tube reduced the permeation zone to the central 14 cm of the reactor.



*Figure 1 : SEM photograph of a cross section of fresh  $\gamma$ -alumina membrane tube*

### 2.2 Reactor configuration

The modified membrane tube was mounted in the stainless steel membrane reactor housing and sealed with graphite o-rings as illustrated in Figure 2. The reactor consists of Li-B-MgO catalyst packed in the inner side of the membrane tube that acts as an oxygen distributor. Methane and



**Figure 2 :** Schematic of fixed bed membrane reactor (FBMR) configuration

oxygen/nitrogen were fed to the reactor tube-side and shell-side entrance, respectively using mass flow controllers. The pressures at both reactor sides were measured with pressure transducers and displayed by the pressure indicators. The pressure in the shell-side of the reactor was controlled by back-pressure regulator. The permeation of oxygen was carried out only in the central 14 cm region of the membrane tube. A three-zone electrical furnace was used to heat up the reactor. The exit gases were measured using a flow-meter and then directed to the on-line gas chromatograph (HP 6890) equipped with TCD and FID detector where they were analyzed.

Due to brittleness of the membrane and its susceptibility to the mechanical strain, the same packed bed membrane reactor was used for the experimentation for about a month without the need to change for fresh catalyst every time a run was carried out. The Li-B-MgO catalyst was regenerated at least once in the duration of the experimentation to restore catalyst activity near to the activity of fresh catalyst that was deactivated due to coking caused by prolong exposure to the experimentation.

### 2.3 Membrane characterization

The characterization of the modified membrane was carried out to analyze the physical properties of membrane and catalyst. Specifically, membrane was characterized for its surface morphology, stability and pore size. The lanthanum modified  $\gamma$ -alumina membrane (that was originally having average pore size of 5 nm) was characterized using Nitrogen adsorption measurement (AUTOSORB), Thermal Gravimetric Analysis (TGA) and X-ray Diffraction (XRD).

Nitrogen adsorption method was used to obtain BET surface area measurements, the pore size distribution as well as the mean pore radius of catalyst and membrane. AUTOSORB-1 supplied by QUANTACHROME Corporation, USA was used for this purpose. The thermal stability of catalyst and membrane was checked using thermal gravimetric analysis (TGA) by monitoring the change in weight of sample as its temperature was increased. In TGA, the temperature at which the sample loses its weight is determined, which also indicates the changes in the thermal stability of the material. These temperature changes are physical properties of chemical compounds and can be used for their identifications. Powder XRD measurement was carried out to identify

component phases present and to determine the crystallinity of the sample. In XRD unit, appropriately oriented grains in the sample diffract the x-rays into a detector. By sweeping the angle of incidence and detection, a spectrum of diffraction peaks corresponding to the crystal lattice spacing is produced.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) was used for the analysis of surface morphology and component detection of membrane. Images of the surface of the inside, outside and cross-section of the membrane were produced in SEM. Meanwhile, EDX digital mapping was used to identify the element in the sample. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) analysis were carried out using an electron microscope (Leica Cambridge S-360) equipped with Camscan Editor for the EDX analysis.

### 3. RESULTS

#### 3.1 Surface area and pore diameter

The results in this section show the difference of surface area of the  $\gamma$ -alumina for fresh and after OCM experimentation. Table 1 summarizes the results of nitrogen adsorption analysis for the modified membrane.

**Table 1 :** Nitrogen Adsorption Analysis Lanthanum modified  $\gamma$ -alumina membrane used in the OCM experiment

Material	BET surface area ( $\text{m}^2/\text{g}$ )	Average pore size (nm)
Modified $\gamma$ -alumina (fresh)	1.385	7.652
Modified $\gamma$ -alumina (used)	1.295	15.10

The BET surface area of the modified  $\gamma$ -alumina membrane was found to be in line with the reported silica modified  $\alpha$ -alumina with BET surface area of around 0.76 to 2.42  $\text{m}^2/\text{g}^3$ . BET surface area of the lanthanum modified  $\gamma$ -alumina membrane showed a slight drop after the experiment at high temperature. The slight drop in the membrane surface area was probably due to the sintering process that took place at high temperature. Doping of membrane with Lanthanum was used to retard the phase transformation process by reducing the number of nucleation sites or increasing the nucleation activation energy<sup>(9)</sup>. This is contrary to what was expected, where the introduction of Lanthanum does not seem to significantly decrease the rate of loss of surface area when alkali compounds are present.

It was observed that the value of average pore size of the modified  $\gamma$ -alumina membrane was increased after the experiment. This is due to the enlargement of pore size of the  $\gamma$ -alumina membrane due to phase change from  $\gamma$ -alumina to  $\alpha$ -alumina at temperature higher than

900°C<sup>(10,11)</sup>. Furthermore, the commercial  $\gamma$ -alumina membrane that was typically calcined at 400 - 600°C was subject to potential structural changes as was revealed by alumina chemistry at temperature beyond 600°C<sup>(10)</sup>. Therefore, at operating temperature of 700-900°C employed in the experiment, some slight pore size enlargement due to the transition phase change did indeed occur even after the modification of the  $\gamma$ -alumina membrane. Pore sizes of the membrane were still in the range of mesoporous (2-50 nm) area, where Knudsen diffusion is the major transport<sup>(12)</sup>. Therefore, the resulted gas permeation will be both ways between the tube side and the shell side of the membrane based on the molecular weight of the permeating species and the pressure difference between the tube and the shell side. The increment in pore size in this paper is slightly higher than reported in the literature (7.9 to 9.6 nm)<sup>(9)</sup>. However, as mentioned, the current experiment was carried out over a month while the measured pore size in literature was done after 48 hours of operation only.

### 3.2 Thermal stability

Figures 3 and 4 show the TGA results for fresh and used modified  $\gamma$ -alumina membrane, respectively. Both fresh and used modified  $\gamma$ -alumina membrane showed a total weight loss of

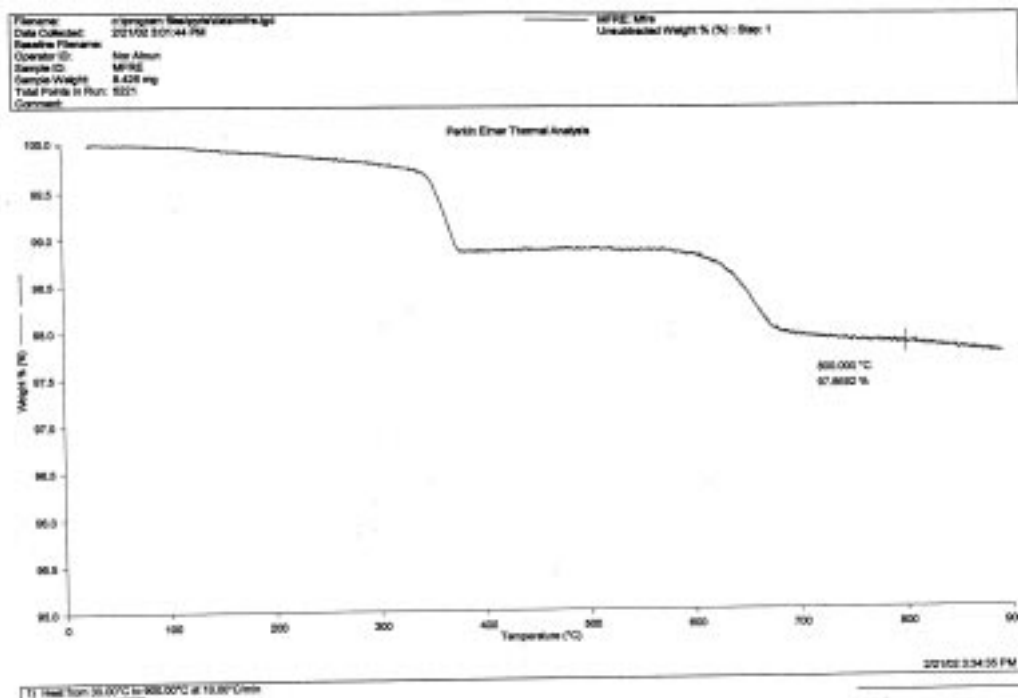


Figure 3 : TGA Analysis of Fresh Lanthanum Modified  $\gamma$ -alumina Membrane

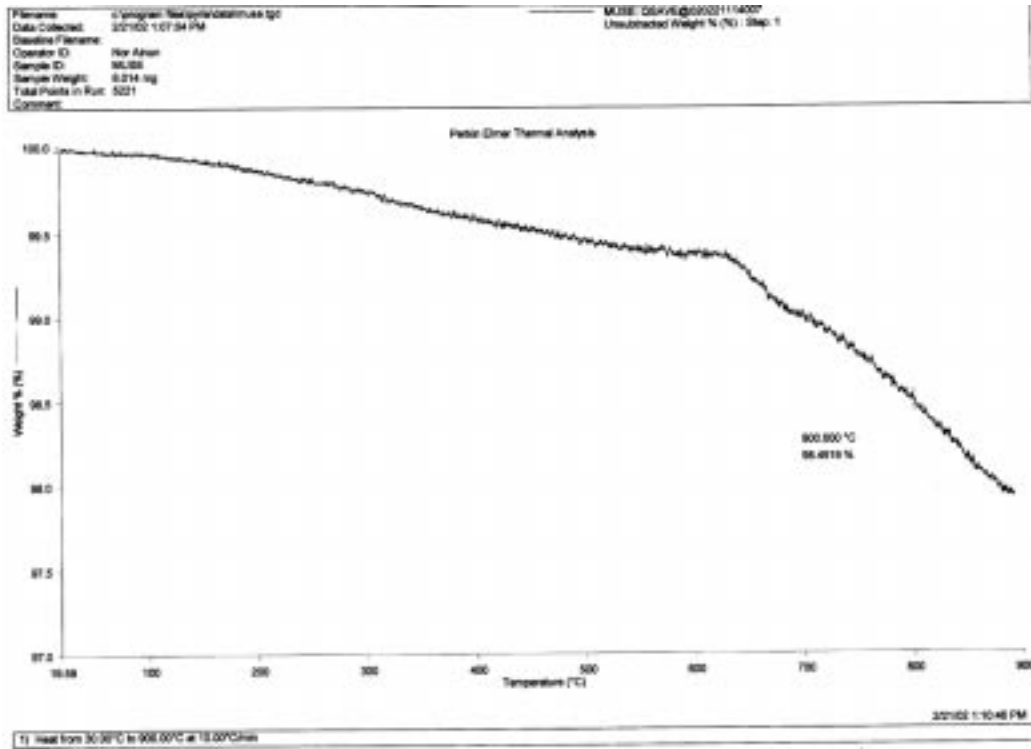


Figure 4 : TGA Analysis of Lanthanum Modified  $\gamma$ -alumina Membrane after Experimentation

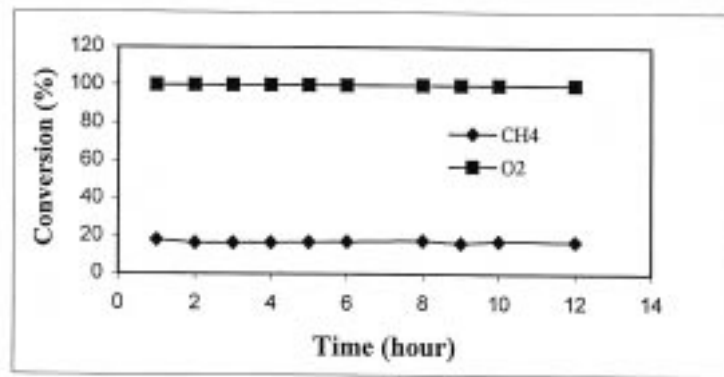


Figure 5 : The effect of time on-stream on methane and oxygen conversion at  $T = 750^{\circ}\text{C}$ ,  $\text{CH}_4/\text{O}_2$  ratio = 4,  $\text{SV} = 6.241 \times 10^{-7} \text{ m}^3/\text{g}_{\text{cat}}\cdot\text{s}$  and  $\text{N}_2$  flow rate = 120 ml/min.

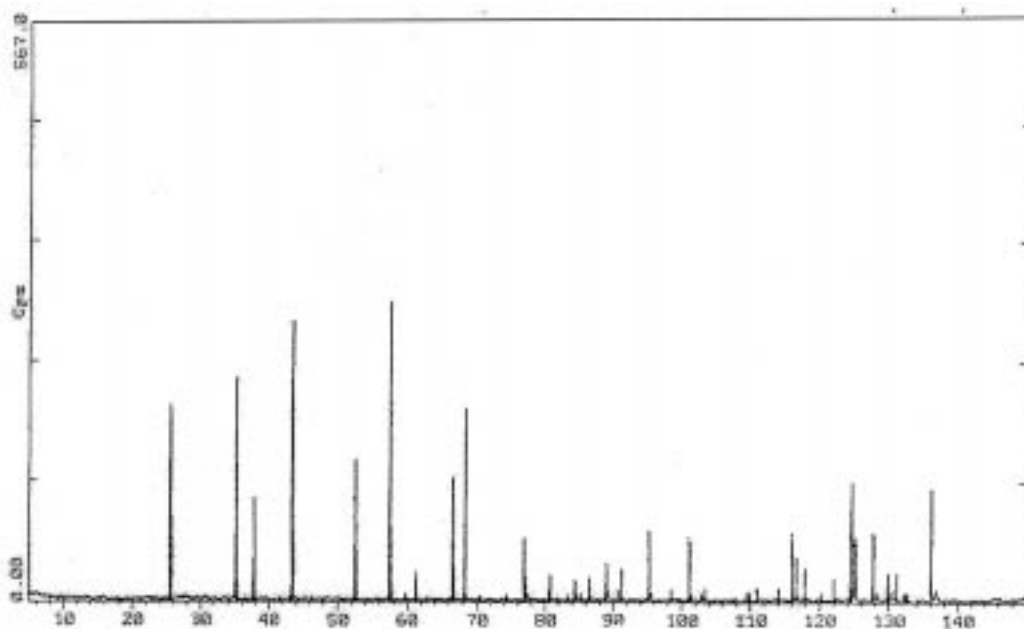
about 2.2-2.3% from the initial weight. The weight loss was probably due to the fact that lanthanum nitrate has reacted with the alumina to produce lanthanum aluminate releasing the nitrate compound<sup>(8)</sup> in addition to the evaporation of water. However, the weight loss for



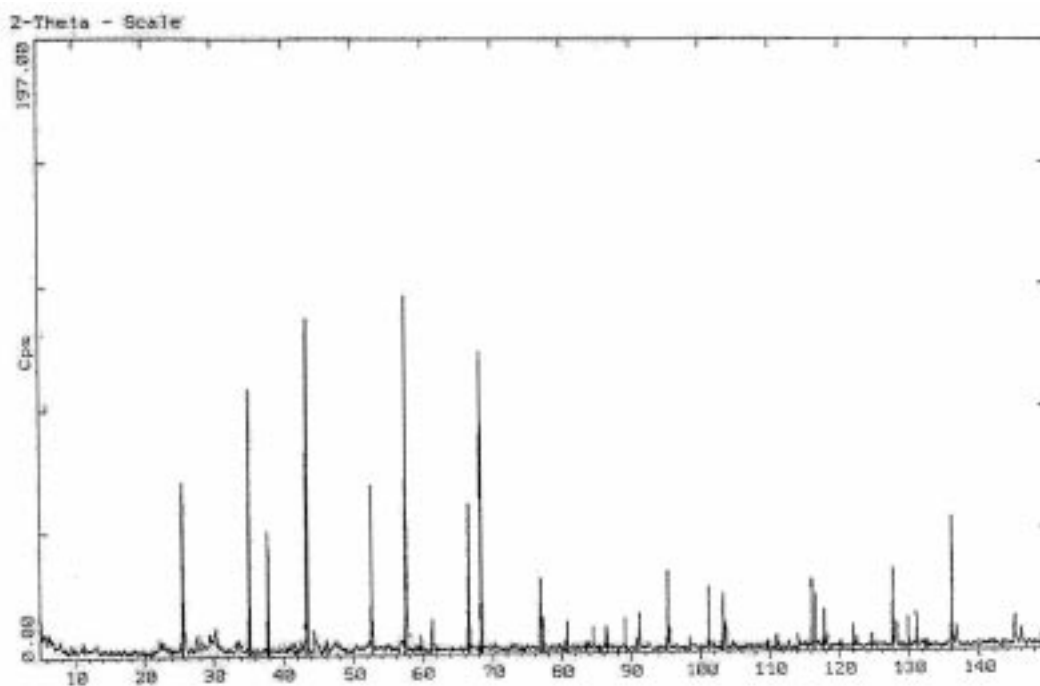
membrane and catalyst can still be considered low thus showing that the membrane is stable at reaction temperature. The stability of the membrane (as well as catalyst) is further confirmed with the time used for OCM operation. A total of 12-hour operation was used to show the stability of membrane under prolong exposure in high temperature. Figure 5 shows methane and oxygen conversion with respect to time on-stream. Both oxygen and methane conversion remained almost constant throughout the reaction time, which shows that the membrane and catalyst were stable up to 12 hours. Furthermore, the results of the experimental runs for the study of all operating conditions carried out using the same reactor without changing the catalyst and membrane for over a month was observed to check on the stability of the membrane or catalyst. The membrane was stable for the whole month while the catalyst was regenerated once to regain its activity.

### 3.3 Crystalline structure

Lanthanum modified  $\gamma$ -alumina membrane subjected to reaction temperature of 700-900°C was analyzed using XRD. Figures 6 and 7 show the XRD analysis results of fresh and used modified  $\gamma$ -alumina membrane, respectively. As seen, alumina crystalline structures were detected in both fresh and used  $\gamma$ -alumina membrane. The comparison of XRD analysis results between fresh and used  $\gamma$ -alumina membrane has shown that the crystalline phases did not change with temperature and reactions. Therefore, XRD analysis confirms the stability of both catalyst and membrane employed in the experiment.



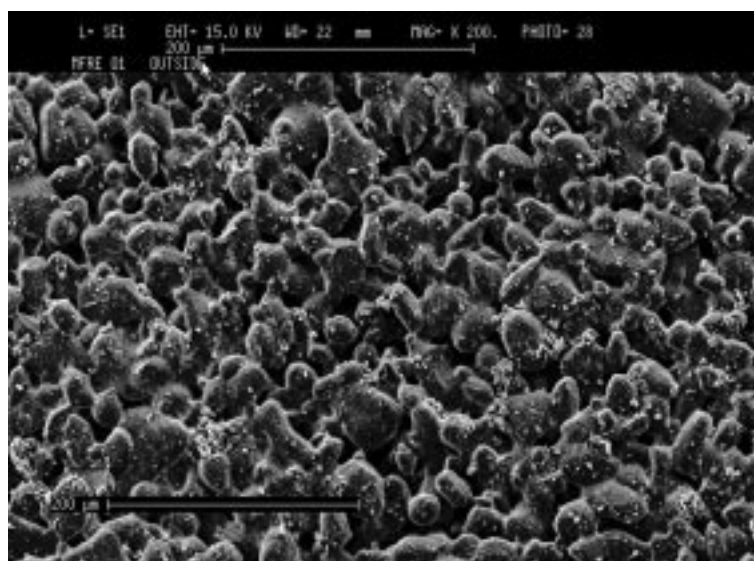
**Figure 6 :** XRD Analysis of Fresh Lanthanum Modified  $\gamma$ -alumina Membrane



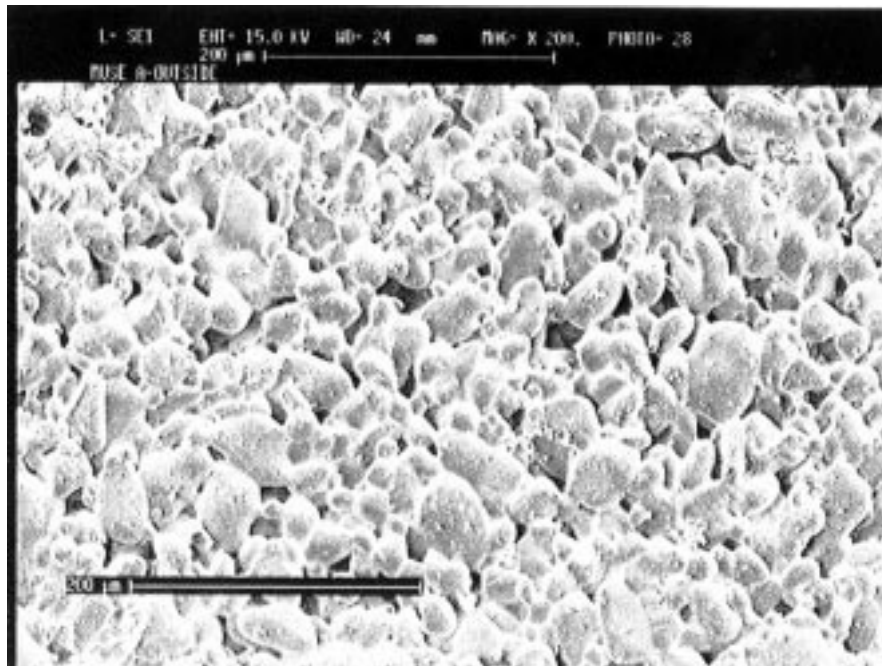
**Figure 7 :** XRD Analysis of Used Lanthanum Modified  $\gamma$ -alumina Membrane, subjected Temperature of 700-900°C

### 3.4 Surface morphology

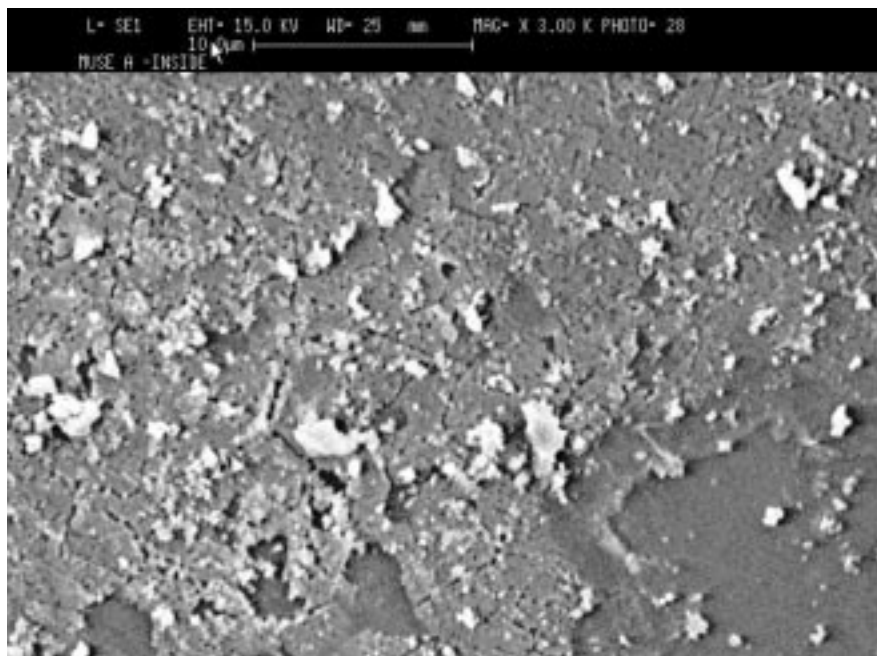
Figure 8 shows the surface morphology of the outer surface of fresh modified  $\gamma$ -alumina membrane at magnification of 200. Here, porous surface was observed. Figure 9 shows the surface



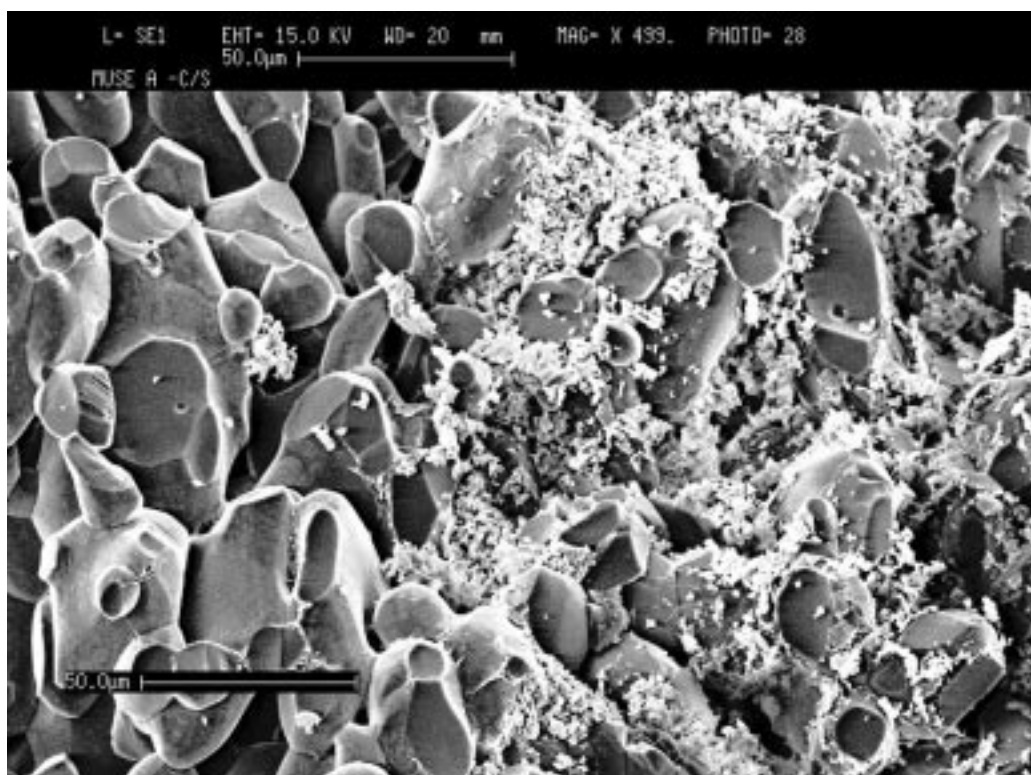
**Figure 8 :** SEM Photograph of the outer surface of fresh unmodified  $\gamma$ -alumina membrane



*Figure 9 (a) : SEM photograph of the outside surface of the lanthanum modified  $\gamma$ -alumina membrane*



*Figure 9 (b) : SEM photograph of the inside surface of the lanthanum modified  $\gamma$ -alumina membrane*



*Figure 9 (c) : SEM photograph of the cross section of lanthanum modified  $\gamma$ -alumina membrane*

morphology of the (a) outer surface (magnification X 200) (b) inside surface (magnification X 3000) and (c) cross section of membrane thickness (magnification X 499) for modified  $\gamma$ -alumina membrane after experimentation. The outer surface morphology of the used membrane was also detected for its porous structure. The coating of lanthanum oxide solution can be detected in the inside surface of the membrane where layers of the coated solution was observed. It was found that the coating employed did not result in uniform coating layer as cracks can be clearly seen on the membrane surface. Despite that, the coating can be considered successful as the layers of the coated solution were observed. Figure 9 (c) shows a part of the membrane cross-section surface where the border can be seen between the infiltrated lanthanum oxide regions with the original membrane structure. Here, it can be clearly seen how lanthanum oxide particles have filled up the pores of the membrane, thus reducing the pore size of the membrane at the region. Not only that, EDX digital mapping of the cross-section of the modified  $\gamma$ -alumina membrane tube showed that lanthanum was present across the entire thickness of the membrane tube wall. Almost 22.7% of lanthanum element was found present in the cross-section area as shown by Figure 10. Therefore, it can be concluded that the deposited lanthanum oxide solution did indeed help to stabilize the  $\gamma$ -alumina membrane thermally as shown in SEM picture and with only enlargement of average pore size from 7 to 15 nm as was found in nitrogen adsorption.

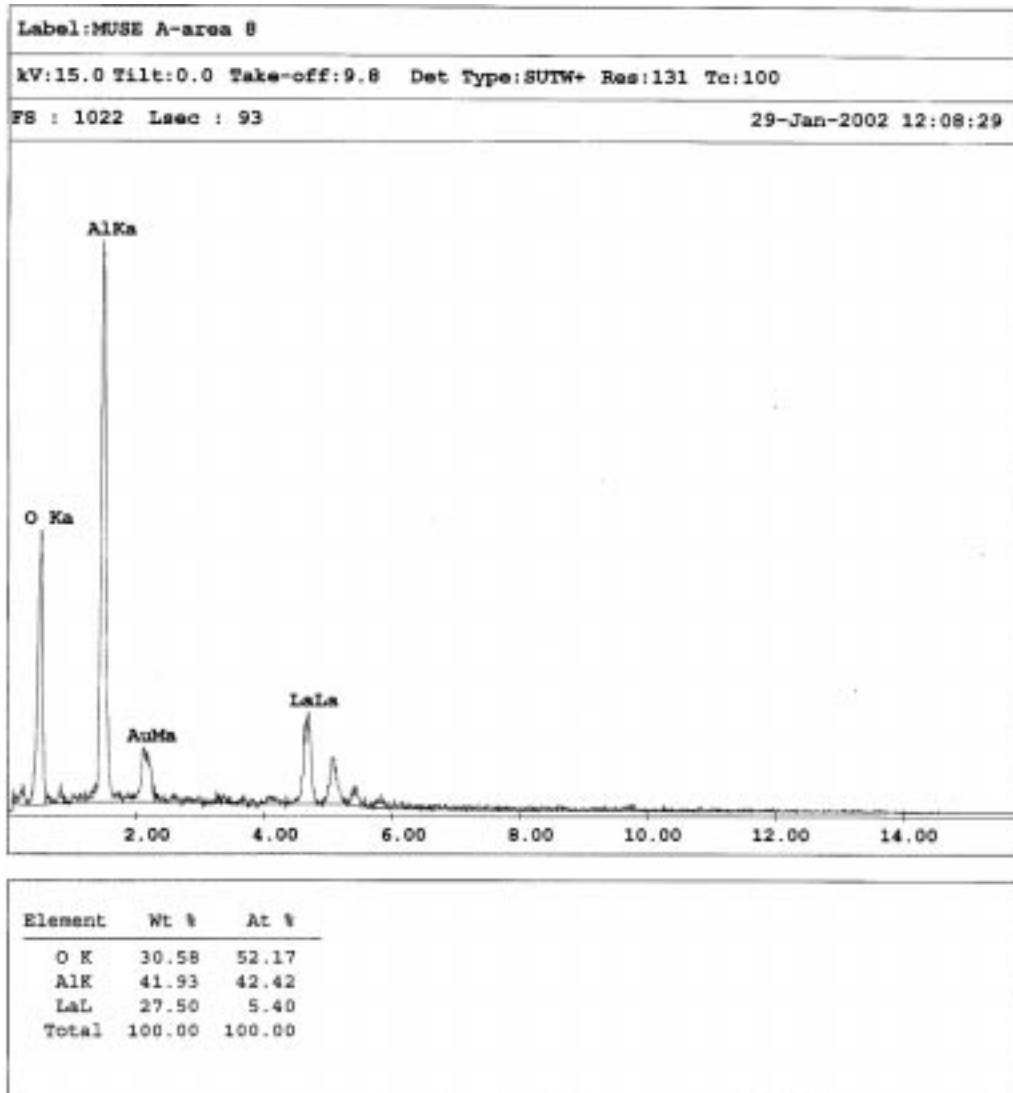
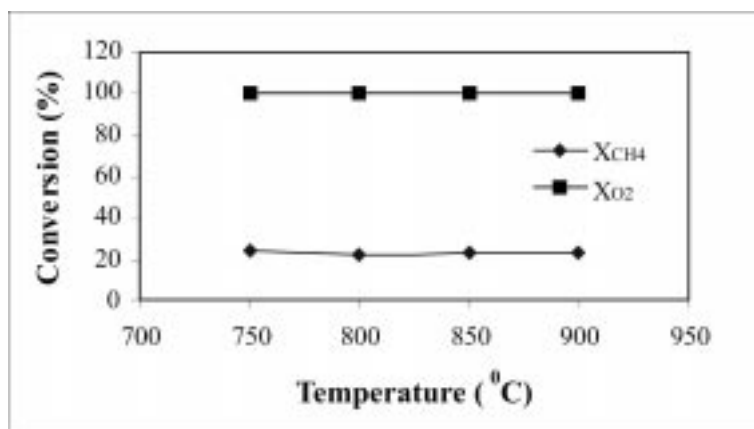


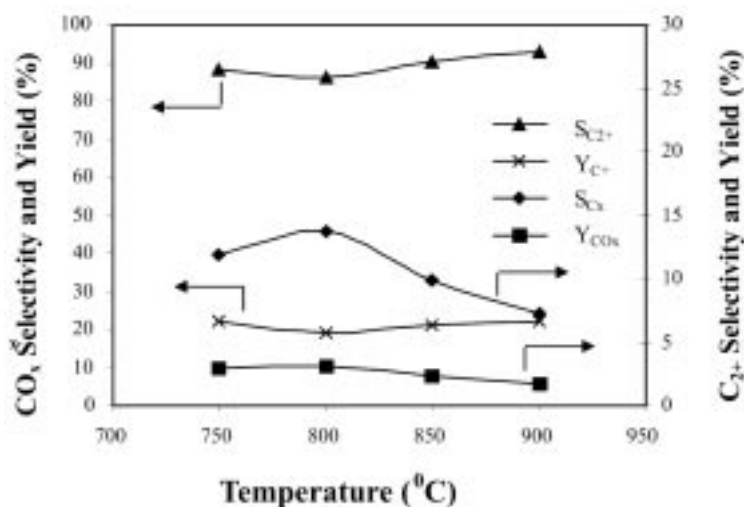
Figure 10 : EDX Analysis of Cross-section of Modified  $\gamma$ -Alumina Membrane Tube

### 3.5 Oxidative coupling of methane (OCM) experimentation

The results of OCM experimentation are shown for the effect of temperature on the performance of the modified FBMR. The operating temperature was varied between 700 to 900°C in the packed bed membrane reactor loaded with Li-B/MgO catalyst at  $\text{CH}_4/\text{O}_2 = 4$ ,  $\text{SV} = 7.046 \times 10^{-7} \text{ m}^3/\text{g}_{\text{cat}} \text{ s}$  and  $\text{N}_2$  flow rate = 120 ml/min. Figure 11 shows the temperature profile of methane conversion in OCM process. Oxygen conversion is always 100%, showing all the oxygen fed was used up. Similarly, methane conversion was changed little over the temperature. It only fluctuated between 33 to 36% with only a marginal increase at 892°C. The trend of methane conversion was almost constant since all oxygen was used up at the whole range of the operating temperature.



**Figure 11 :** Effect of reaction temperature on conversion of methane and oxygen at operating conditions of  $CH_4/O_2 = 4$ ,  $N_2$  flow rate = 120 ml/min and  $SV = 7.046 \times 10^{-7} m^3/g_{cat}s$



**Figure 12 :** Effect of reaction temperature on selectivity of  $C_{2+}$  and  $CO_x$  and yield of  $C_{2+}$  and  $CO_x$  at operating conditions of  $CH_4/O_2 = 2$ ,  $N_2$  flow rate = 120 ml/min and  $SV = 7.046 \times 10^{-7} m^3/g_{cat}s$

As shown in Figure 12,  $C_{2+}$  selectivity decreased with respect to the increasing  $CO_x$  selectivity with respect to temperature. Therefore, the resulted yield of  $C_{2+}$  hydrocarbons was also decreased. Meanwhile, yield of  $CO_x$  showed a slight fluctuation with increasing temperature. This was due to even though the reaction was more selective towards the formations of carbon oxides at higher temperature; the resulted  $CO_x$  yield was limited by the constant methane conversion over the temperature.

#### 4. CONCLUSIONS

Mesoporous inorganic membrane has been developed and characterized for oxidative coupling of methane reactions. The fixed bed membrane reactor consists of a modified commercial  $\gamma$ -alumina and Li/B-MgO catalyst packed inside the membrane tube. The characterization of the membrane was carried out to analyze the physical properties of the membrane. The BET surface area of membrane was found to be in the range reported in the literature. The increase in pore size of membrane was due to membrane exposure to heat at a very long period. Similarly, TGA analysis and experimentation have shown that membrane was stable under the operating conditions during the experiments. The surface morphology of the membrane obtained from SEM analysis shows that the membrane was successfully modified even though the resulted coating was inhomogeneous.

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