การพัฒนาตัวเร่งปฏิกิริยา Mn-Na_2WO_4 บนตัวรองรับ La_2O_3, Y_2O_3 และ YSZ สำหรับปฏิกิริยาการคู่ควบมีเทนในเครื่องปฏิกรณ์แบบเบดนิ่งและเซลล์เชื้อเพลิงชนิดออกไซด์แข็ง

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DEVELOPMENT OF Mn-Na_2WO_4 CATALYST ON La_2O_3, Y_2O_3 AND YSZ SUPPORTS FOR OXIDATIVE COUPLING OF METHANE REACTION IN FIXED BED AND SOLID OXIDE FUEL CELL REACTORS

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ฤษฎา คำโมนะ : การพัฒนาตัวเร่งปฏิกิริยา Na_2WO_4-Mn บนตัวรองรับ La_2O_3, Y_2O_3 และ YSZ สำหรับปฏิกิริยาการคู่ควบมีเทนในเครื่องปฏิกรณ์แบบ เบดนิ่งและเซลล์เชื้อเพลิงชนิดออกไซด์แข็ง DEVELOPMENT OF Mn-Na_2WO_4 CATALYST ON La_2O_3, Y_2O_3 AND YSZ SUPPORTS FOR OXIDATIVE COUPLING OF METHANE REACTION IN FIXED BED AND SOLID OXIDE FUEL CELL REACTORS. อ.ที่ปรึกษาวิทยานิพนธ์หลัก:ศ.ดร.สุทธิชัย อัสสะบำรุงรัตน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร.วิศิษฏ์ศรี วิยะรัตน์, 122 หน้า.

การศึกษาการพัฒนาตัวเร่งปฏิกิริยา Mn-Na_2WO_4 บนตัวรองรับ La_2O_3, Y_2O_3 และ YSZ สำหรับปฏิกิริยาการคู่ควบมีเทนแบ่งการศึกษาออกเป็น 2 ส่วนคือ ในเครื่องปฏิกรณ์แบบเบดนิ่งและเซลล์ปฏิกรณ์เชื้อเพลิงชนิดออกไซด์แข็ง ซึ่งการศึกษาในเครื่องปฏิกรณ์แบบเบดนิ่ง เป็นลักษณะของการไหลผสมของก๊าซมีเทน, ก๊าซออกซิเจนรวมทั้งก๊าซไนโตรเจนในอัตราส่วน 4:1:5 เพื่อศึกษาตัวเร่งปฏิกิริยาและช่วงอุณหภูมิ 973-1173 K โดยตัวเร่งปฏิกิริยาที่สนใจศึกษาคือ Mn-Na_2WO_4 บนตัวรองรับ La_2O_3, Y_2O_3 และ YSZ ซึ่งได้มีการพัฒนาด้วยการเติม ซัลเฟอร์, ฟอสฟอรัส, และซีเรียม ลงไป เพื่อดูประสิทธิภาพของตัวเร่งปฏิกิริยา พบว่าตัวเร่งปฏิกิริยาที่มีประสิทธิภาพคือ ตัวเร่งปฏิกิริยา Mn-Na_2WO_4 บนตัวรองรับ YSZ ที่มีการเติมซัลเฟอร์และฟอสฟอรัสลงไป โดยที่อุณหภูมิ 1073 K การเติมซัลเฟอร์(S-Mn-Na_2WO_4/YSZ)ให้ค่าการเลือกเกิดผลิตภัณฑ์ C_2 เท่ากับ 60.3% และค่าการเปลี่ยนแปลงของมีเทนเท่ากับ 31.1% ในขณะที่การเติมฟอสฟอรัส (P-Mn-Na_2WO_4/YSZ) ให้ค่าการเลือกเกิดผลิตภัณฑ์ C_2 เท่ากับ 59.8% และค่าการเปลี่ยนแปลงของมีเทนเท่ากับ 34.1% ที่อุณหภูมิเดียวกัน ส่วนการศึกษาในเครื่องปฏิกรณ์แบบเซลล์เชื้อเพลิงชนิดออกไซด์แข็งนั้น ได้เลือกตัวเร่งปฏิกิริยา S-Mn-Na_2WO_4/YSZ, P-Mn-Na_2WO_4/YSZ และตัวเร่งปฏิกิริยา Mn-Na_2WO_4 บนตัวรองรับ YSZ มาเป็นขั้วแอโนดในเซลล์ปฏิกรณ์เชื้อเพลิงชนิดออกไซด์แข็ง โดยใช้ขั้วแคโธดคือ $La_{0.8}Sr_{0.2}MnO_3$ (LSM) อิเล็กโตรไลท์คือ 8% โมล yttria-stabilized zirconia (YSZ) พบว่าตัวเร่งปฏิกิริยา P-Mn-Na_2WO_4/YSZ ให้ประสิทธิภาพดีที่สุด โดยให้ค่าการเลือกเกิดผลิตภัณฑ์ C_2H_4 เท่ากับ 89.0% และค่าการเปลี่ยนแปลงของมีเทนเท่ากับ 10.5% ที่ 1123 K โดยกำลังไฟฟ้าที่ได้รับคือ 13.2 W/m^2 นอกจากนั้นได้มีการศึกษาค่าความเสถียรของตัวเร่งปฏิกิริยา P-Mn-Na_2WO_4/YSZ ที่ 1123 K พบว่ามีความเสถียร 29 ชั่วโมง

ภาควิชา......วิศวกรรมเคมี...... ลายมือชื่อนิสิต..............................

สาขาวิชา......วิศวกรรมเคมี...... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก....................

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##5370396721: MAJOR CHEMICAL ENGINEERING
KEY WORDS: SOLID OXIDE FUEL CELL (SOFC), OXIDATIVE COUPLING OF METHANE (OCM), CO-GENERATION

KRIDSADA KHAMMONA: DEVELOPMENT OF Mn-Na_2WO_4 CATALYST ON La_2O_3, Y_2O_3 AND YSZ SUPPORTS FOR OXIDATIVE COUPLING OF METHANE REACTION IN FIXED BED AND SOLID OXIDE FUEL CELL REACTORS. ADVISOR: PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., CO-ADVISOR: WISITSREE WIYARATN, Ph.D., 122pp.

This research studies the development of Mn-Na_2WO_4 catalysts on La_2O_3, Y_2O_3 and YSZ supports for oxidative coupling of methane reaction. It can be divided into two parts; (1) study in fixed bed reactor (FBR), and (2) study in solid oxide fuel cell reactor (SOFC). In part I, the experiments were performed using co-feeds of methane, oxygen and nitrogen inert gas at a ratio of 4:1:5 for different temperatures (973-1173 K). Mn-Na_2WO_4 catalyst on supports La_2O_3, Y_2O_3 and YSZ were doped with sulfur, phosphorous, and cerium in order to improve its catalytic reactivity. The results indicated that sulfur and phosphorous showed the good improvement for Mn-Na_2WO_4 catalyst on YSZ support. At 1073 K, S-Mn-Na_2WO_4/YSZ provided C_2 selectivity of 60.3% and methane conversion of 31.1%, while P-Mn- Na_2WO_4/YSZ offered C_2 selectivity of 59.8% and methane conversion of 34.1%. S-Mn-Na_2WO_4/YSZ, P-Mn-Na_2WO_4/YSZ and Mn-Na_2WO_4/YSZ catalysts part I were selected as anode catalysts for further study in the SOFC reactor. The experiments were carried out using $La_{0.8}Sr_{0.2}MnO_3$ (LSM) as the cathode catalyst, 8mol% yttria-stabilized zirconia (YSZ) as the electrolyte. P-Mn-Na_2WO_4/YSZ exhibited the best performance, providing C_2H_4 selectivity of 89.0%, methane conversion of 10.5% and electrical power density of 13.2 W/m^2 at 1123 K. In addition, the stability of the P-Mn-Na_2WO_4/YSZ catalyst was tested at 1123 K. Good stability of the reaction system could be observed at least for twenty nine hours.

Department:……Chemical Engineering…...	Student's Signature……………………..
Field of Study:.Chemical Engineering…...	Advisor's Signature……………….….
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CHAPTER I
INTRODUCTION

1.1 Introduction

Fuel cell is an electrochemical cell that converts chemical energy of a fuel into electrical energy with water and heat as its by-products. It has a number of advantages particularly its high efficiency and low emission of pollutants. The main components of fuel cell consist of electrolyte, anode electrode, cathode electrode, and external load. There are six main types of fuel cell classified by type of electrolyte: alkaline fuel cell (AFC), polymer electrolyte membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), direct methanol fuel cell (DMFC), and solid oxide fuel cell (SOFC). SOFCs are the most attractive fuel cell because of a possibility of using a wide variety of fuel, high efficiency, long-term stability and low emissions. Although in conventional operation, the main objective of SOFC is to generate electricity, some researchers have focused on the application of SOFC as a multifunctional reactor for co-generation of chemicals and electrical power. Various valuable industrial compounds such as ethylene, hydrogen, hydrogen cyanide, nitric oxide, styrene, and formaldehyde have been considered (Alcaide *et al*., 2006). In this study, the focus is on the production of ethylene as it is one of the most important feedstock in the petrochemical industry. At present most worldwide ethylene is produced from cracking of hydrocarbon feedstocks. However, many researchers have been devoted to find alternative routes for the production of ethylene. Methane is considered a promising feedstock for production of ethylene and other chemicals because it is the major component of natural gas and a by-product from oil refining and chemical processing. Oxidative coupling of methane (OCM) becomes an interesting route for ethylene production as it requires only one reaction step unlike the conventional route via production of synthesis gas (carbon monoxide and hydrogen) which requires many steps. The concept of chemicals and electrical power co-generation in SOFC reactor can be applied to this OCM reaction. However, the major problem of the OCM is the poor reaction selectivity with carbon monoxide and carbon dioxide as major by-products.

In the past two decades, researchers have attempted to develop active and selective catalysts as well as to understand reaction mechanisms. In SOFC reactor, White *et al.* (1992) investigated anode for solid oxide fuel cells to generated C_2 hydrocarbon included $Sm_{0.5}Ce_{0.5}CuO_3$, $Tb_{0.8}Sm_{0.2}CuO_3$, $Gd_{0.9}Th_{0.1}CuO_3$, $Gd_{0.9}Na_{0.1}MnO_3$ and $Th_{0.8}Yb_{0.2}NiO_3$. The cell was CH_4, (anode) electrocatalyst/$ZrO_2(8\%Y_2O_3)/La_{0.9}Sr_{0.1}MnO_3$, O_2 (air). The experiment result shows almost anode catalyst exhibit high C_2 selectivity more than 70% but provides low conversion. Moreover, Tagawa *et al.* (1999) studied in a membrane reactor for OCM reaction for a tube type cell unit (LSM/YSZ/LaA1O) and showed low yield only 7-8%. Lapeña-Rey and Middleton (2003) investigated OCM to C_2 hydrocarbon in solid oxide electrolyte reactor. Three different catalyst–electrode systems based on silver and two trimetallic formulations of Mn modified alkali (Na and K) tungstates supported on silica were used. The $Mn/K_2WO_4/SiO_2$ catalyst shows the best C_2 selectivity but provide the C_2 yield only 4%. In part of $Mn/Na_2WO_4/SiO_2$ catalyst showed the best C_2 yield (7% yield). It was found that SOFC reactor showed low yield consequently the anode catalyst was necessary to develop appropriate anode catalyst. One of problem to apply $Mn/K_2WO_4/SiO_2$ and $Mn/Na_2WO_4/SiO_2$ into anode catalyst for SOFC is SiO_2 support ,which has low the electrical conductivity, moreover the thermal expansion coefficient of SiO_2 mismatch with YSZ electrolyte. In part of conventional reactor the catalyst for OCM has been study reasonable. One of the active and selective catalysts was $Mn\text{-}Na_2WO_4/SiO_2$. Ji *et al.* (2002, 2003) investigated in the performance of $Mn\text{-}Na_2WO_4/SiO_2$ catalysts for OCM in a fixed-bed reactor. $Mn\text{-}Na_2WO_4/SiO_2$ was reported to be a good catalyst for the OCM reaction. The reaction was found to perform best with the contents of Na, W, and Mn in the catalyst between 0.4–2.3%, 2.2–8.9%, and 0.5–3.0%, respectively. The active sites of the catalysts included Na-O-Mn and Na-O-W species. After that study, M–W–Mn/SiO_2 catalysts (M = Li, Na, K, Ba, Ca, Fe, Co, Ni, and Al) were tested. Na– and K–W–Mn/SiO_2 catalysts offered CH_4 conversion and C_2 hydrocarbon selectivity in the OCM reaction higher than the others (C_2 yield ~ 20 %). Zheng *et al.* (2010) doped S and P in Na–W–Mn–Zr/SiO_2 catalyst; the results showed that addition of 2% S and 0.4%P to the Na-W-Mn-Zr/SiO_2 catalyst helped the formation of active phases, such as α-cristobalite, Na_2WO_4, ZrO_2, and Na_2SO_4. In the experiment result showed that higher methane conversion and C_2 yield, conversion of methane and yield of C_2 hydrocarbons reached about 45% and 23.5%, respectively, were obtained from the six-components Na-W-Mn-Zr-S-P/SiO_2 catalyst. In addition, rare earth oxides (REOs) are also promising catalysts for OCM reaction. Lanthanum (La_2O_3), as the most basic one in REOs provided a C_{2+} yield around 9%. While the addition of 10 wt% of ceria to La-MgO promoted C_{2+} yield up to 20–22% (Dedov *et al.*, 2003). In addition, La_2O_3 showed the strong basicity catalyst, which many investigators reported the catalysts possessing higher surface basicity showed lower selectivity to CO_2 and increased C_2 Selectivity. Shahri and Pour (2010) studied the performance of Mn-Na_2WO_4/SiO_2 catalyst to promote Ce that increased its activity and stability. The maximum value for selectivity and yield of C_{2+} hydrocarbons was 75.3% and 21.1%, respectively. In addition, Y_2O_3 was an interesting support because it offered 29.9 % conversion and 26.2% selectivity (Au *et al.*, 1998). Although some catalysts in convectional process have possible to use in anode catalyst in SOFC reactor ,but the essential properties for anode catalyst such as high electrical conductivity, ionic conductivity and matching thermal expansion with electrolyte have been still explored. Thus, the support to use for develop anode catalyst has a suitable properties, selective with OCM reaction, high electrical and ionic conductivity and matching with electrolyte. Thus in this study we studied three supports for sodium tungsten manganese catalyst which these supports active and selective with OCM reaction. La_2O_3, Y_2O_3 and YSZ supports have the thermal expansion nearby YSZ electrolyte to avoid cracking during the cell operation and selective with OCM reaction; thus we interest to apply to anode support catalyst for SOFC and preliminary research investigated in fixed bed reactor. In addition, applied YSZ support to anode catalyst can reduce thickness of electrolyte impact to high oxygen permeate to anode side lead to increase reaction rate. Therefore, in this work, the OCM over Mn-Na_2WO_4 with La_2O_3, Y_2O_3 and YSZ supports to produce C_2 hydrocarbon in a fixed bed reactor and to produce simultaneously C_2 hydrocarbon and electrical power for SOFC typed reactor are investigated.

1.2 Objective

To develop anode catalysts and suitable supports for oxidative coupling of methane to co-generate C_2 hydrocarbons and electrical power in SOFC reactor.

1.3 Scope of work

1. Study the suitable supports: Y_2O_3 and La_2O_3 and YSZ are selected as potential supports for preparing 5wt% Na_2WO_4–2wt%Mn catalyst. The co-impregnation method is used in the catalyst preparation.
2. Promote 5wt% Na_2WO_4–2wt%Mn/Y_2O_3, YSZ or La_2O_3 catalysts with S, P, Ce.
3. Characterize the catalyst samples using X- ray diffraction (XRD), BET surface area, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS).
4. Compare the catalytic performance in term of CH_4 conversion, C_2 selectivity aC_2 yield and stability.

1.4 Research plan

To achieve the research objective, the research methodology is provided as follows:

1. Review literatures on related topics, i.e. catalysts ,OCM, SOFC
2. Prepare raw materials and chemical substances.
3. Prepare 5 wt% Na_2WO_4 -2 wt% Mn supported on La_2O_3, YSZ or Y_2O_3 supports by incipient wetness impregnation method.
4. Characterize the physical properties of the catalysts.
5. Study OCM reaction for C_2 hydrocarbons in a fixed bed reactor
6. Prepare anode electrode by incipient wetness impregnation and cathode by commercial.
7. Test the catalytic activity of the catalyst in OCM by SOFC.
8. Study effect of promoters (2wt% S, 2wt% P, 2wt% Ce) in 5 wt% Na_2WO_4 -2 wt% Mn supported on La_2O_3, Y_2O_3 and YSZ catalysts.
9. Study OCM reaction for C_2 hydrocarbons and electricity production in SOFC reactor.

10. Analyze the obtained data to find the conclusion of the research.
11. Write the thesis and prepare the thesis presentation.

CHAPTER II
THEORIES

2.1 Oxidative coupling of methane (OCM) process

Methane is the main component of natural gas. During the past two decades, there has been a global interest in the convert methane to high value chemical products, especially ethane and ethylene. OCM is a promising way to convert methane into ethylene and ethane. Ethylene is base chemical in the petrochemical industries such as polyethylene (PE), polyvinyl chloride (PVC), polyethylene terephthalate (PET) etc. Moreover it can be easy to liquefy C_2 products. However, makes its use in ethylene production difficult, figure 2.1 OCM is a reaction of two methyl radicals coupled into ethane after the abstraction of one hydrogen atom from the methane molecule. Ethylene is the secondary product occurred from dehydrogenation of ethane. This reaction is highly exothermic.

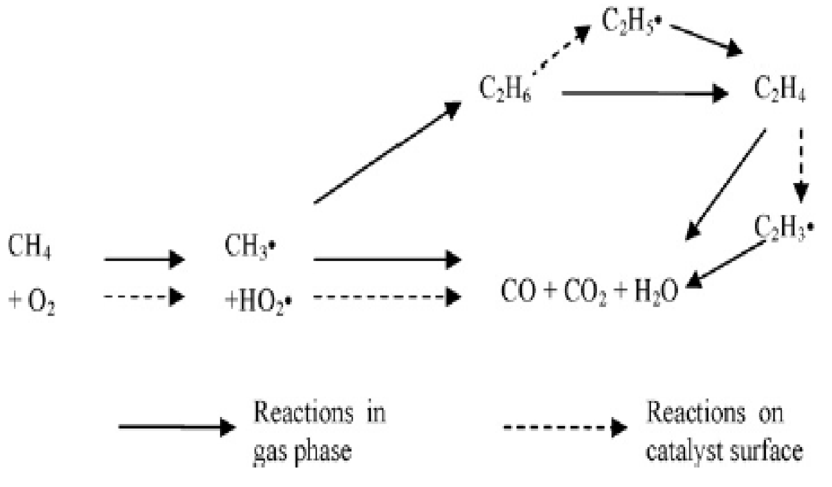


Figure 2.1 A general scheme of the reaction network in oxidative coupling of methane (Sun *et al*., 2008)

2.1.1 Definition

OCM is one of the promising potential routes for direct conversion of natural gas (methane) to higher hydrocarbons, especially ethylene, which are raw materials in the production of petrochemical compounds, polymers and liquid fuels. Ethylene is formed by coupling two methyl radicals after the abstraction of a hydrogen atom from each methane molecule; respectively however, the selectivity of ethylene is always reduced due to the formation of carbon oxides (CO and CO_2) from the combustion of methane and C_2 products with oxygen.

2.1.2 Mechanism of OCM reaction

The mechanism, it is generally accepted that methane molecule is first activated on catalyst surface to form methyl radicals then methyl radical couple into ethane in gas phase. Ethylene is a secondary product, formed from dehydrogenation of ethane. The carbon oxides (CO and CO_2) are usually considered to be formed due to oxidation of methane, C_2 hydrocarbon molecules and hydrocarbon radicals. The reactions are shown below (Gao *et al.*, 2010).

$$CH_4 + O^* \rightarrow CH\bullet_3 + HO^* \qquad (1)$$

$$HO^* + HO^* \rightarrow H_2O + O^* \qquad (2)$$

$$CH\bullet_3 + CH\bullet_3 \rightarrow C_2H_6 \qquad (3)$$

Overall reaction of the three steps above is shown below

$$2CH_4 + O^* \rightarrow C_2H_6 + H_2O \qquad (4)$$

Ethylene is a secondary product, formed from dehydrogenation

$$C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O \qquad (5)$$

$CH\bullet_3$ is methyl radical.

O^* is surface active oxygen species.

2.2 Conventional reactor

The most common reactor for OCM reaction is fixed bed reactor. Traditional OCM process used this reactor to studies because of it was easiest to design. The investigators have effort to found the catalytic performance, especially the selectivity to ethylene. Many catalysts showed the good performance such as rare earth oxides (REO), A few transition metal oxides that contain Group IA ions or transition metal-based catalyst. For OCM in fixed bed reactor the mode of operation focus on the co-feed mode (methane with oxygen). Figure 2.2 shows scheme of fixed bed reactor.

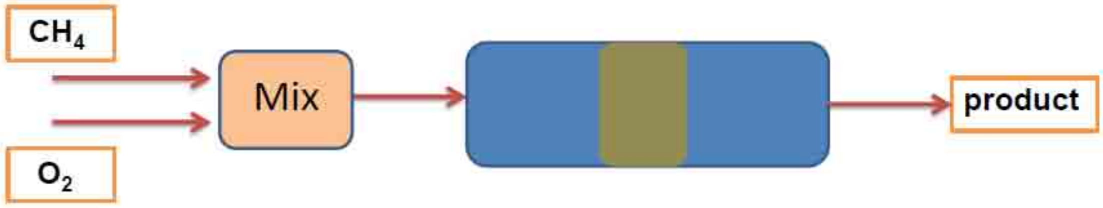


Figure 2.2 Scheme of fixed bed reactor (Chua *et al*., 2008).

2.3 Fuel cell principles

2.3.1 Basic principles

Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy with environment friendly. When fuel (hydrogen) has chemical interaction with oxygen in air will generate water and heat moreover energy (electron) in the call will transfer in form current. The main composition of fuel cell consist with anode electrode, cathode electrode and separate by electrolyte layer. Figure 2.3 exhibits single cell of fuel cell and figure 2.4 Electrode reactions and charge flow for an alkaline electrolyte fuel cell. Hydrogen fuel is fed into the anode of the fuel cell. Oxygen or air enters the fuel cell through the cathode. Under influence of a catalyst, the hydrogen atom splits into a proton and an electron, which take different paths to the cathode. The proton passes through the electrolyte. The electrons create a separate current that can be utilized before they return to the cathode, to be reunited with the hydrogen and oxygen in a molecule of water.

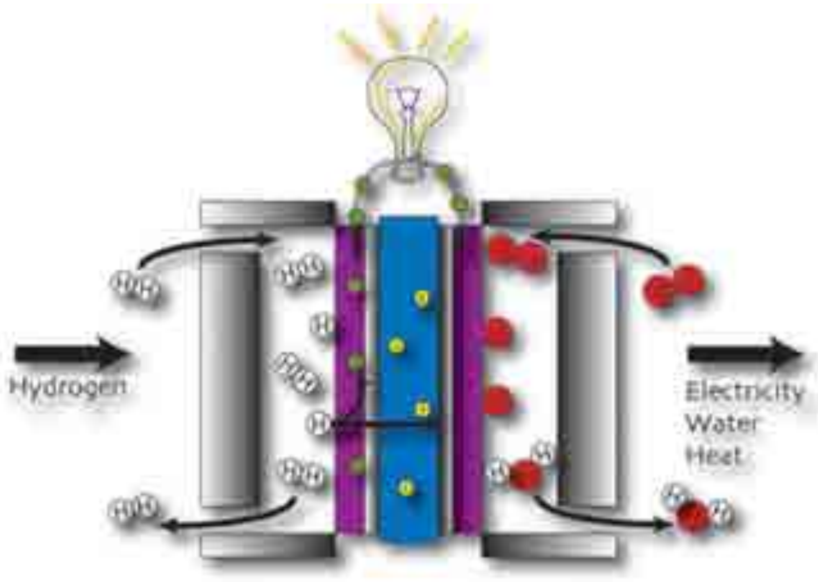


Figure 2.3 Single cell of fuel cell
http://ssrl.slac.stanford.edu/nilssongroup/nilsson_projects.html (2011).

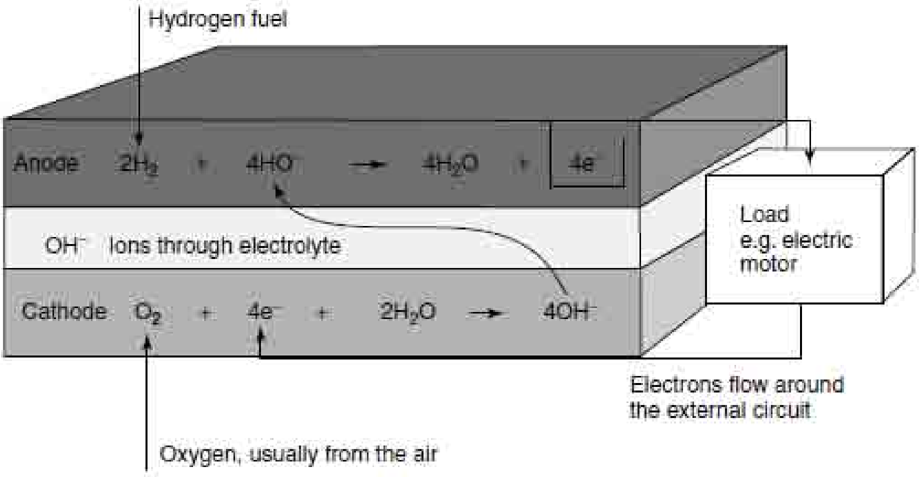


Figure 2.4 Electrode reactions and charge flow for an alkaline electrolyte fuel cell. Electrons flow from anode to cathode, but conventional positive current flows from cathode to anode (Larminie, 2003).

2.3.2 Different type of fuel cell

Fuel cell can be classified into several groups depend on fuel, working temperature, their electrolyte material (http://www.fuel cell.org/basics/types.html#sofc (2011)). The example Alkaline Fuel Cells (AFCs), Proton Exchange Membrane Fuel Cells (PEMFCs), Direct Methanol Fuel Cells (DMFCs), Phosphoric Acid Fuel Cells (PAFCs), Molten Carbonate Fuel Cells (MCFCs), Solid Oxide Fuel Cells (SOFCs), as shown in table 2.1.

Table 2.1 The different type of fuel cells (http://www.fuel cell.org/basics/types.html#sofc (2011)).

	Low temperature fuel cell			**High temperature fuel cell**		
	Direct Methanol Fuel Cells (DMFC)	Proton Exchange Membrane Fuel Cells (PEMFC)	Alkaline Fuel Cells (AFC)	Phosphoric Acid Fuel Cells (PAFC)	Molten Carbonate Fuel Cells (MCFC)	Solid Oxide Fuel Cells (SOFC)
Electrolyte	Proton-conducting membrane	Proton-conducting membrane	Caustic potash solution	Concentrated phosphoric acid	Molten carbonate	Ceramic
Temperature range	< 373 K	< 373 K	< 373 K	~473 K	~923 K	1073-1273 K
Fuel	Methanol	Hydrogen	Hydrogen	Hydrogen	Natural gas, Coal	Natural gas, Coal
Power rang	Watts/kilowatts	Watts/kilowatts	Watts/kilowatts	Kilowatts	Kilowatts/megawatts	Kilowatts/mega watts
Application area (Example)	Vehicles, small appliances	Vehicles, small generators, and power generation	Space	Block-type heat and power stations	Power plants, combine heat and power	Power plants, combine heat and power

2.4 Solid oxide fuel cell reactor (SOFC)

SOFC differs in many respects from other fuel cell technologies. First, they are composed of all solid state materials. SOFC use a solid, non-porous ceramic compound as the electrolyte such as YSZ electrolyte. Second, the cells can operate at temperatures range 1073-1,273 K, which this temperature is significantly than others. Third, the cells can be configured either as tubular or as flat plates. SOFC are expected in applications electro co-generation by converting fuel to chemical production with electric power generation, which is different from fuel cell mode just release water and electricity. Figure 2.5 shows principle of co-generation. Methane is one choice of fuel in SOFC because methane is the low value and glut, which able applied to SOFC reactor. The objectives to used methane for provide ethylene production with electric power (http://www.fuelcelltoday.com (2011)).

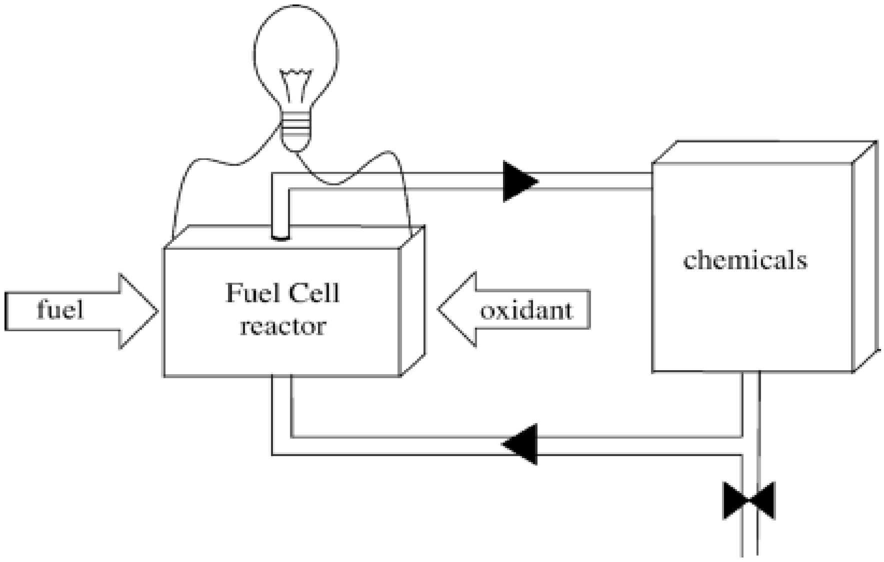


Figure 2.5 Principles of operation of a fuel cell reactor generating chemicals and energy (Alcaide *et al.*, 2006).

2.4.1 Principle of SOFC reactor

SOFC reactor is electrochemical cell similar battery usually used as a power generator but difference between SOFC and battery is lifetime. The cell is making with two porous electrodes, which sandwich is an electrolyte. In SOFC reactor reactant (methane, oxygen) always feed to reactor lead to long term of production. The SOFC is the expansive technology because of it operated at high and wide range of temperature between 1073-1,273 K. Briefly, At the high operating temperatures, oxygen ions are formed from air into the cathode the reduction of O_2 to O^{2-} anions occur, the anions transfer through an YSZ electrolyte and the oxidation of the methane fuel with O^{2-} anions at the anode. Electrons generated at the anode move out through an external circuit, creating electricity. Effectively, the chemical energy produced when the methane fuel is oxidized is given up to the electrons produced at the anode.

2.4.2 Materials selection and processing

Each material must have the electrical properties required to perform its function in the cell. There must be enough chemical and structural stability to endure fabrication and operation at high temperatures. The fuel cell needs to run at high temperatures in order to achieve sufficiently high current densities and power output; operation at up to 1273 K is possible using the most common electrolyte material, yttria-stabilized zirconia (YSZ). Reactivity and interdiffusion between the components must be as low as possible. The thermal expansion coefficients of the components must be as close to one another as possible in order to minimize thermal stresses which could lead to cracking and mechanical failure. Table 2.2 shows electrical conductivity and thermal expansion of support.

Table 2.2 electrical conductivity and thermal expansion of different supports

Support	Electrical conductivity (S/cm)	Thermal expansion coefficient ($x10^6/^oC$)	ionic conductivity (S/cm)
SiO_2	-	~10.3	-
La_2O_3	-	~10.5 at 900°C	-
Y_2O_3	-	~8.4 at 900°C	-
8%YSZ	$\sim 8.11\times10^{-4}$ at 600°C	~10.5 at 25-1000°C	0.16 at 1000°C

2.4.2.1 Cathode

The cathode must be porous in order to allow oxygen molecules to reach the electrode/electrolyte interface. Today the most commonly used cathode material is lanthanum manganite ($LaMnO_3$), a p-type perovskite. Typically, it is doped with rare earth elements (eg. Sr, Ce, Pr) to enhance its conductivity. Most often it is doped with strontium and referred to as LSM ($La_{1-x}Sr_xMnO_3$) because it displays good electrical conductivity, catalytic activity and high thermal and chemical stability between 1073 K and 1273 K.

The properties for cathode;

•Adequate electronic and ionic conductivity.

•High catalytic activity for oxygen reduction.

•Chemical stability and relatively low interactions with the electrolyte.

•High compatibility with other cell components.

2.4.2.2 Electrolyte

Once the molecular oxygen has been converted to oxygen ions it must migrate through the electrolyte to the fuel side of the cell. In order for such migration to occur, the electrolyte must possess a high ionic conductivity and no electrical conductivity. It must be fully dense to prevent short circuiting of reacting gases through it and it should also be as thin as possible to minimize resistive losses in the cell. As with the other materials, it must be chemically, thermally, and structurally stable across a wide temperature range. YSZ has occurred as the most suitable electrolyte material. Yttria serves the dual purpose of stabilizing zirconia into the cubic structure at high temperatures and also providing oxygen vacancies.

2.4.2.3 Anode

The anode (the fuel electrode) must meet most of the identical requirements as the cathode for electrical conductivity, thermal expansion compatibility and porosity, and must function in a reducing atmosphere. The reducing conditions combined with electrical conductivity requirements make metals attractive candidate materials. For oxidative coupling of methane the anode catalyst has been widely investigated such as; (i) Group IA or IIA ions supported on basic oxides for example, Li/MgO, Ba/MgO and Sr/La_2O_3, (ii) A few transition metal oxides that contain Group IA ions or transition metal-based catalyst for example Mn/Na_2WO_4/SiO_2.

2.4.3 Advantages and disadvantages of SOFC reactor

Solid oxide fuel cell reactor compared with conventional reactor.

2.4.3.1 Advantages

- Provide high C_2 selectivity more than convectional reactor
- Generate co-generation ethylene and electrical power, which possible future technology developments
- Decrease hot spot inside reactor
- Provide heat energy

2.4.3.2 Disadvantages

- Solid oxide fuel cells use expensive materials because operate at high temperature
- Catalyst deactivation

CHAPTER III
LITERATURE REVIEW

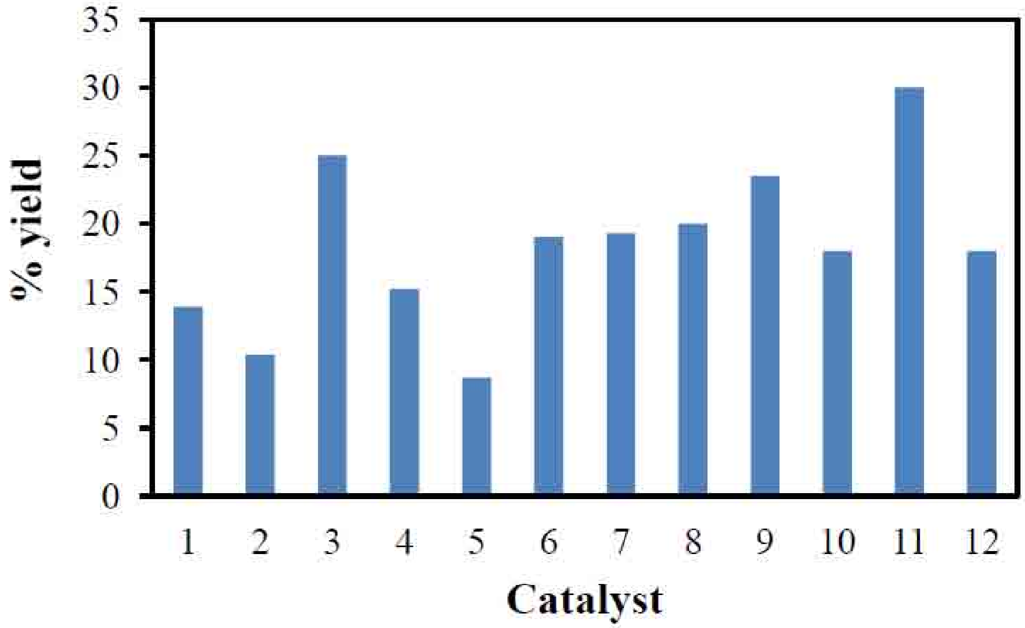
3.1 Oxidative coupling of methane (OCM)

Worldwide efforts have been invested to develop efficient catalysts such as oxygen capacity on surface catalyst, catalyst activity, and catalyst stability for this reaction system. Main interest of the research on the reaction was to look for a more active catalyst to increase C_2 hydrocarbons production. Many investigators caught the catalytic performance can be significantly improved by halides. Long *et al*., (1995) investigated alkaline-earth-metal fluoride by promoting effect of F- on Sr/La oxide catalysts for the OCM in packed bed reactor the maximum C_2 yields of 18-20% were achieved over the LaF_3/SrO and SrF_2/La_2O_3 catalysts at 923-1023 K. In some case halides, especially chlorides and bromides have been added to the oxides to improve the catalytic activity and selectivity. Au *et al*., (1998) proposed BaF_2, $BaCl_2$, or $BaBr_2$ can significantly improve the catalytic performance of Gd_2O_3. 30 mol% $BaCl_2/Gd_2O_3$ provided the best C_2 yield of 21.1% with a CH_4 conversion of 36.6% and C_2 selectivity of 57.6%. From the experiment result halides can improve performance in BaX_2/Gd_2O_3. Moreover, alkaline was interesting. Fakhroueian *et al*., (2008) studied the $XBaSrTiO_3$ (X = Li, Na, Mg) perovskite in OCM it was found the NaBST showed the maximum catalytic effect provided 42% methane conversion and 51% ethylene selectivity at the temperature of 1073 K. Au *et al*., (1997) reported performance of LaOCl was promoted by $BaCO_3$ in OCM reaction. When the mol%$BaCO_3$ was added, there was little change in CH_4 conversion, but C_2 selectivity was increased from 37% to 66%. Hong and Yoon, (2001) studied on $CaCl_2$-promoted calcium chlorophosphate catalysts for OCM at 1023 K, the highest C_2 yield of around 22% was obtained with the C_2 selectivity of 56–59%. Although, there are many researches about this reaction but remained not successful. Thus, it was attempted to a new approach for improve performance of reaction such as membrane brought into use or applied in SOFC. Various types of reactors such as fixed bed reactor, membrane reactor and SOFC reactor have been reported. Most reported studies on OCM were carried out in fixed-bed reactors in co-feed operation mode because it was easiest to design but this reactor presented the low C_2 yield. SOFC systems are one alternative, which could convert the energy of combustion directly into electric power with high efficiency. These systems also have another application as a membrane reactor for selective oxidation. It is also possible to convert the chemical energy directly into electrical power during the selective oxidation. Several studies seek to develop OCM reaction from these technologies.

3.2 Reactor for OCM process

3.2.1 Fixed bed reactor

In a fixed-bed reactor the catalysts are held in place do not move with a fixed reference frame and operating by co-feed methane and oxygen through the catalyst the chemical reaction takes place on the surface of the catalyst. Generally, the reaction occurred at temperature between 873-1273 K. Most researches about OCM process emphasized development of the catalyst performance for increase simultaneously the methane conversion and C_2 selectivity. Many catalysts have been found to be effective in OCM. Rare earth oxide catalysts (La_2O_3, CeO_2, Sm_2O_3) provided a high performance in this reaction. Rane *et al.*, (2008) reported alkali metal promoted CaO in OCM reaction the experiment result exhibited increasing in the surface basicity and the C_{2+} selectivity and yield of the catalysts in the OCM process. Murata *et al.*, (1998) investigates Li-doped sulfated-zirconia catalysts it was found effective for oxidative coupling of methane. In addition, alkaline-earth-metal fluoride such as SrF_2-La_2O_3, SrO-LaF_3, BaF_2-CeO_2 showed good catalytic performance in OCM. Chao *et al.*, (1995) studied on BaF_2/LaOF in fixed-bed quartz reactor at atmospheric pressure. Catalyst had CH_4 conversion of 33.08% and a C_2 selectivity of 62.47% was achieved at CH_4:O_2 = 3:1. The best OCM reaction results were obtained over BaF_2/LaOF with BaF_2 content in 10 to 18 mol% another interest option that are a few transition metal oxides that contain Group IA ions or transition metal-based catalyst for example Mn/Na_2WO_4/SiO_2. Ji *et al.*, (2002, 2003) have the great attention in the Na_2WO_4-Mn/SiO_2 catalyst system because of its excellent catalytic performance. They are proposed the relationship among structure and the performance of Na-W-Mn/SiO_2 catalysts. It was found that Na-O-Mn and Na-O-W species is an active site and suitable percent contain of Na=0.4–2.3%, W=2.2–8.9%, and Mn=0.5–3.0%. Recently, Liu *et al*., (2008) scale up and stability test for oxidative coupling of methane over Na_2WO_4-Mn/SiO_2 catalyst the highest C_2 (ethylene and ethane) yield of 25% was achieved. When increased temperature from 913 to 1073 K the C_2 yield decreased and the CO_x certainly increased. In addition, CH_4/O_2 ratio was the significant for OCM. The reaction mechanism of OCM was very complicated and there was considerable disagreement concerning the nature of the active centers in the catalyst. Several studies proposed a surface W species containing W=O and three W–O–Si bonds as the OCM active site. The same catalyst was studied by Wang *et al*., (1995) although they suggested that Na–O–Mn species were the most probable active sites, in which Mn was an active component, Na was required for high selectivity, and W ions were required to stabilize the catalyst. Zhang *et al*., (2007) proposed on CeO_2-W-Mn/SiO_2 catalyst for OCM reaction at 1073 K in fixed bed reactor. Modifying of Na_2WO_4-Mn/SiO_2 catalysts with CeO_2 provided the reaction stable for 500 hr and obtained 22 % of C_2H_4 yields. Moreover, the difference of dilution gas was significant to performance of reaction. Shahri and Pour, (2010) studied addition of Ce into Mn/Na_2WO_4/SiO_2 catalyst for OCM. The result showed excellent stability during a long-term reaction. Moreover, the addition of Ce promoter increased its activity. It also enhanced the dispersion of Na_2WO_4. The maximum value for selectivity and yield of C_2 hydrocarbons was 75.3% and 21.1%, respectively. Zheng *et al*., (2010) reported catalytic performance of S and P promoted Na-W-Mn-Zr/SiO_2 catalyst for OCM at 1023 °K. The XRD result showed addition of S and P to the Na-W-Mn-Zr/SiO_2 catalyst helps the formation of active phases, such as α-cristobalite, Na_2WO_4, ZrO_2, and Na_2SO_4 and increase the surface-active oxygen species. Improvements of catalyst by add S and P lead to increase the catalytic performance of these catalysts, and the maximum C_2 yield was 16%. From comparison the Na-W-Mn/SiO_2 showed better performance than overall and it was interesting. Both Na-O-Mn and Na-O-W acted as the active centers of the catalysts for OCM. Although, Na-W-Mn/SiO_2 exhibited good performance in fixed bed reactor but the problem in fixed bed reactor still appear: (1) the oxygen species is an one of main problem to study because in co-feed the partial oxidation to CO and H_2 can be generated lead to low C_2 selectivity; (2) low selectivity at higher conversion on the other hand good selectivity and conversion extremely difficult. Traditional OCM process used this reactor to studies because it was easiest to design and base on catalytic activity of catalyst. Figure 3.1 shows the performance of catalyst in literature review.



1. La_2O_3	(Dedov *et al*., 2003)
2. Y_2O_3	(Dedov *et al*., 2003)
3. Na_2WO_4-Mn/SiO_2	(Wang *et al*., 2008)
4. Na-CaO	(Rane *et al*., 2008)
5. Li-CaO	(Rane *et al*., 2008)
6. Li/SZ	(Murata *et al*.,1998)
7. BaF_2/LaOF	(Chao *et al*., 1995)
8. CeO_2-W-Mn/SiO_2	(Li *et al*., 2007)
9. Na-W-Mn-Zr-S-P/SiO_2	(Chen *et al*., 2010)
10. BaF_2/Y_2O_3	(Au *et al*., 1998)
11. Na-W-Mn/SiO_2	(Bhatia *et al*., 2008)
12. Ce-Mn/Na_2WO_4/SiO_2	(Shahri and Pour, 2010)

Figure 3.1 Performance of catalyst in literature review

3.2.2 SOFC for chemical and electrical cogeneration

The past two decade, new application for fuel cell reactors has been developed for more efficiency many researches proposed chemicals and energy co-generation. This application converts of fuel (i.e. H_2, CO, CH_4) to desired chemicals as chemicals as the main product with energy generation is the by-product. SOFC reactor distinguishes it from the conventional reactor. Moreover, chemicals and energy co-generation provides an advantage over a conventional fuel cell which just produces electrical and pure water as a by-product. This system includes of fuel cell reactor and external load. The fuel and oxidant are supplied separately to electrochemical cell (anode and cathode electrode) at fuel cell reactor, after that useful chemical and electricity are occurred. Electricity is supplied to an external load and useful chemical produced is collected. Alcaide *et al*., (2006) reported cogeneration technology:

- To simplify a complicated chemical industrial process in a one-step production.
- To develop alternative process when the demand of a final product decays.
- For environmental reason.

Although, the cogenerating energy and chemical substances are very similar to those relate in conventional catalytic but the cogeneration method provide advantage over the conventional catalytic as follows:

- Cogeneration of electricity and chemical products is efficient.
- The use of the reactants is efficient and they can be re-circulated.
- Corrosion of reactors and pipelines is smaller.
- Production in the electrochemical reactor is mainly controlled by the external load.
- The selectivity of the process can be controlled by changing the external load (which can vary the electrode potential) or the electrode catalyst.

The SOFC co-generation process has become one of the new applications for fuel cell system. Usually, the fuel which is supplied for SOFC is hydrogen (H_2) but pure hydrogen is expensive and gives only water as by-product. The most interesting fuel for SOFC is methane (CH_4) because almost of methane are used as fuel for heat and electricity generation. OCM is the promising way to increase value of methane to C_2 hydrocarbon (ethylene, ethane) that is a useful chemical in petrochemical industrial such as polyethylene (PE), polyvinyl chloride (PVC), polyethylene terephthalate (PET) etc. Therefore, SOFC for chemical and electricity cogeneration using methane as a fuel is very attractive. The OCM reactions at anode, cathode, and overall reaction in SOFC electro catalytic reactor are presented in the equation (6), (7), and (8) respectively. Figure 3.2 shows the scheme of OCM reaction for SOFC reactor (Tagawa *et al*., 1999).

$$2CH_4 + 2O^{2-} \rightarrow 2C_2H_4 + H_2O + 4e \qquad (6)$$

$$O_2 + 4e \rightarrow 2O^{2-} \qquad (7)$$

$$2CH_4+O_2 \rightarrow C_2H_4+2H_2O \qquad (8)$$

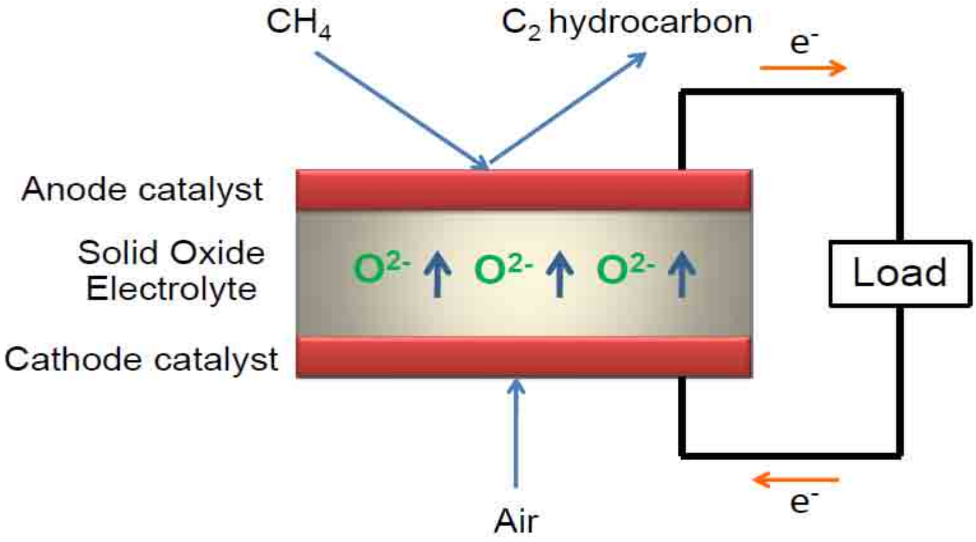


Figure 3.2 Scheme of the OCM reaction for SOFC reactor (Tagawa *et al*., 1999).

Stoukides *et al*., (1996) presented SOFC co-generation plant that uses methane as fuel. The 100 MW electrical power plant produces simultaneously 0.21 x 10^9 lb of ethylene. And then Hugill *et al*., (2005) reported co-generation of ethylene and electricity through OCM reaction in 2003 compared with a scheme in which ethylene and electricity are generated separately by conventional processes. It found that the co-generation reduced significantly CO_2 emissions. In addition, the catalyst such as $Pt/Sm_2O_3/La_{0.89}Sr_{0.10}MnO_3$, KF, $BaCO_3$, $NaCl/MnO_2$, Sm_2O_3, $La_{1.8}Al_{0.2}O_3$, $Sm_{0.5}Ce_{0.5}CuO_3$, $Tb_{0.8}Sm_{0.2}CuO_3$, $Gd_{0.9}Th_{0.1}CuO_3$, $Gd_{0.9}Na_{0.1}MnO_3$, and

$Th_{0.8}Yb_{0.2}NiO_3$ has been investigated (White *et al.*, 1992; Lapeña-Rey, N., and P.H. Middleton, 2003; Pujare and Sammells, 1988; Otsuka *et al.*, 1990; Tagawa *et al.*, 1998).

3.2.3 Material properties for OCM in SOFC reactor

Presently, a substantial research was highly relevant to the development of materials suitable for use for SOFC. However, there are the required properties of the oxides for using as SOFC electrolyte materials such as durable high temperature, high oxide ion conductivity, high stability and low cost.

3.2.3.1 Solid Electrolyte

Electrolyte is a main component of SOFC. The electrolyte is a dense layer of ceramic that conducts oxygen ions. Electrolyte for SOFC in commercial is 8% yttria - stabilized zirconia (YSZ). It is outstanding mechanical stability. It can operate at high temperatures (about 1273 K). Bismuth oxide, doped ceria, and doped lanthanum are three materials known to have a higher conductivity in air (Ralph *et al.*, 2001). Tu *et al.*, (2011) synthesized scandia ceria stabilized zirconia use as the electrolyte of anode-supported solid oxide fuel cell (SOFC). It's much higher ionic conductivity than that of YSZ. Moreover, Mizutani *et al.*, (1994) investigated the electrical conductivity and mechanical properties of Sc_2O_3-ZrO_2 (ScSZ) and compare with YSZ electrolyte. The result showed 8 mol% Sc_2O_3-ZrO_2 provide higher electrical conductivity than 8 mol% YSZ at 1273 °C. Bozza *et al.*, (2009) proposed $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ electrolyte for intermediate temperature solid oxide fuel cells. Anode supports were made of $La_{0.4}Ce_{0.6}O_{2-x}$ (LDC) and a $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSFC) is cathode using H2 as fuel and air as oxidant the result showing a maximum power density of 150 mW/cm^2 at 973 K. Ahn *et al.*, (2010) investigated $Sm_{0.075}Nd_{0.075}Ce_{0.85}O_{2-\delta}$ electrolyte under fuel cell operating conditions. The results confirm that $Sm_{0.075}Nd_{0.075}Ce_{0.85}O_{2-\delta}$ is a promising alternative electrolyte for intermediate temperature solid oxide fuel cells. Baker and Fuentes, (2009) proposed $Gd_{0.1}Ce_{0.9}O_{1.95}$ electrolyte in SOFC and provided the highest total ionic conductivity (1.91×10−2 S cm^{-1} at 873 K). Presently, the most studied in SOFC focus to increase the cell performance at decreased operating temperatures (773-1073 K) for some applications the reaction does not require high temperatures and another importance thing is chemical compatibility among electrodes. Although, several researches aim at a new electrolyte for solve low ionic conductivity problem but the YSZ continues to be popular in commercial because of low electronic conductivity, and stability under reducing and oxidizing atmosphere. In this OCM reaction, YSZ electrolyte is still interested because of high thermal stability at high temperature (1073-1273 K). Table 3.1 exhibits the advantages and disadvantages of possible electrolyte candidates for SOFC (Ivers-Tiffée *et al.*, 2001).

Table 3.1 Advantages and disadvantages of possible electrolyte candidates for SOFC (Ivers-Tiffée *et al.*, 2001).

Electrolyte	Advantages	Disadvantage
YSZ **(Yttria stabilized zirconia)**	•Excellent stability in oxidizing and reducing environment •Excellent mechanical stability •High quality raw materials Available	•Low ionic conductivity •Incompatible with some cathode materials
GCO **(Gd doped CeO_2)**	•Good compatibility with cathode materials. •Mixed electronic-ionic conductor at low pO_2 (application in anode cermets)	•Mechanical stability •Electronic conduction at low pO_2 → low open circuit voltage.
LSGM **(Lanthanum gallate (LSGM: $(La,Sr)(Ga,Mg)O_3$))**	•Good compatibility with cathode materials.	•Ga-evaporation at low pO_2 •Incompatible with NiO •Mechanical stability
ScSZ **(Sc-doped ZrO_2)**	•Excellent stability in oxidizing and reducing environment.	•Availability and price of scandium

3.2.3.2 Anode

The anode layer must be stability for high temperature and chemical reaction as well as high catalytic activity. Anode is important for catalytic properties to oxidation. Generally, the anode is active catalyst to change CH_4 to C_2 hydrocarbon. Keller and Bhasin, (1982) proposed the most active catalysts for C_2 formation were the oxides of Sn, Pb, Sb, Bi, Tl, Cd, and Mn, while Li, Mg, Zn, Ti, Zr, MO, Fe, Cr, W, Cu, Ag, Pt, Ce, V, B, and Al showed little or no activity. After that the most studies interest in fixed bed reactor there are a few research to propose anode in SOFC. Pujare and Sammells, (1988) studied OCM with SOFC reactor. Using the SOFC cell was CH_4, Pt/Sm_2O_3/$La_{0.89}Sr_{0.10}MnO_3$/YSZ/ $La_{0.89}Sr_{0.10}MnO_3$/Pt, O_2 (air). High C_2 hydrocarbon selectivity (90%) was observed, although the methane conversion was relatively low. Thereafter Otsuka *et al.*, (1990) investigated OCM reaction in SOFC reactor over several catalysts (i.e. KF, $BaCO_3$, NaCl/MnO_2, Sm_2O_3) deposited on Au-electrode. The result showed that $BaCO_3$ on Au was the most active and selective catalyst. Gold continues to be interesting in anode electrode Tagawa *et al.*, (1998) proposed the anode catalyst was $La_{1.8}Al_{0.2}O_3$ in SOFC system (air/$La_{0.85}Sr_{0.15}MnO_3$/YSZ/$La_{1.8}Al_{0.2}O_3$/methane). The experiment result showed C_2 composition and electrical were obtain. In addition, compared with Ni-Zr cermet and Ag anode. The Ni-Zr anode exhibited high current value but the conversion trends to the complete oxidation. Ag anode was not active for oxidative coupling of methane and low current value. Moreover, White *et al.*, (1992) investigated perovskite anode electrocatalysts in SOFC system (anode) electrocatalyst/YSZ/$La_{0.9}Sr_{0.1}MnO_3$,O_2 (air), which showed to possess activity towards promoting the electrochemical OCM to C_2 hydrocarbons included $Sm_{0.5}Ce_{0.5}CuO_3$, $Tb_{0.8}Sm_{0.2}CuO_3$, $Gd_{0.9}Th_{0.1}CuO_3$, $Gd_{0.9}Na_{0.}1MnO_3$ and $Th_{0.8}Yb_{0.2}NiO_3$. In 2003 Lapeña-Rey and Middleton, (2003) investigated the trimetallic catalyst formulations such as Mn/Na_2WO_4/SiO_2 and Mn/K_2WO_4/SiO_2WO_4 in electrochemical reactor for OCM reaction. Kiatkittipong *et al.*, (2004) proposed SOFC reactor using $La_{0.85}Sr_{0.15}MnO_3$/8mol%Y_2O_3-ZrO_2/$La_{1.8}Al_{0.2}O_3$ for C_2 hydrocarbon production. The influence of increasing methane flow rate affected to the decreasing methane conversion whiles C_2 selectivity slightly increases. In addition, Carrillo *et al.*, (2001) presented mist pyrolysis method to preparation of Ni/ZrO_2 anode catalyst for SOFC reactor and compared with paste method. Ni/ZrO_2 from mist pyrolysis method powders was spherical, well dispersed and homogeneous. The paste method was actived for the oxidation of methane to CO and CO_2. That the mist method active for OCM reaction than paste method. Presently, investigators try to find the appropriate properties of anode electrode in OCM reaction. The good properties of anode are (1) high oxygen ion capacity on surface area; (2) high physical and chemical stability; (3) high electrical conductivity and activity. Table 3.2 show the performance of catalyst in SOFC reactor to produce C_2 hydrocarbon

Table 3.2 Performance of catalyst in SOFC reactor to produce C_2 hydrocarbon

Electrolyte	**Working electrode (Catalyst)**	**Temperature (K)**	**C_2 Yields**	**References**
YSZ tube	Bi_2O_3-Au	1073	<2.0	K. Otsuka *et al.* (1990)
YSZ tube	BiO_3-Au	1073	<2.0	K. Otsuka *et al.* (1990)
YSZ	Au-$SrCeO_3$	973-1123	3.1	A.G. Anderson *et al.* (1994)
YSZ plate	$La_{1.8}Al_{0.2}O_3$	973	3.8	T. Tagawa *et al.* (1998)
YSZ tube	LaSrMnO/LaAlO	1273	4.0	T. Tagawa *et al.* (1999)
YSZ plate	Ni/ZrO_2	1223	4.5	A.S. Carrillo *et al.* (2003)
YSZ tube	Mn/ Na_2WO_4/SiO_2-Ag	773-1273	4.0	N. L apeña-Rey *et al.* (2003)
YSZ tube	$Mn/K_2WO_4/SiO_2$-Ag	773-1273	4.0	N. L apeña-Rey *et al.* (2003)
YSZ tube	$La_{1.8}Al_{0.2}O_3$	973-1273	4.3	W. Kiatkittipong *et al.* (2005)

Anode side reaction:

$$2CH_4 + 2O^{2-} \rightarrow 2C_2H_4 + H_2O + 4e^- \qquad (9)$$

The Mn/Na_2WO_4 catalyst is attractive from many investigators to use in fixed bed reactor for OCM reaction. Moreover, still studied in electrochemical reactor used $Mn/Na_2WO_4/SiO_2$ and $Mn/K_2WO_4/SiO_2$ catalyst and YSZ tube electrode but poor electrical conductivity of the as-received catalyst. YSZ was attracted to use for supported in Mn/Na_2WO_4 for solve ionic and electrical conductivity problem, in addition, compatibility is the important factor.

3.2.3.3 Cathode

Perovskite materials have been widely used as cathode materials in SOFCs. Figure 3.3 shows unit cell of the ABO_3 perovskite structure. The A-site cation is a mixture of rare and alkaline earths (such as La and Sr, Ca or Ba), while the B-site cation is a reducible transition metal such as Mn, Fe, Co, or Ni. The octahedral symmetry around the transition metal often promotes a metallic or semiconducting band structure at high temperatures leading to high electronic conduction. The most common cathode is Sr doped La-manganese (LSM) which using at 1073–1273 K. The strontium can enhance expansion coefficient and electronic conductivity. Properties of cathode: (1) a high rate of oxygen diffusion through the material; (2) a high electronic conductivity; (3) a high oxygen-ion conductivity; (4) a high catalytic activity and stability for the reduction of oxygen; (5) a suitable thermal-expansion coefficient to assure chemical and mechanical compatibility between electrode materials and the electrolyte; and (6) low cost (Sun *et al.*, 2010). Although, LSM is the usually cathode but other oxides, such as gadolinia-doped ceria (GDC), scandia-stabilized zirconia, samaria-doped ceria (SDC), and lanthanum strontium gallium magnesium oxide (LSGM), are also under consideration because they have higher ionic conductivities at reduced operating temperatures.

Cathode side reaction:

$$O_2 + 4e^- \rightarrow 2O^{2-} \qquad (10)$$

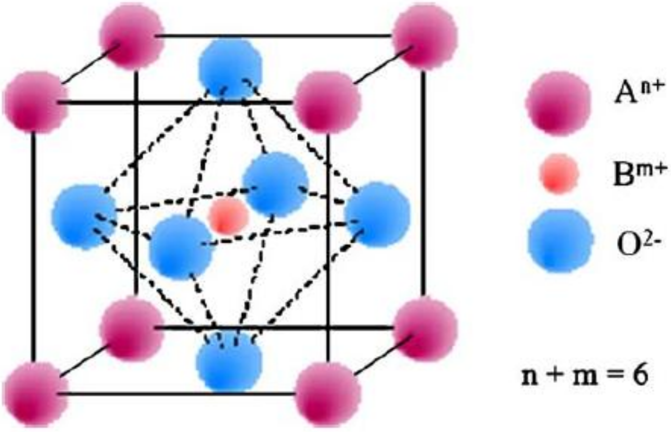


Figure 3.3 Unit cell of the ABO_3 perovskite structure (Sun *et al*., 2010).

SOFC is a complex process. The problem in SOFC was low oxygen permeates flux through membrane, methyl radical coupling to deep oxidation to form COx, complete oxidation to CO_2 and H_2O or partial oxidation to H_2 and CO. Although, the electrolyte provides high oxygen permeable was not guarantee high product depends on several factors such as rate of methane consumption. So if we can solve these problems which lead to development of Co-generation (electrical energy and chemical product). In addition, high efficiency promises reduced CO_2 emissions and there are virtually no NO_x emissions. This technology can apply to vehicle, power generation, etc.

3.2.4 Effect of applied voltage for SOFC reactor

Tagawa *et al*., (1999) proposed effect of applied electric potential during the reaction. The electric potential was applied between the cathode and anode, which experiment result showed when applied potential, the total yield was increased. This showed that enhance of permeated oxygen. Next time in 2003 studied effect of applied potential on $La_{0.85}Sr_{0.15}MnO_3$/YSZ/$La_{1.8}Al_{0.2}O_3$ SOFC reactor. When increased the applied potential lead to increase the amount of adsorbed oxygen at the surface active site. It was found that the rate of C_2 formation was not affected by an applied potential. The positive potential increased the rate of CO formation, while the negative potential suppressed the rates of CO and CO_2 formation (Tagawa et al., 2003). Lapeña-Rey and Middleton, (2003) reported the electrochemically-supplied oxygen gave higher overall C_2 selectivities than the co-fed method under low current conditions on $Mn/Na_2WO_4/SiO_2$ and $Mn/K_2WO_4/SiO_2WO_4$ in electrochemical reactor for OCM reaction. In addition, Andersen *et al.*, (1994) studied in an electrochemical membrane cell of the type: CH_4, (O_2), $SrFeO_{3-\delta}$, Au/8%Y_2O_3: ZrO_2/Ag, air. And studied influence by the potentials in the electrochemical reactor. The data showed an increasing resistance with applied potential, indicating a chemical limitation.

3.2.5 Side reaction for OCM in SOFC reactor

Every reaction must be occur side reaction which led to low production yield from the desire reaction including OCM reaction it has side reactions such as partial oxidation to H_2 and CO, complete oxidation to CO_2 and H_2O.

3.2.5.1 Partial oxidation of methane

Partial oxidation of methane is route for synthesis gas production, a mixture of CO and H_2. The reaction similar OCM reaction but will selective to H_2 and CO more than C_2. In SOFC the partial oxidation of methane was investigate similar OCM, interest in chemical product and electrical energy. Generally, Pt, Rh, Ru, Pd or Ni metal are being widely considered as the anode catalyst. Vollmar *et al.*, (2000) proposed the concepts for the coproduction of electricity and synthesis gas with solid oxide fuel cells. In same experiment Ishihara *et al.*, (1999) investigate the partial oxidation of methane in SOFC reactor. The experiment result showed $LaGaO_3$ provided highly effective for increasing oxide ion conductivity Fe or Co doped $LaGaO_3$ as electrolytes for fuel cells lead to increase the power density and the yield of synthesis gas. Hamakawa *et al.*, (2000) investigated $Ni_{1.0}/Ca_{0.8}Sr_{0.2}Ti_{0.9}Fe_{0.1}O_{3-\alpha}$ as the anode catalyst has achieved the selective oxidation of CH_4 to synthesis gas at 900°C. Nowadays, the most investigators have efforted to find alternative energy source**.** Hydrogen is one of the most interests because high efficiency and environmentally friendly.

Partial oxidation of methane:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad (11)$$

3.2.5.2 Deep oxidation of C_2 product

It is very difficult to prevent the oxidation of the C_2 hydrocarbon. The C_2 hydrocarbon is more selective than methane; the formation of carbon dioxides cannot be avoided.

Deep oxidation of C_2:

$$C_2H_4+O_2 \rightarrow 2CO_2+2H_2O \tag{12}$$

$$C_2H_6+O_2 \rightarrow 2CO_2+3H_2O \tag{13}$$

The main reaction is oxidative coupling of methane to C_2 hydrocarbon when the side reaction occur lead to decrease desire product and increase undesired product such as carbon monoxide, carbon dioxide, water, and hydrogen.

3.3 Factors affecting for OCM process

OCM is a reaction that depends on several factors such as catalysts preparation, CH_4/O_2 ratio and GHSV. We try to know about those factors for develop this process however, so difficult to find suitable operating condition.

3.3.1 Catalyst preparation

Catalyst preparation has several methods such as mist method is spray of the precursor solution into anode electrode, incipient wetness impregnation method and paste into anode electrode, precipitation method, sol-gel method but the most common method is impregnation this method was proposed in many papers. Mahmoodi *et al.*, (2010) synthesized Mn/SiO_2 nanocatalysts by incipient wetness impregnation and studied the affect of different promoters such as W, Mo, V, Cr, Nb on the catalytic performance in the oxidative coupling of methane. Na_2WO_4–Mn/SiO_2 shows the best catalytic performance at the OCM reaction conditions. Rane *et al.*, (2010) presented catalyst preparation in difference methods among physical mixing and co-precipitated for the La-promoted CaO catalyst in OCM. Moreover, influence of catalyst precursors used in the catalyst preparation has been studied. The experiment result showed the both method influence on the surface properties such as higher basicity observed for the catalyst prepared by co-precipitation method the physical mixing and in difference precursors exhibit different catalytic performance in OCM. The relationship among surface basicity and high activity promotes high C_2

selectivity. Gao and Shi, (2010) modified surface of impregnation La_2O_3/MgO catalyst with nitric acid for suppressed formation of CO_2 and H_2O in the OCM. Khodadadian *et al.*, (2010) studied affects of various barium precursors and promoters on catalytic activity of Ba–Ti perovskite catalysts for oxidative coupling of methane. Carrillo *et al.*, (2001) compared the Ni/ZrO_2 catalyst preparation method among paste and mist method the mist method was selective for the OCM, while the Ni/ZrO_2 cermet prepared by the ordinary paste method was active for CO and CO_2 formation. The most research focus on this topic. A wide variety of oxide catalyst has been studied for the OCM. Au *et al.*, (1997) studied OCM over $BaCO_3$/LaOCl catalysts at 1073 K. The addition of $BaCO_3$ over LaOCl provided the best performance is 40% methane conversion, 56% C_2 selectivity, and 22% C_2 yield. Research on the OCM to C_2 hydrocarbons has shown that alkali, alkaline earth, rare earth, rare earth oxide/alkaline earth oxide mixed catalysts, and transition metal oxides are catalytically active materials. After that C.T. Au proposed BaF_2/Y_2O_3 catalyst for OCM reaction. It found that quantity composition of BaF_2 have effected to performance of catalyst when the CH_4:O_2:N_2 = 2.47 : 1 : 11.4 and a total flow rate of 50 mLmin-1, after 4 h at 1023 K, the CH_4 conversion and C_2 selectivity over Y_2O_3 were 29.9 and 26.2%, respectively, giving a C_2 yield of 7.8%. When 30 mol% of BaF_2 was added, the CH_4 conversion, C_2 selectivity, and C_2 yield were enhanced to 35.3, 55.4, and 19.5%, respectively. With a 95 mol% BaF_2/Y_2O_3 catalyst, we could achieve a 22.4% C_2 yield with 36.1% CH_4 conversion and 62.1%.C_2 selectivity [10]. In 2000 Zeng *et al.*, (2001) studied catalytic properties of dense fluorite-structured $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) pellets in a packed-bed reactor. C_2 yields of 20–27%, C_2 selectivity of 50–62% were obtain and CH_4/O_2 ratio and He/(CH_4 + O_2) ratio had significant affects on OCM performance over BYS catalyst. In addition, Papa *et al.*, (2010) proposed the relationship among the surface basicity and catalytic activity for C_2 formation over equimolecular mixtures of alkaline-earth oxides (BeO, MgO, CaO and SrO) and Nd_2O_3. The catalyst basicity was the efficiency for selectively converting methane to C_2. Which consistent with Rane *et al.*, (2008) studied influence of alkali metal (Li, Na, K, Rb, and Cs) doped CaO catalysts in OCM reaction. The result of addition alkali metal showed a decreasing in the surface area but an increasing in the surface basicity and the C_2 selectivity and yield for the catalysts in the OCM process. The Na-CaO catalyst showed best catalytic performance, C_2 selectivity of 68.8% with 24.7% methane conversion in the OCM. In addition, the literatures exhibited the basicity of surface catalyst have the influent to performance of catalyst. The relationship among basicity of surface catalyst and performance of catalyst found that the catalytic performance in OCM of investigated metal oxides coincided with their basicity. However, the only few catalysts have been a good performance for OCM. Na-W-Mn/SiO_2 is one of the widely studied catalysts in OCM reaction. Wang *et al.*, (1995) studied on Mn–Na_2WO_4/SiO_2, Mn–Na_2WO_4/MgO and $NaMnO_4$/MgO for OCM at 1073 K, 1 atm. The three catalysts provided about 80% C_2 selectivity and 20% methane conversion. The sodium is required for high selectivity, tungsten is required for stabilize and Manganese is highly dispersed. Figure 3.4 shows an example Lunsford’s catalyst preparation.

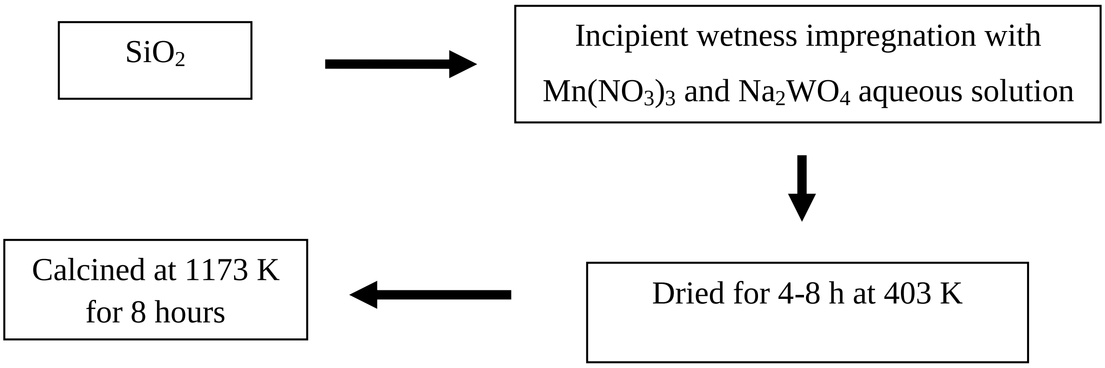


Figure 3.4 Preparation of Mn-Na_2WO_4/SiO_2 (Wang *et al.*, 1995).

In the same catalyst Ji *et al.*, (2002, 2003) report performance of M–W–Mn/SiO_2 catalysts (M = Li, Na, K, Ba, Ca, Fe, Co, Ni, and Al) in OCM reaction. In the trimetallic catalysts studied, there was evidence for WO_4 tetrahedron on the surface in the Li–, Na–, and K–W–Mn/SiO_2 catalysts. The WO_4 tetrahedron on the catalyst surface appears to an essential role in achieving high CH_4 conversion and high C_2 hydrocarbon selectivity in the OCM reaction. Chua *et al.*, (2008) reported Na-W-Mn/SiO_2 catalyst for OCM providing the stability and activity of the catalyst system. The Na_2WO_4 and Mn_2O_3 very important in achieved high selectivity of C_2 products. Zhang *et al.*, (2007) studied stability of CeO_2-Na_2WO_4-Mn/SiO_2 catalyst. 22 % of C_2H_4 yields were obtained and excellent stability in long-term reaction. Zheng *et* *al*., (2010) presented effect of S, P Addition on Na–W–Mn–Zr/SiO_2 catalyst. The conversion of methane and yield of products have been improved. The highest methane conversion is 43.8% and C_2 yield is 23.5%.

From the literatures reported showed two behaviors, when higher methane conversion but the C_2 selectivity must be lower on the other hand, when higher C_2 selectivity but methane conversion is lower. The most studies effort to develop new reactor for compare with a conventional process. The solid oxide membrane has been applied to this process. Solid oxide membrane role is to separate oxygen ion from non-reaction side into methane reaction side. It found that provide higher selectivity and yields because the oxygen ion more selective than gas-phase oxygen in the reaction.

3.3.2 CH_4/O_2 ratio and GHSV

There are many research interests in this factor for oxidative coupling of methane believe which guide to a better performance of this process. Jiang *et al*., (1997) studied effect of the ratio of CH_4 to O_2 on C_2 selectivity and CH_4 conversion at 1088 K CH_4 space velocity, 104 hr^{-1} in a fixed-bed reactor used $CaTiO_3$ catalysts. The highest C_2 yield at 1088 K is obtained at a CH_4/O_2 ratio around 3.5. When increased or decreased the CH_4/O_2 ratio lead to a decreasing in C_2 yield. At CH_4/O_2 ratio 3.5 when increased the CH_4 space velocity from 2500 to 30000 hr^{-1} made C_2 selectivity increased from 29.3 to 85.7 % but first a slightly increasedthen a rapidly decreased in CH_4 conversion. The highest yield of 17% was obtained around 15000 hr^{-1}. Wu *et al*., (2007) studied the effect of CH_4/O_2 ratio on Na_2WO_4/Co–Mn/SiO_2 catalyst for coincident production of syngas and ethylene from CH_4. Increasing the CH_4/O_2 ratio from 2.0 to 4.0 lead to increase in C_2 selectivity from 51.3 to 62.4, but methane conversion was slightly decreased and provided the best C_2 yield 15.5%. Rane *et al*., (2008) studied factors affected to performance of alkali metal (Li, Na, K, Rb, and Cs) doped CaO. The GHSV results showed that the methane conversion for all the catalysts, except Rb-doped CaO (Rb/Ca = 0.4) was decreased with increasing GHSV from 5140 to 20550 $cm^3 \cdot g^{-1} \cdot h^{-1}$and at high CH_4/O_2 ratio provided high C_2 selectivity ,but methane conversion was slightly decreased. Wang *et al*., (1995) presented the CH_4/O_2 ratio affected to performance of CeO_2-W-Mn/SiO_2 catalyst for methane oxidation to ethylene at 1073 K, methane GHSV = 6667 ml•g^{-1}•h^{-1}. Increasing of CH_4/O_2 ratio, C_2 selectivity increased and CO_x selectivity decreased, accompanying that CH_4 and O_2 conversions decreased sharply.

Effects of CH_4/O_2 ratio and GHSV are the importance factors bring about to appropriate operating condition from the literatures when increasing the GHSV lead to increasing of C_2 selectivity on the other hand, decreased in CH_4 conversion. Generally, increased the CH_4/O_2 ratio leads to high selectivity, but occur low methane conversion. Moreover, some cases exhibit effect of dilute gas when increased flow rate of dilution gas, the C_2 selectivity will be high. On the other hand, if decreases the flow rate of dilution gas lead to low C_2 selectivity.

3.3.3 Oxygen permeable

It is generally accepted that the type and state of oxygen used is an importance in achieving C_2 yields. For oxygen permeable membranes, oxygen is uniformly transported through the membrane as oxygen ions (O^{2-}). These oxygen species may be more selective for the OCM reaction. Although, the theoretical or experimental studies present an intensive consideration for use of the mixed conducting catalytic membranes to supply oxygen ions from the non-reaction side to the reaction side. There are many materials to use in selective oxygen. A perovskite oxides with oxygen-ionic conductivity have been reported as promising OCM catalysts, which are very active, stability and selective in converting methane into C_2 (C_2H_4, C_2H_6) products (Lin and Zeng, 1996). Haag *et al.*, (2007) reported that the oxygen flux and its permeability control the methane conversion and C_2 selectivity during OCM reaction in a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO), $Ba_{0.5}Sr_{0.5}Mn_{0.8}Fe_{0.2}O_{3-\delta}$ (BSMFO) and $BaBi_{0.4}Fe_{0.6}O_3$ (BBFO) membrane reactor using dense perovskite membrane coated with Pt/MgO catalyst. Jiang *et al.*, (2011) investigated the influence of Pt, Ag catalysts and thickness of membrane on oxygen permeation through the disk-shaped $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_x$ perovskite dense membrane found that a thickness has significant more than catalyst. Zeng *et al.*, (1998) studied on $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ perovskite-type ceramic membrane, oxygen permeation and membrane reactor performance for oxidative coupling of methane at temperatures higher than 1123 K, high C_2 selectivity (70-90%) and yield (10-18%) were achieved. Shao *et al.*, (2001) reported a mixed-conducting perovskite-type $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) ceramic membrane reactor in OCM reaction provided C_2 selectivity 40–70% but methane conversion rate was low about 0.5-3.5% at 1073–1173 K oxygen permeation flux for the BSCFO membrane was far higher than that required for methane activation the permeation flux was only slightly improved. Although, increment of oxygen permeate flux will increase methane conversion but catalyst is equally important. Tan and Li, (2006) studied a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\alpha}$ (LSCF) perovskite hollow-fiber membrane in oxidative coupling of methane at 1223 K. The membrane has been prepared via a combined phase inversion/sintering technique. The experimental results showed the LSCF hollow-fiber membrane exhibits good oxygen permeation and provided a better performance than a conventional disk-shaped membrane. 15.3% was the highest C_2 yield. Tan *et al.*, (2007) presented $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) hollow fiber membranes prepared by via the phase inversion and sintering technique with $SrTi_{0.9}Li_{0.1}O_3$ catalyst. The resulted showed that increasing methane conversion and oxygen permeation rate was observed whereas the C_2 selectivity decreased. The experiment results showed the maximum C_2 yield was 21%.

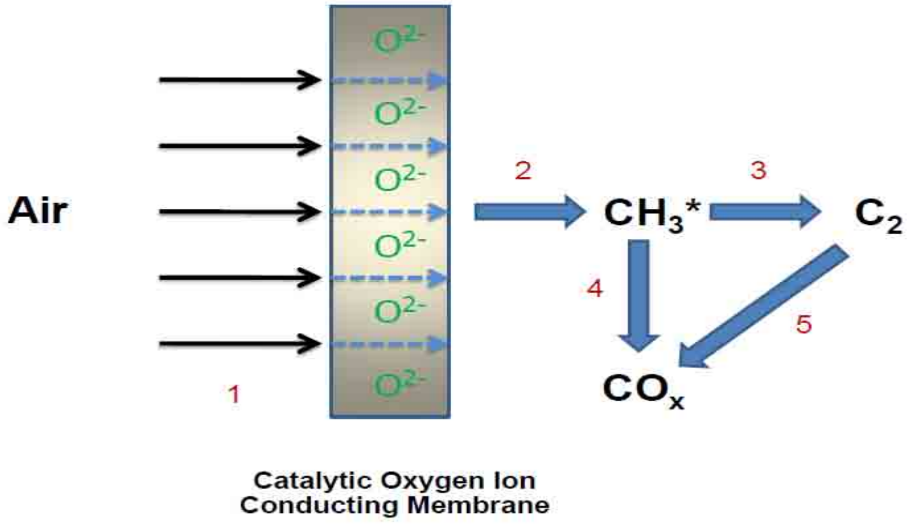


Figure 3.5 Scheme of oxygen through the membrane reactor and product. (Liu *et al.*, 2001)

Presented in figure 3.5 when the permeation rate of O^{2-} of Step one is lower than the rate consumed in Step 2, the product rate is low. Contrarily, if the permeation rate of O^{2-} is bigger high than the methane consumption step the O^{2-} passed through the membrane may combine to form gaseous O_2 and both Steps 4 and 5, which lead to lower the C_2 yields. If the oxygen-ion permeation rate is controlled and comparable to the consumption rate of oxygen in the reactor, any complete oxidation reactions on the membrane surface as well as in the gas phase can be limited, lead to high C_2 selectivity for OCM in the membrane reactor. Consequently, the O^{2-} permeation flux and catalytic methane reaction rate is the importance factor to make a maximum C_2 yield. The key to achieving high C_2 yields in solid oxide membrane reactors are the both good activity and selectivity for OCM and high oxygen permeate for oxygen transport (Liu *et al*., 2001).

3.3.4 Ion and mixed conducting oxides as catalysts

Ion and mixed conducting oxides as catalysts is the catalytic properties of solid oxides which display oxygen ion or mixed (i.e. ionic + electronic) conductivity. Particular consideration is given to the oxidation-reduction reactions of gas phase components, but attention is also devoted to oxygen exchange between gas and oxide. An attempt has been made to relate and explain the observed phenomena such as catalytic activity and selectivity in terms of the electrical conducting properties of the oxides, which depend on their crystal and defect structures of ion and mixed conducting oxides as catalysts (Gellings *et al*., 1992)

CHAPTER IV
EXPERIMENT

In this chapter explained the catalysts preparation and operation reaction in fixed bed and SOFC reactor for OCM reaction. Moreover, described in term of catalyst preparation, technique characterization of catalyst, catalytic performance.

4.1 Catalyst Preparation

The 5%Na_2WO_4-2%Mn/La_2O_3, Y_2O_3 or YSZ catalysts were prepared by the incipient wetness impregnation method following the method described in literature (Wang *et al.*, 1995). The La_2O_3, Y_2O_3 or YSZ support was first impregnated with an aqueous solution of $Mn(NO_3)_2$, and then dried for 10 h at room temperature. After that it was dried at 373 K overnight. Next the impregnation method was repeated using an aqueous solution containing an appropriate amount of Na_2WO_4. The 2 wt% S, 2 wt% P and 2 wt%Ce were added into the catalyst by the incipient wetness impregnation method after impregnating Na_2WO_4. Finally, the catalysts were calcined in air for 5 h at 1123 K.

Table 4.1 Chemicals for catalyst synthesis

Reagent		Company
Lanthanum (III) oxide	La_2O_3	Sigma-Aldrich
Yttrium (III) oxide	Y_2O_3	Sigma-Aldrich
8% YSZ	YSZ	Tosoh
Manganese (II) nitrate tetrahydrate	$MnN_2O_6 \bullet 4H_2O$	Sigma-Aldrich
Sodium tungstate dihydrate	$Na_2\ WO_4 \bullet 2H_2O$	Sigma-Aldrich
Cerium (III) nitrate hexahydrate	$CeN_3O_9 \bullet 6H_2O$	Sigma-Aldrich
Lanthanum strontium manganite	$La_{0.8}Sr_{0.2}MnO_3$	Sigma-Aldrich

Table 4.2 The catalysts for used in experiment

Catalyst	**Support**
-	La_2O_3
Na_2WO_4-Mn	
S-Na_2WO_4-Mn	
P-Na_2WO_4-Mn	
Ce-Na_2WO_4-Mn	
-	Y_2O_3
Na_2WO_4-Mn	
S-Na_2WO_4-Mn	
P-Na_2WO_4-Mn	
Ce-Na_2WO_4-Mn	
-	8%YSZ
Na_2WO_4-Mn	
S-Na_2WO_4-Mn	
P-Na_2WO_4-Mn	
Ce-Na_2WO_4-Mn	

4.2 Physical and structural characterizations

The synthesized catalysts were determined their properties by various techniques; XRD, BET, XPS, SEM.

X-Ray Diffractometer (XRD): The crystalline phases of prepared samples were identified by x-ray diffraction technique using Cu-Kα radiation. The x-ray diffractograms were recorded in range of 10° to 80° (2ϴ).

Brunauer-Emmett-Teller (BET): The specific surface area and pore size of catalysts was measured by BET instrument. This method used nitrogen (N_2)

adsorption isotherm. Adsorption always occurs when a solid surface is exposed to vapor.

X-ray photoelectron spectroscopy (XPS): The XPS is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within catalysts.

Scanning Electron Microscopy (SEM): The surface morphology and particle size of prepared samples were investigated by using scanning electron microscope at magnification of 15,000x

4.3 Catalytic activity experiment

4.3.1 Fixed bed reactor

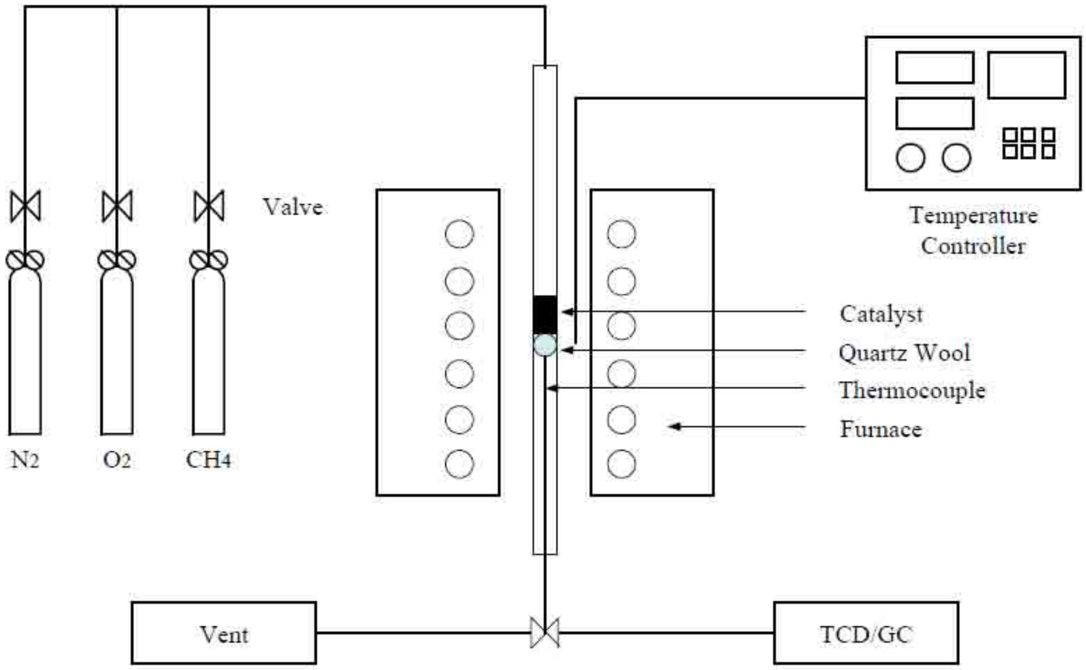
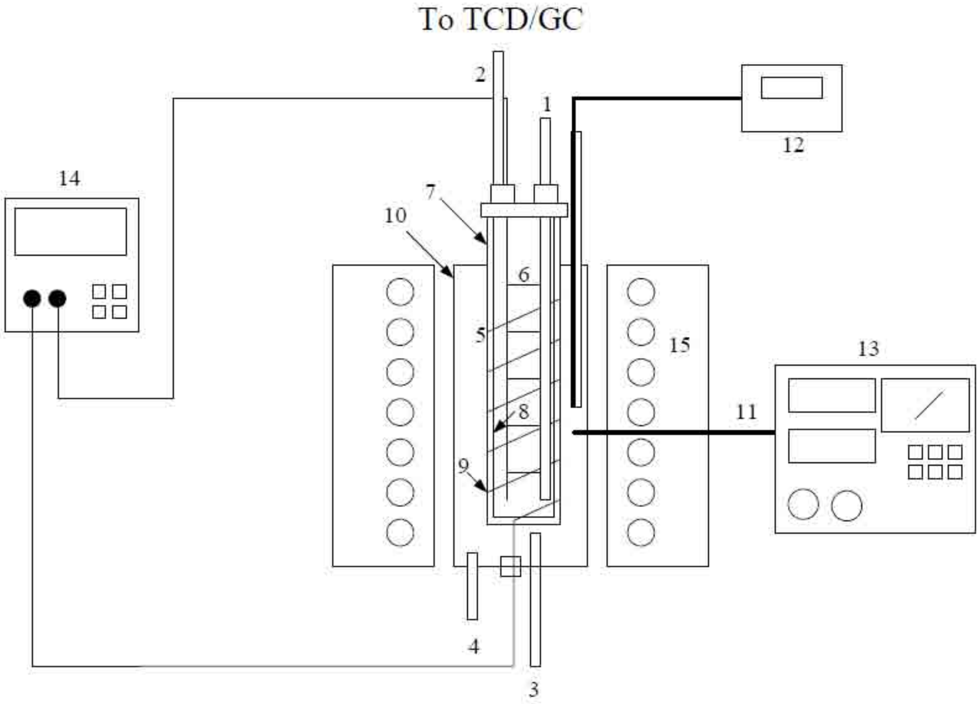


Figure 4.1 Schematic diagram of oxidative coupling of methane in fixed bed**.**

Activity tests were carried out in a quartz fixed-bed microreactor (i.d. 6 mm), using 0.2 g of catalyst (figure 4.1). A thermocouple was attached in the inside wall of the reactor to monitor the reactor temperature and to control the furnace. The catalyst bed was heated to a desired temperature (973-1173 K) under nitrogen flow 25 ml•min^{-1}and 1 atm. The reactant consists of methane, oxygen and nitrogen at a ratio of 4:1:5. Then the samples were analyzed by a TCD gas chromatograph (Shimadzu GC8A) to determine the product concentrations using a PorapakQ column for the separation of CH_4, CO_2, C_2H_4, and C_2H_6, and a 5 Å molecular sieve column for the separation of O_2, CH_4, and CO.

The supplied gases were composed of nitrogen, methane, and oxygen. For each gas cylinder, the pressure regulator was installed at the outlet in order to set pressure to the valve controller. The valve controllers were installed for adjusting the flow rate of inlet gases.

4.3.2 SOFC reactor



1. Anode side feed (Ar/CH_4)
2. Exit gas from anode side
3. Cathode side feed (O_2)
4. Exit gas from cathode side
5. Platinum wire
6. Platinum wire
7. YSZ tube
8. Anode catalyst
9. Cathode (LSM)
10. Quartz tube
11. Thermocouple
12. Thermocouple indicator
13. Temperature controller
14. Ammeter/Voltmeter/Potentiostat
15. Furnace

Figure 4.2 Schematic diagram of oxidative coupling of methane in SOFC reactor

4.3.2.1 Apparatus

The schematic diagram of the SOFC reactor was illustrated in figure 4.2. A tube-type YSZ membrane (8mol% Y_2O_3, thickness = 1.5 mm, inside diameter = 18 mm, outside diameter = 21 mm, length 100 mm, effective surface area is 0.006126 m^2) was used as an electrolyte. The anode catalyst on the inner surface of the tube while $La_{0.85}Sr_{0.15}MnO_3$ (abbreviated as LSM) prepared by a conventional paste method on the outer side was used as the cathode. Platinum wire has diameter size 0.5 mm, which was connected with cathode and anode side for measure the current by multi-meter. The reactor was heated to a desired temperature (973-1273 K) under argon flow 50 ml•min^{-1}at anode side and oxygen was allowed to continually flow into the cathode catalyst at a total flow rate 100 ml•min^{-1} at 1 atm. At 973 K the argon was transposed to methane continually flow into anode catalyst side at total flow rate 5 ml•min^{-1}. Then the samples were analyzed by a TCD gas chromatograph (Shimadzu GC8A) to determine the product concentrations using a PorapakQ column for the separation of CH_4, CO_2, C_2H_4, and C_2H_6, and a 5 Å molecular sieve column for the separation of O_2, CH_4, and CO.

4.3.2.2 Anode and cathode preparation

The anode catalyst was prepared on the inside of YSZ tube by the paste method. The 1.0 g catalyst powder was mixed with grycerol and pasted into film on the inside of YSZ tube and heated at 1123 K for about 3 h in air.

The 0.2 g LSM powder was mixed with grycerol and pasted into film on the outside of YSZ tube and heated at 1123 K for about 3 h in air.

4.4 Experiment procedures

In the first step of this research was to study the capability of catalysts for OCM reaction. The 5wt%Na_2WO_4-2wt%Mn/SiO_2 is the most interesting catalyst for this reaction (Ji *et al.*, 2002, 2003; Shahri and Pour, 2010; Liu *et al.*, 2008; Wang *et al.*, 1995). There are many different ways to prepare this catalyst but the impregnation method is the suitable because simple and provides high performance (Wang *et al.*, 2006). Moreover, the operating parameters that effect to OCM reaction, for example, CH_4:O_2 ratio, operating temperature, weight hourly space velocity (WHSV).

The experimental procedures are divided into two parts.

Part I: This part studied the OCM reaction in fixed bed reactor and selected the suitable catalyst in term of performance, determining good operating temperature from all catalysts.

Part II: Selected catalyst and some conditions from part I has been used to optimize in SOFC reactor for OCM reaction and were investigated in order to achieve C_2 product.

In this work the desire products are C_2H_4 (ethylene), and C_2H_6 (ethane). Consequently, the catalytic performance of catalyst consider in term of conversion of methane, selectivity to C_2 hydrocarbon product, and yield of C_2 hydrocarbon product. Moreover, the stability of catalysts for SOFC reactor has been examined. The results were evaluated according to the gas composition before and after reaction as the following equations in table 4.3-4.6.

Table 4.3 Conversion of reactants (Shao *et al*., 2001)

Reactant Conversion	**OCM Reaction**
CH_4	$X_{CH_4} = \left(\frac{CH_{4,in} - CH_{4,out}}{CH_{4,in}}\right) \times 100$ (4.1)
O_2	$X_{O_2} = \left(\frac{O_{2,in} - O_{2,out}}{O_{2,in}}\right) \times 100$ (4.2)

Where CH_4,in is concentration of influent methane
CH_4,out is concentration of effluent methane
O_2,in is concentration of influent oxygen
O_2,out is concentration of effluent oxygen

Table 4.4 Product Selectivity (Shao *et al*., 2001)

Product Selectivity	**OCM Reaction**
C_2H_4 **C_2H_6**	$\mathrm{S}_{\mathrm{C}_2} = \frac{2 \times (C_2H_{4,out} + C_2H_{6,out})}{CO_{out} + CO_{2,out} + 2 \times (C_2H_{4,out} + C_2H_{6,out})} \times 100$ (4.3)

Table 4.5 Product Yield (Shao *et al*., 2001)

Product Yield	**OCM Reaction**
C_2H_4 **C_2H_6**	$\mathrm{Y}_{\mathrm{C}_2} = X_{CH_4} \times S_{C_2}$ (4.4)

Table 4.6 Product Distribution

Product Distribution	**OCM Reaction**	
C_2H_4 **C_2H_6**	$D_{C_2} = \left(\frac{C_{2,out}}{Total\ Product_{out}}\right) \times 100$	(4.5)
CO	$D_{CO} = \left(\frac{CO_{out}}{Total\ Product_{out}}\right) \times 100$	(4.6)
CO_2	$D_{CO_2} = \left(\frac{CO_{2,out}}{Total\ Product_{out}}\right) \times 100$	(4.7)
H_2	$D_{H_2} = \left(\frac{H_{2,out}}{Total\ Product_{out}}\right) \times 100$	(4.8)

Where $C_{2,out}$ is concentration of effluent C_2 product
CO_{out} is concentration of effluent carbon monoxide
$CO_{2,out}$ is concentration of effluent carbon dioxide
$H_{2,out}$ is concentration of effluent hydrogen

CHAPTER V

RESULTS AND DISCUSSION

The performance of all catalysts was investigated in OCM reaction for fixed bed reactor and selects the best catalyst performance to use in SOFC reactor as anode material. The results of each part are described as the following:

5.1 Characteristic of catalyst

5.1.1 Phase identification

The fresh catalysts with difference supports were characterized by XRD as shown in figure 5 .1, 5.2, 5.3. Which the importance phases in the catalyst is Na_2WO_4, $Na_2W_2O_7$, Na_2SO_4, Mn_2O_3 (Zheng *et al*., 2010). For La_2O_3 support catalyst did not observe the active phase such as Na_2WO_4 (17°), Na_2SO_4 (34°, 49°) in all catalysts but found the active phase $Na_2W_2O_7$ (15.5°) in P-Na_2WO_4-Mn/La_2O_3 and Ce-Na_2WO_4-Mn/La_2O_3 catalyst. In addition, found Mn_2O_3 (33°) from all catalysts except only La_2O_3 support. Moreover, the addition of metal into the support caused to change of La_2O_3 structure lead to new structure this can see form peak in figure 5.1.

The Y_2O_3 and YSZ support in XRD pattern involve in part metal loading ,which did not found active phase such as Na_2WO_4 (17°), $Na_2W_2O_7$ (15.5°), Na_2SO_4 (34°, 49°) but found only Mn_2O_3 (33°) in catalyst promoted with manganese except S-Na_2WO_4-Mn/Y_2O_3 and S-Na_2WO_4-Mn/YSZ. The diffraction peaks were unexpanded and remained unchanged this cause may be the formation of the composite oxide Na_2WO_4, $Na_2W_2O_7$, Na_2SO_4, Mn_2O_3 as an amorphous phase. (Li and Wang, 2004).

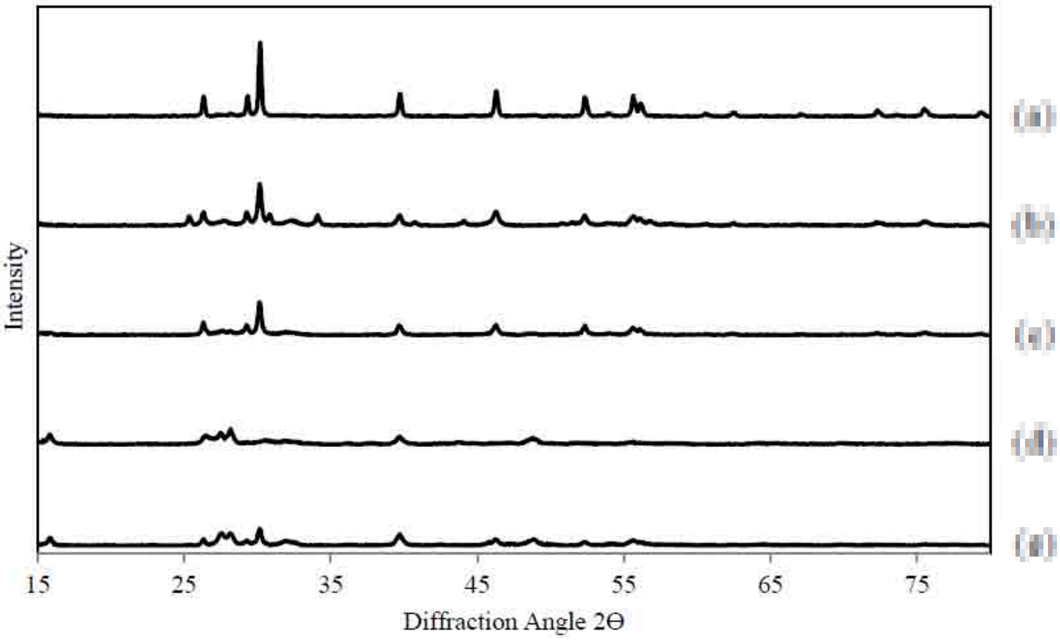


Figure 5.1 The XRD pattern (a) La_2O_3, (b) Na_2WO_4-Mn/La_2O_3, (c) S-Na_2WO_4-Mn/La_2O_3, (d) P-Na_2WO_4-Mn/La_2O_3, (e) Ce-Na_2WO_4-Mn/La_2O_3

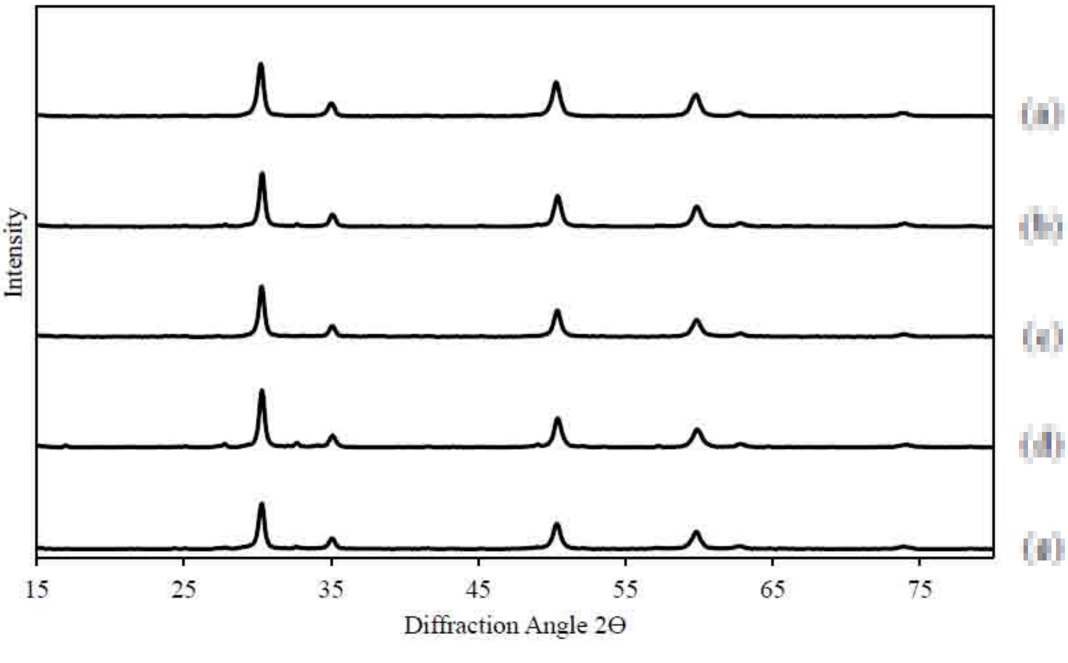


Figure 5.2 The XRD pattern (a) Y_2O_3, (b) Na_2WO_4-Mn/Y_2O_3, (c) S-Na_2WO_4-Mn/Y_2O_3, (d) P-Na_2WO_4-Mn/Y_2O_3, (e) Ce-Na_2WO_4-Mn/Y_2O_3

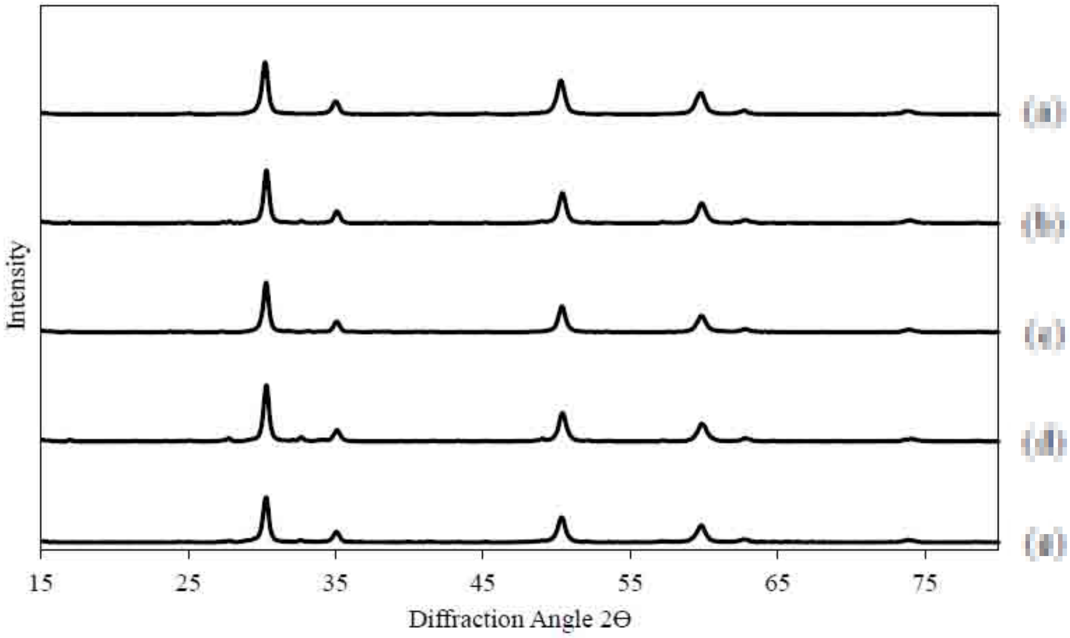
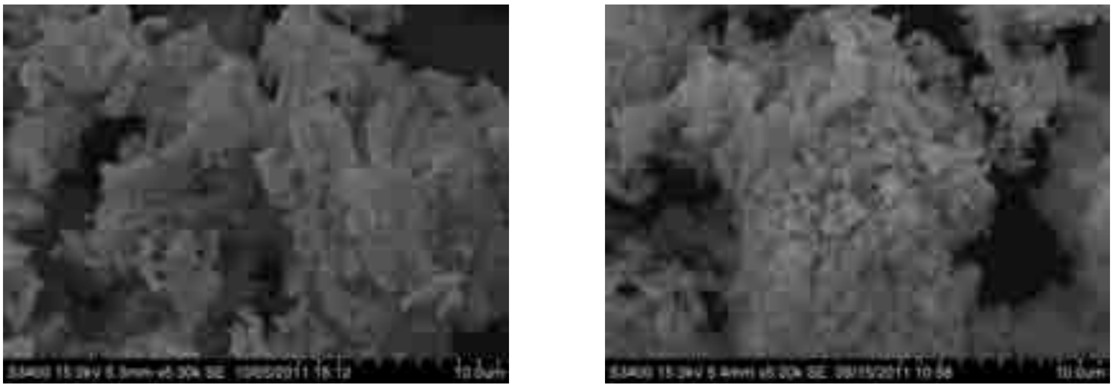


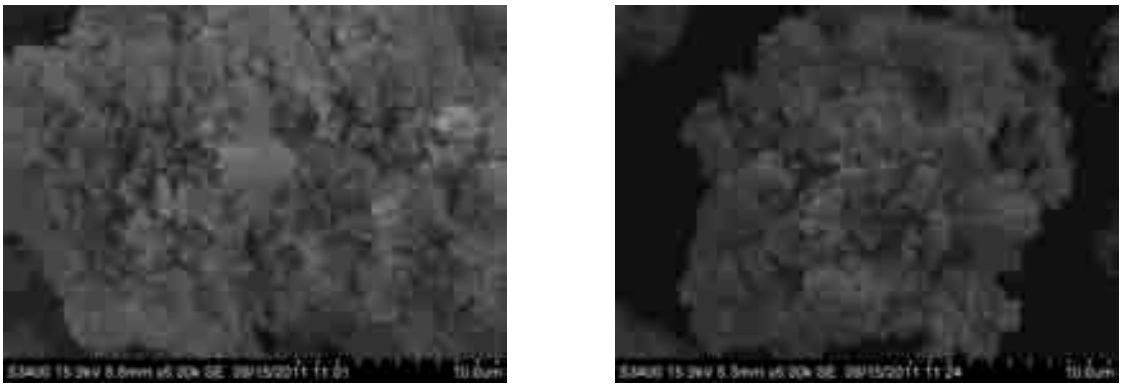
Figure 5.3 The XRD pattern (a) YSZ, (b) Na_2WO_4-Mn/YSZ, (c) S-Na_2WO_4-Mn/YSZ, (d) P-Na_2WO_4-Mn/YSZ, (e) Ce-Na_2WO_4-Mn/YSZ

5.1.2 Surface morphology

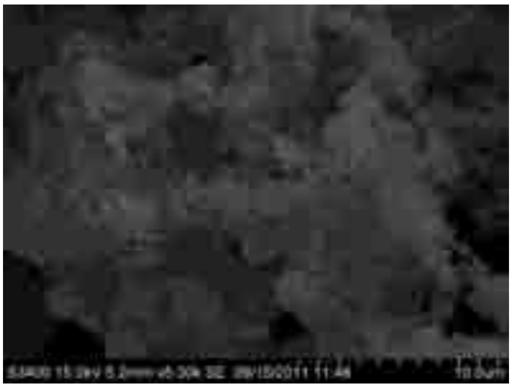
Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) techniques were carried out over the catalysts. The Na, W, Mn, S, P, Ce, La, Sr, Mn, Zr, and O elements detected by EDS technique, and the amount of elements on all supports proximated with theoretical values. In additional the dispersion of elements was good that observed in SEM-EDS elemental mapping. In all the SEM micrographs, the particles with uniform size can be observed together with aggregated clusters consisting of many particles, as shown in figure 5.4, 5.9, and 5.14. However the all SEM micrographs did not show the difference between metal oxide and support.



La_2O_3 Na_2WO_4-Mn/La_2O_3

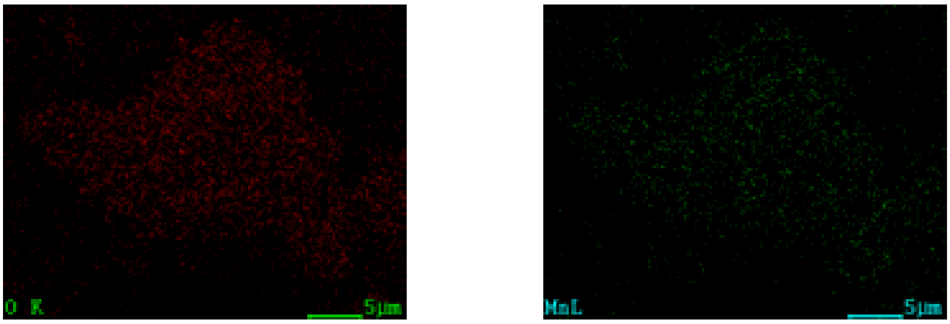


S-Na_2WO_4-Mn/La_2O_3 P-Na_2WO_4-Mn/La_2O_3

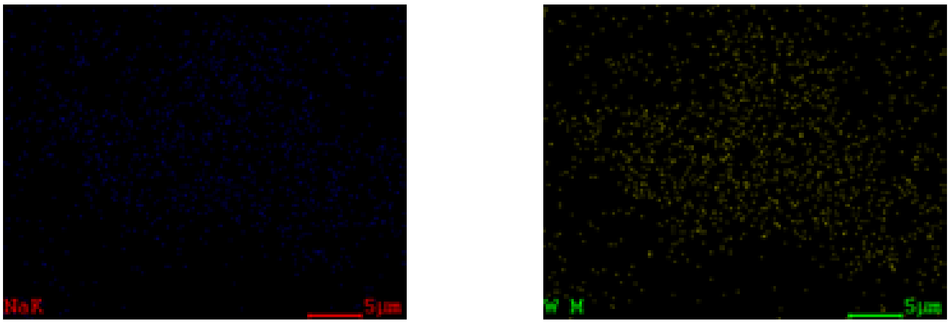


Ce-Na_2WO_4-Mn/La_2O_3

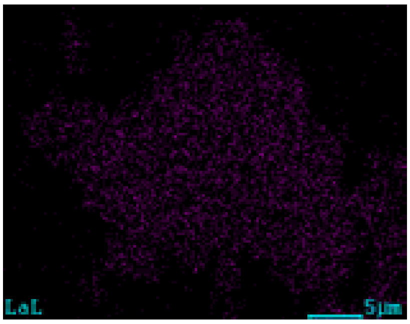
Figure 5.4 Surface morphology of catalyst on La_2O_3 support



O Mn

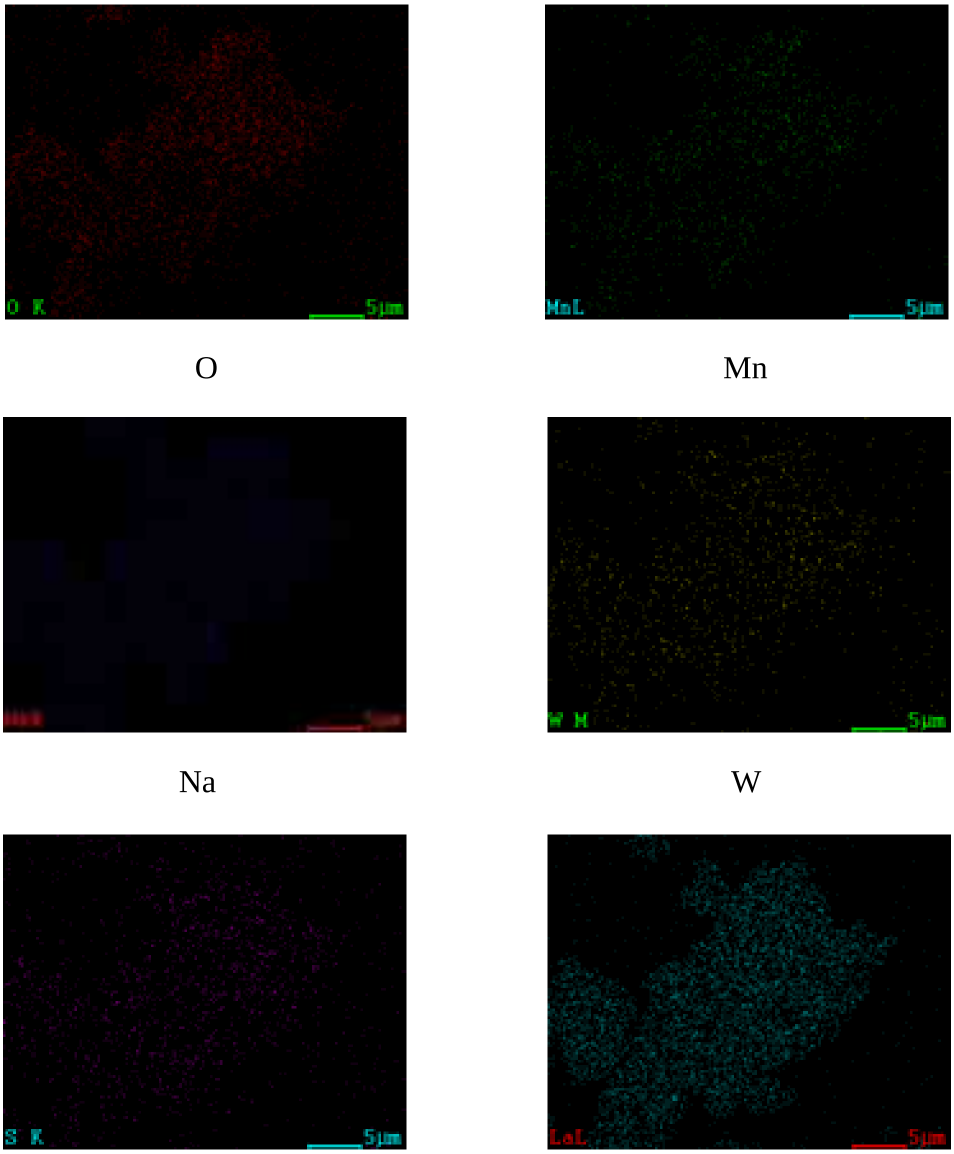


Na W



La

Figure 5.5 The SEM-EDS mapping of elements on Na_2WO_4-Mn/La_2O_3 catalyst



O

Mn

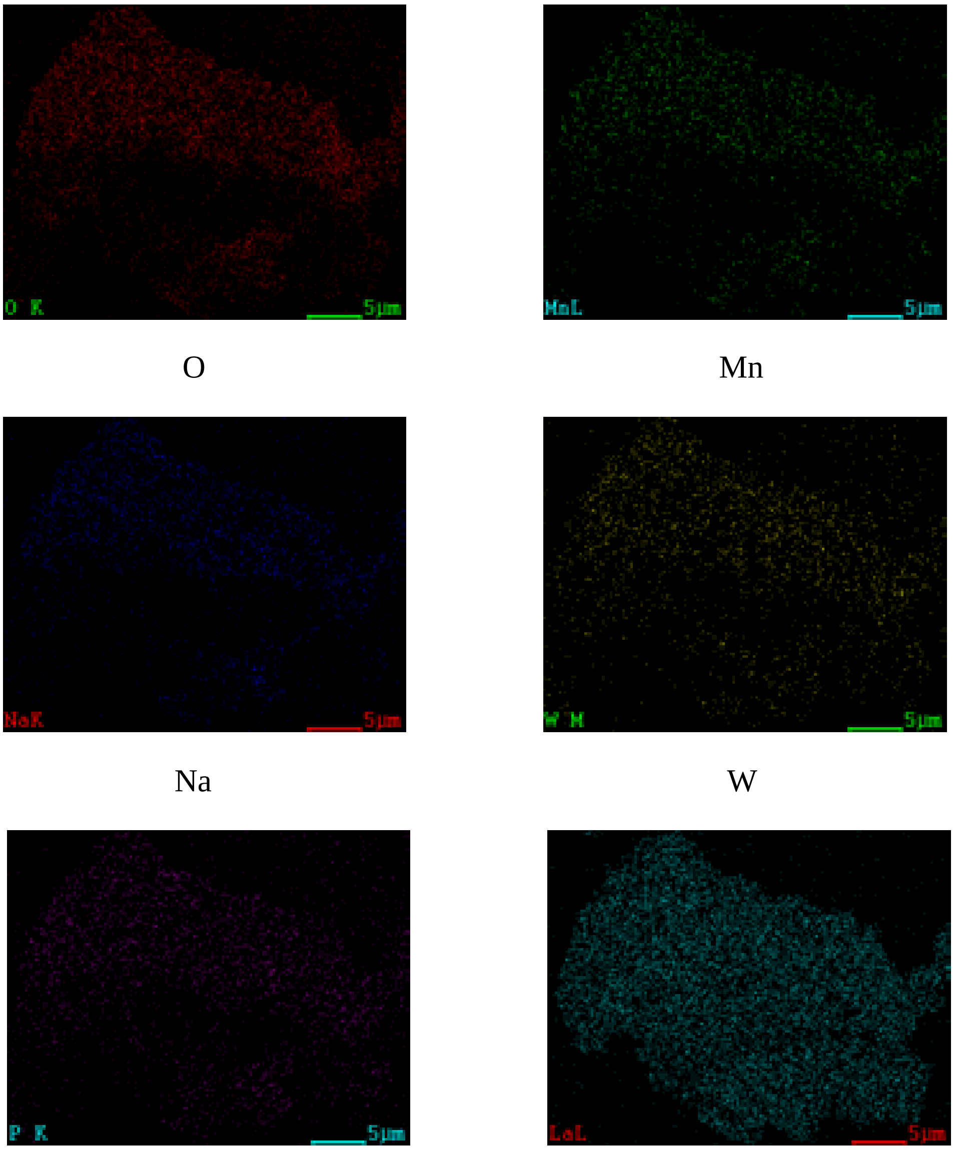
Na

W

S

La

Figure 5.6 The SEM-EDS mapping of elements on S-Na_2WO_4-Mn/La_2O_3 catalyst

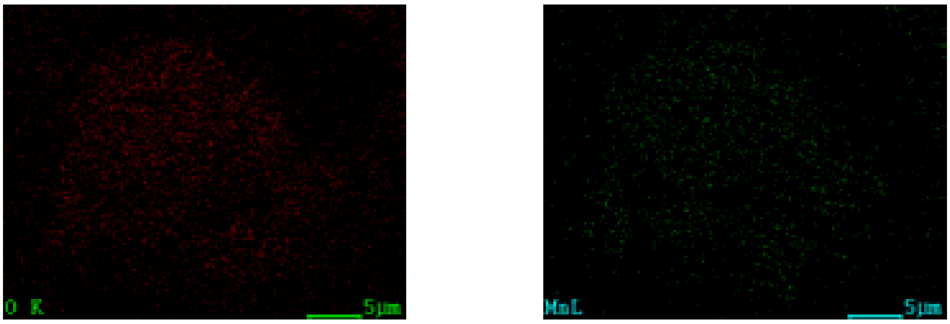


O Mn

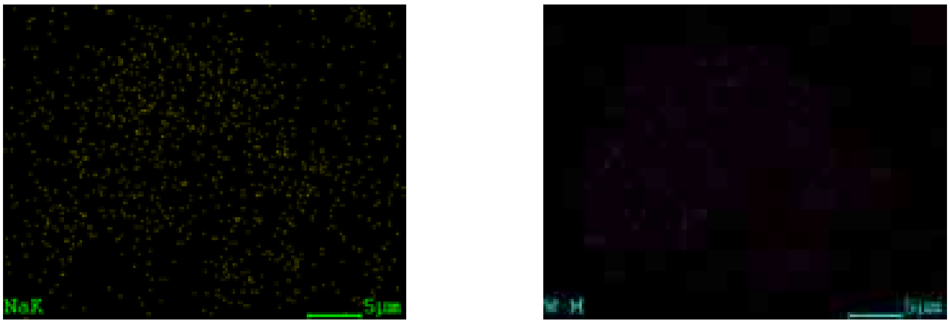
Na W

P La

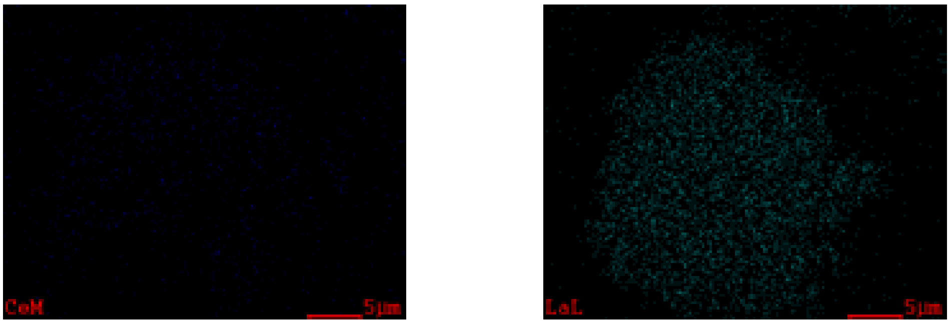
Figure 5.7 The SEM-EDS mapping of elements on P-Na_2WO_4-Mn/La_2O_3 catalyst



O Mn

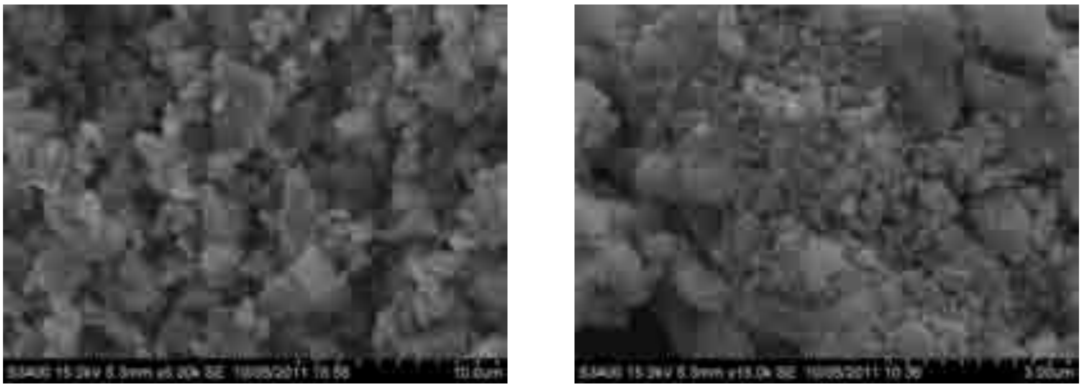


Na W

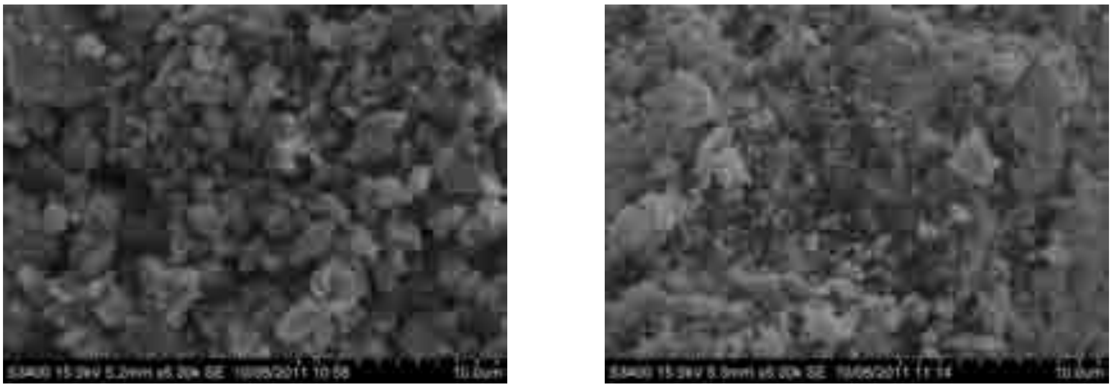


Ce La

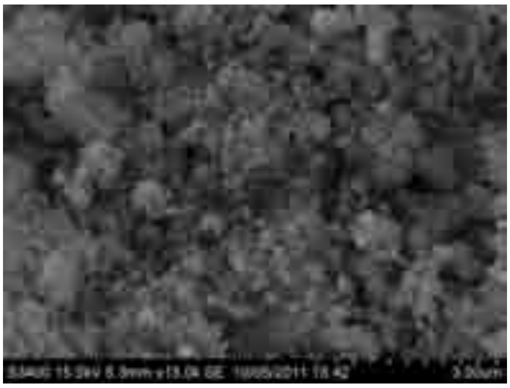
Figure 5.8 The SEM-EDS mapping of elements on Ce-Na_2WO_4-Mn/La_2O_3 catalyst



Y_2O_3　　Na_2WO_4/Y_2O_3

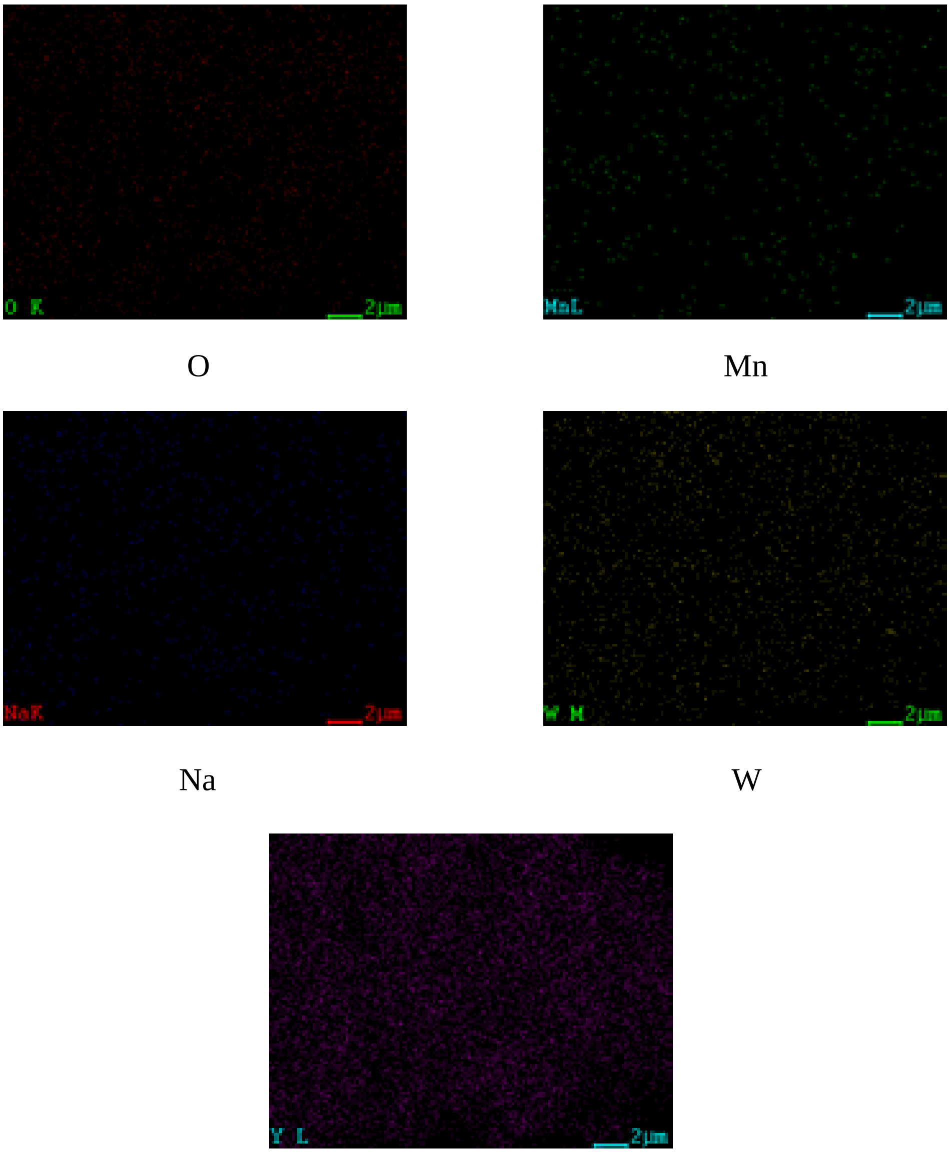


$S\text{-}Na_2WO_4/Y_2O_3$　　$P\text{-}Na_2WO_4/Y_2O_3$



$Ce\text{-}Na_2WO_4/Y_2O_3$

Figure 5.9 Surface morphology of catalyst on Y_2O_3 support



O

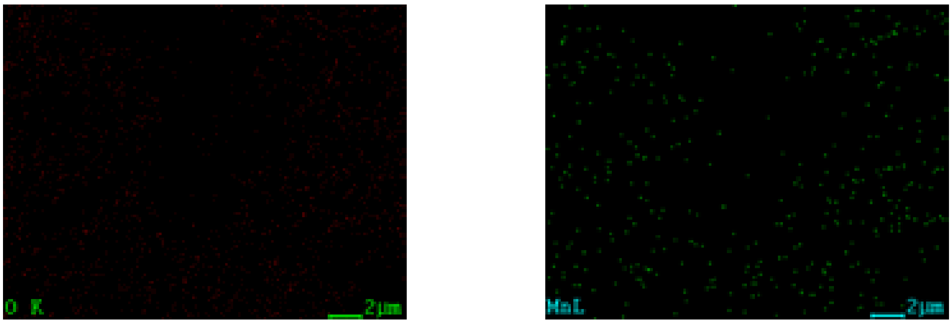
Mn

Na

W

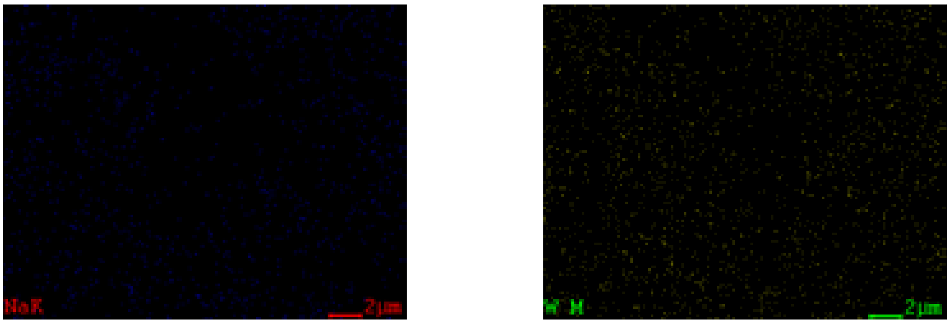
Y

Figure 5.10 The SEM-EDS mapping of elements on Na_2WO_4-Mn/Y_2O_3 catalyst



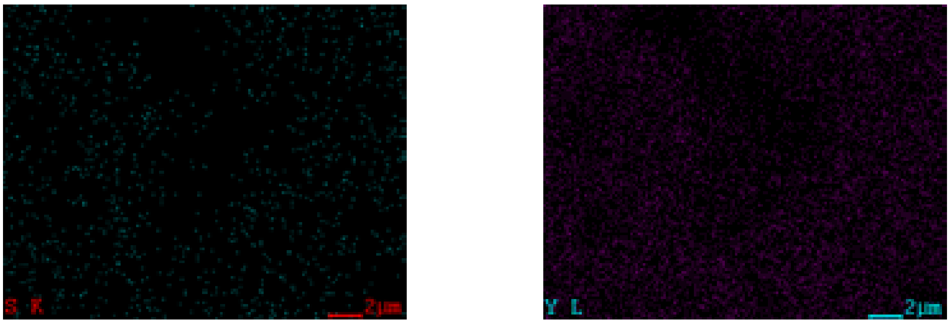
O

Mn



Na

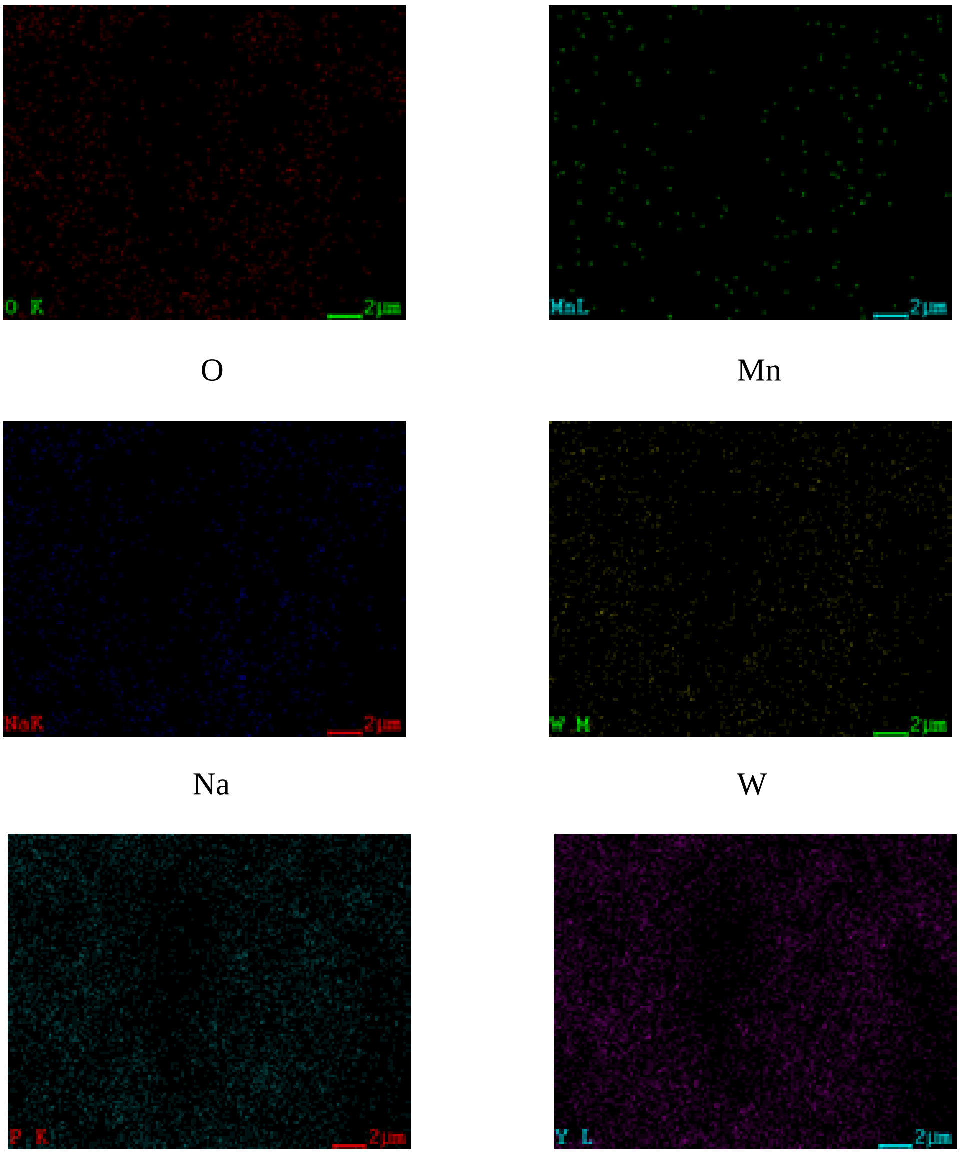
W



S

Y

Figure 5.11 The SEM-EDS mapping of elements on S-Na_2WO_4-Mn/Y_2O_3 catalyst



O

Mn

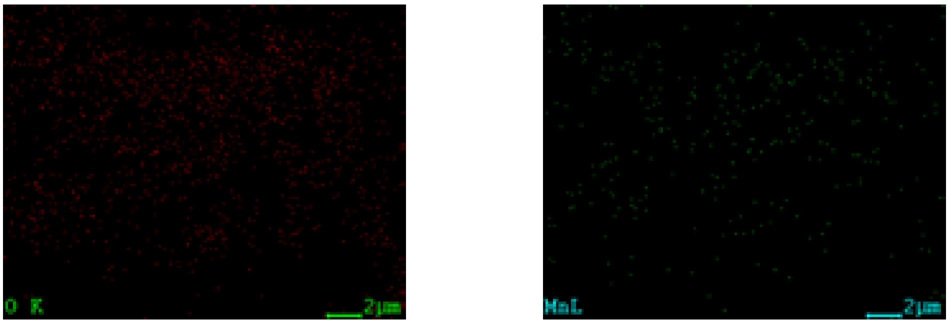
Na

W

P

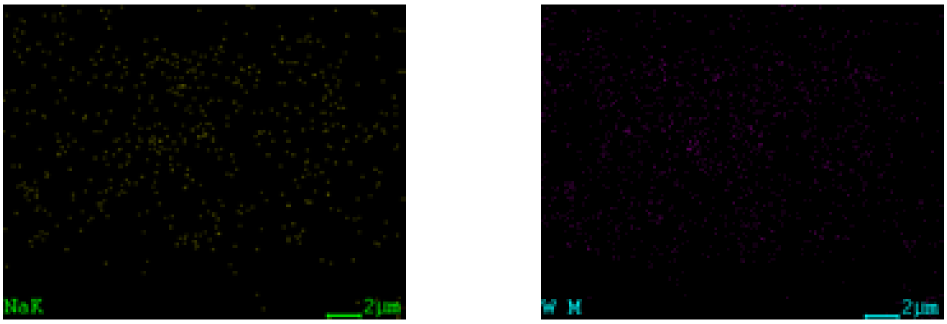
Y

Figure 5.12 The SEM-EDS mapping of elements on P-Na_2WO_4-Mn/Y_2O_3 catalyst



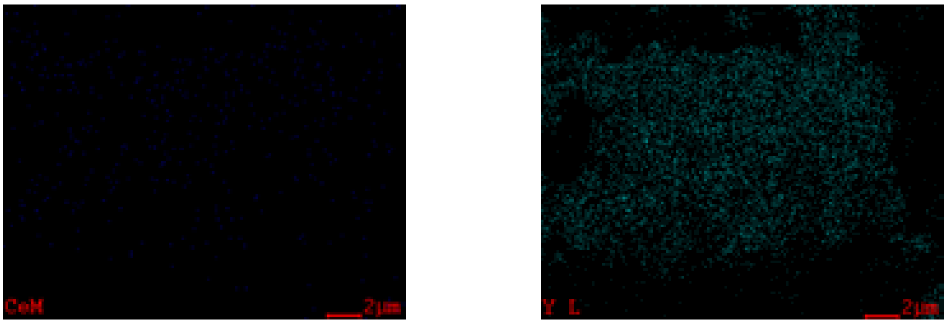
O

Mn



Na

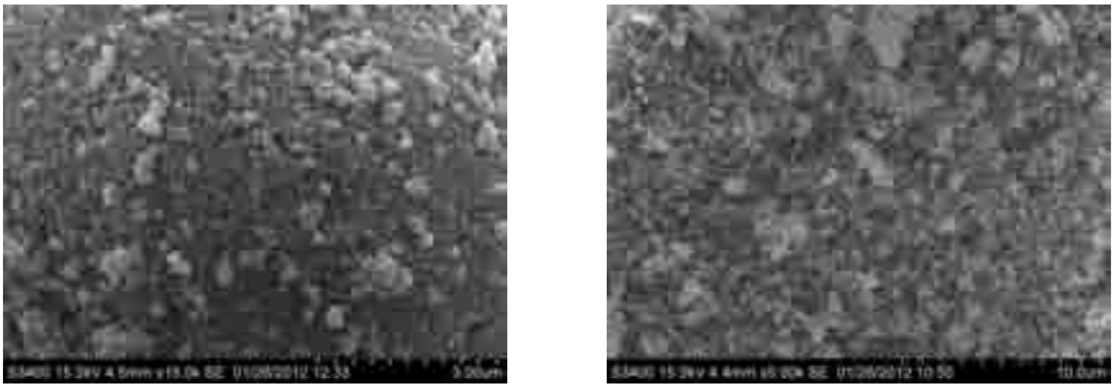
W



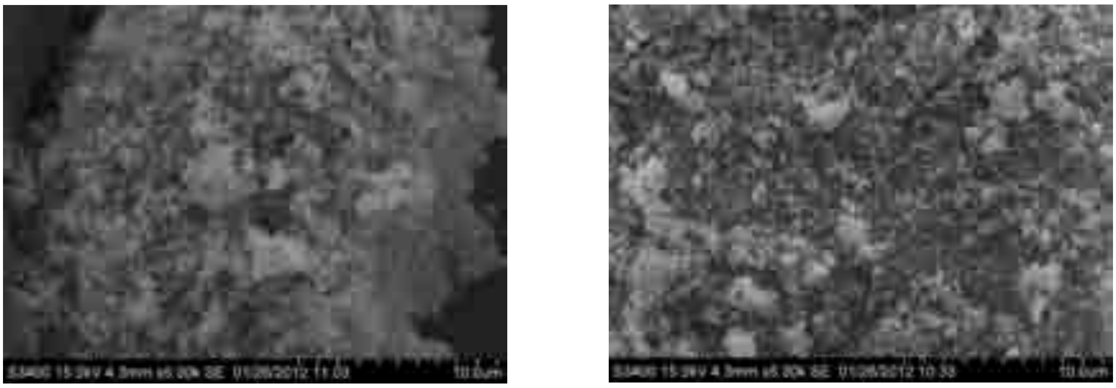
Ce

Y

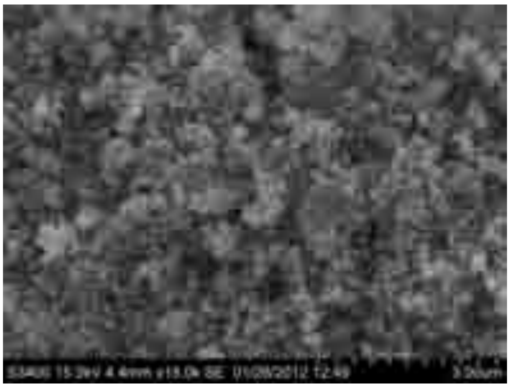
Figure 5.13 The SEM-EDS mapping of elements on Ce-Na_2WO_4-Mn/Y_2O_3 catalyst



YSZ **Na_2WO_4/YSZ**

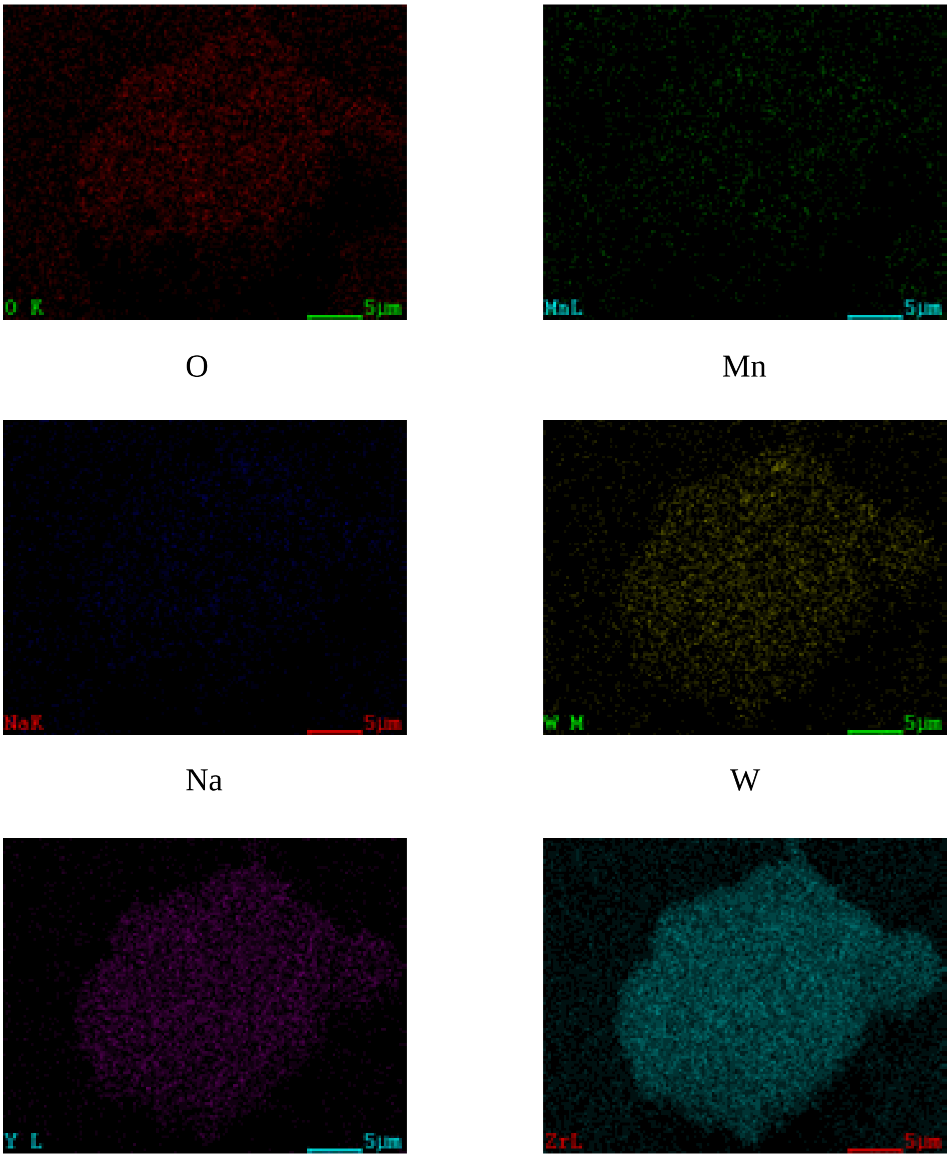


S-Na_2WO_4/YSZ **P-Na_2WO_4/YSZ**



Ce-Na_2WO_4/YSZ

Figure 5.14 Surface morphology of catalyst on YSZ support

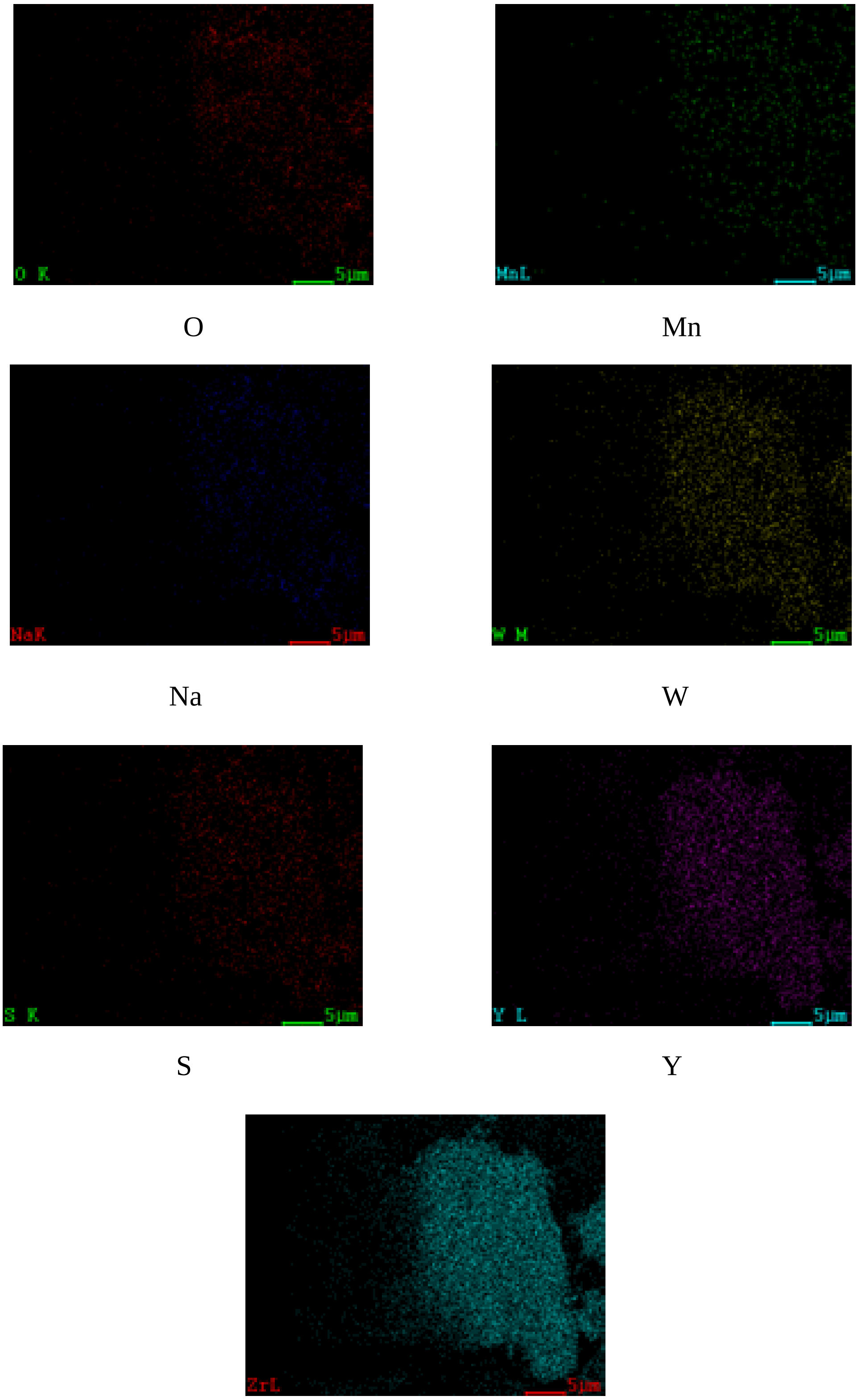


O Mn

Na W

Y Zr

Figure 5.15 The SEM-EDS mapping of elements on Na_2WO_4-Mn/YSZ catalyst



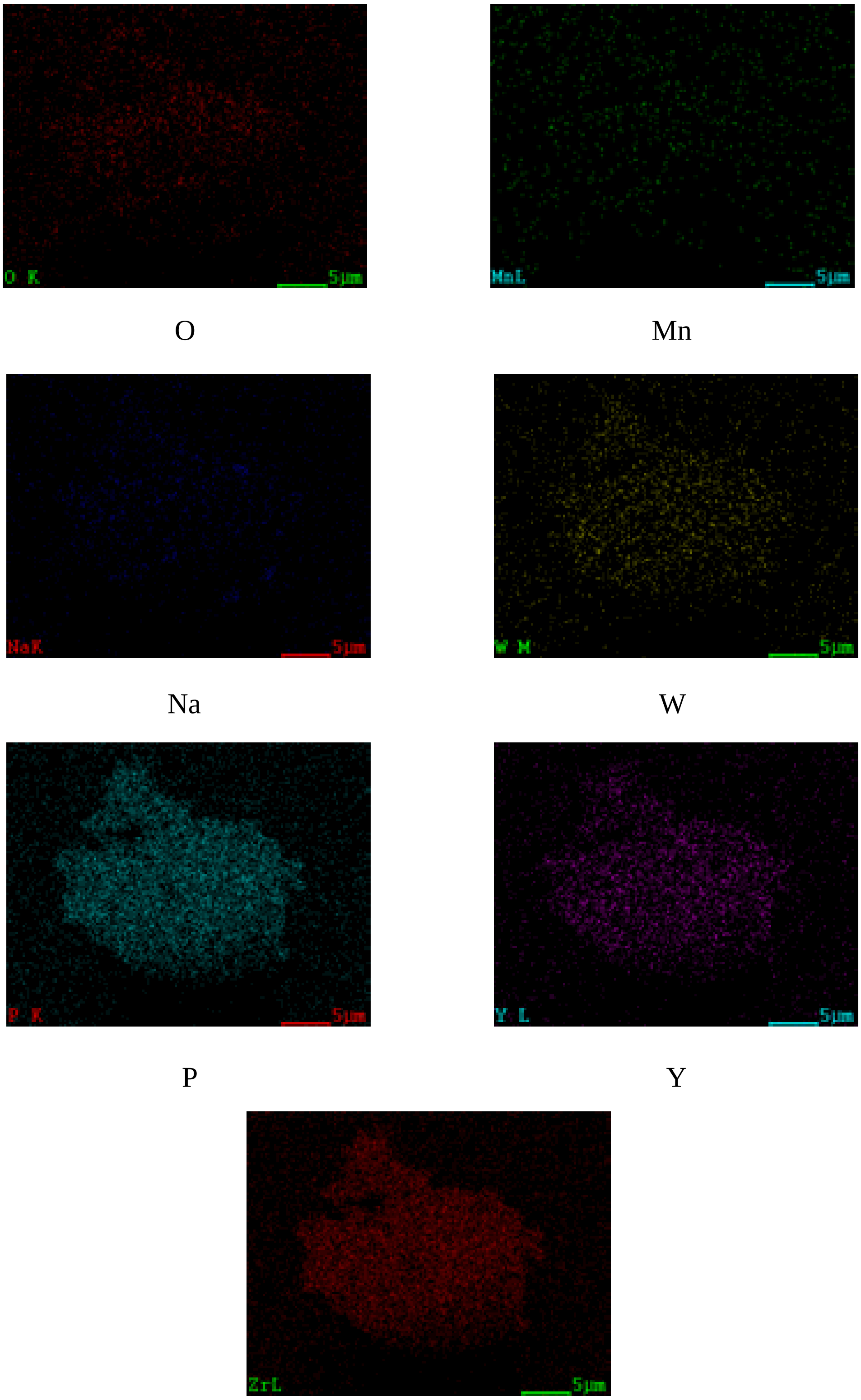
O Mn

Na W

S Y

Zr

Figure 5.16 The SEM-EDS mapping of elements on S-Na_2WO_4-Mn/YSZ catalyst



O

Mn

Na

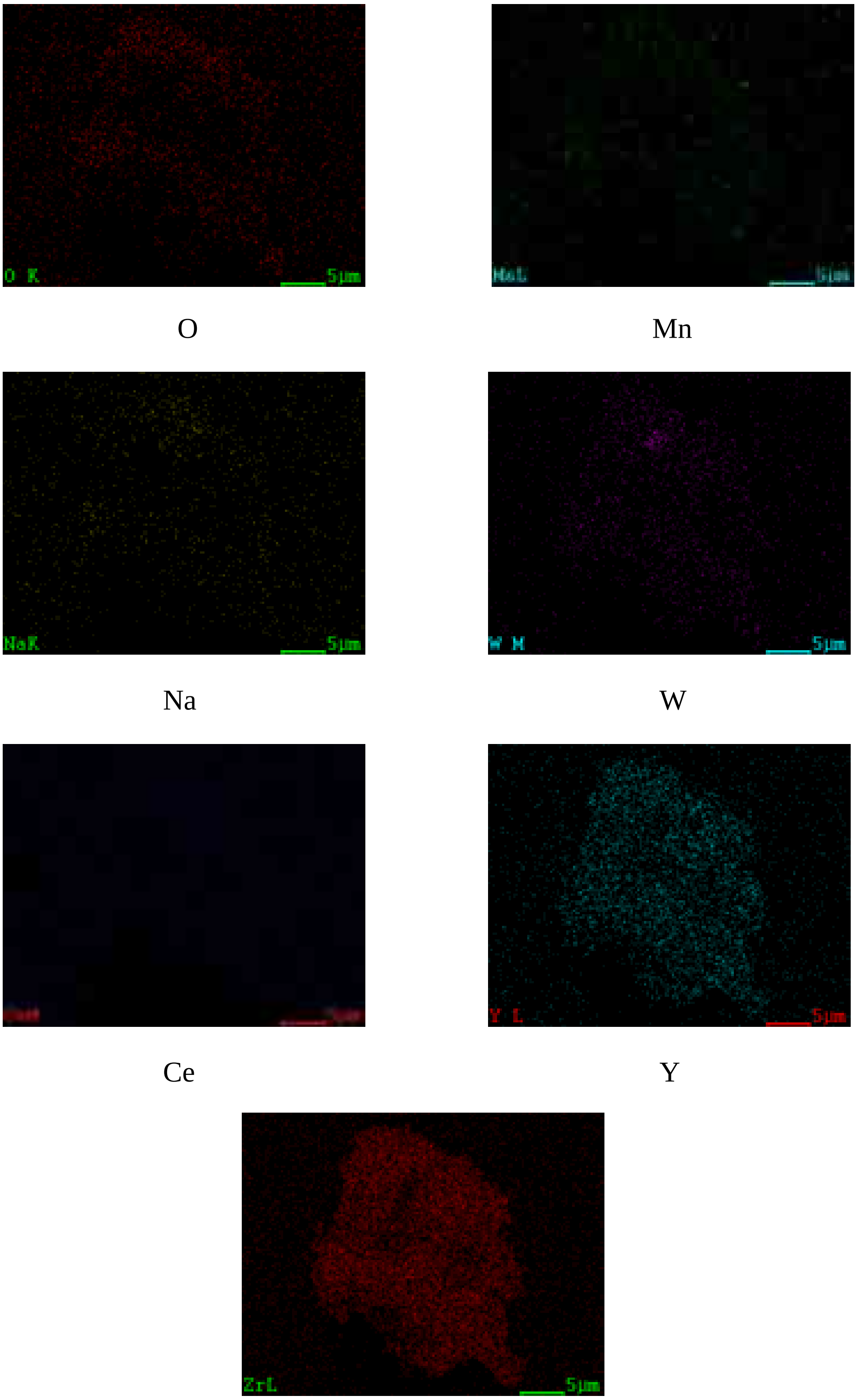
W

P

Y

Zr

Figure 5.17 The SEM-EDS mapping of elements on P-Na_2WO_4-Mn/YSZ catalyst



O

Mn

Na

W

Ce

Y

Zr

Figure 5.18 The SEM-EDS mapping of elements on Ce-Na_2WO_4-Mn/YSZ catalyst

From mapping of element on support La_2O_3, Y_2O_3, and YSZ catalyst it found dispersion of each element on surface support. The contents of Na, W, and Mn in the catalyst between 0.51-3.65%, 3.15-9.02%, and 1.55-5.69%, respectively, which was similar with Ji *et al.*, (2002). They reported high performance of Na_2WO_4-Mn/SiO_2 consist of the content 0.4–2.3% Na, 2.2–8.9% W, and 0.5–3.0% Mn. In other the percent content element did not far from theoretical.

5.1.3 Surface area and pore analysis

The surface area, total pore volume, average pore diameter of all supports and catalyst were analyzed by BET measurement. The BET surface area for the La_2O_3, Y_2O_3 and YSZ was 3.620, 3.886, and 11.263 m^2 g^{-1}, respectively. After the La_2O_3 supports was loaded with catalysts precursor, the BET surface area of the catalyst increased because active catalyst did not deposit in La_2O_3 support. On the other hand, when load the active catalysts to Y_2O_3 and YSZ support the decreasing of surface was observed. Table 5.1, 5.2, 5.3 shows the BET surface area, total pore volume and average pore each supports.

Table 5.1 The results of BET surface area, total pore volume and average pore diameter of La_2O_3 support catalyst

Catalyst	BET (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (nm)
La_2O_3	3.620	0.005	5.559
Na_2WO_4-Mn/La_2O_3	5.369	0.008	5.619
S-Na_2WO_4-Mn/La_2O_3	7.185	0.011	6.108
P-Na_2WO_4-Mn/La_2O_3	5.354	0.011	8.493
Ce-Na_2WO_4-Mn/La_2O_3	7.818	0.012	6.156

Table 5.2 The results of BET surface area, total pore volume and average pore diameter of Y_2O_3 support catalyst

Catalyst	**BET ($m^2\ g^{-1}$)**	**Total pore volume ($cm^3\ g^{-1}$)**	**Average pore diameter (nm)**
Y_2O_3	3.886	0.006	6.213
Na_2WO_4-Mn/Y_2O_3	2.645	0.005	6.928
S-Na_2WO_4-Mn/Y_2O_3	1.185	0.002	5.853
P-Na_2WO_4-Mn/Y_2O_3	1.095	0.002	7.999
Ce-Na_2WO_4-Mn/Y_2O_3	3.292	0.005	5.794

Table 5.3 The results of BET surface area, total pore volume and average pore diameter of YSZ support catalyst

Catalyst	**BET ($m^2\ g^{-1}$)**	**Total pore volume ($cm^3\ g^{-1}$)**	**Average pore diameter (nm)**
YSZ	11.263	0.021	7.534
Na_2WO_4-Mn/YSZ	7.483	0.015	7.875
S-Na_2WO_4-Mn/YSZ	7.716	0.012	6.171
P-Na_2WO_4-Mn/YSZ	5.789	0.009	6.628
Ce-Na_2WO_4-Mn/YSZ	6.954	0.009	5.566

5.1.4 Surface (XPS)

Table 5.7, 5.8, 5.9 showed the near surface elemental compositions of the fresh catalysts. In La_2O_3 support found tungsten between 1.19-5.16%, which was low when compared with other support. Moreover, sodium only found in P-Na_2WO_4-Mn/La_2O_3 catalyst but did not found manganese from all catalysts. In addition, sulfur and cerium did not found in S-Na_2WO_4-Mn/La_2O_3 and Ce-Na_2WO_4-Mn/La_2O_3 respectively. The elements loss from near surface of catalyst which consistent with the decreasing of BET surface area the most of active catalyst can not attach with La_2O_3 support. These effected to performance of the catalyst, which from the literature S and Ce can improve performance of catalyst (Zheng *et al*., 2010; Shahri and Pour, 2010). The missing of them make low performance. In case of Y_2O_3 support catalyst. It found high value of sulfur and oxygen on S-Na_2WO_4-Mn/Y_2O_3 about 22.48% and 39.06%, respectively. In addition, it found the sodium on the surface of P-Na_2WO_4-Mn/La_2O_3 catalyst was the highest value, but tungsten was the lowest. In Ce-Na_2WO_4-Mn/Y_2O_3 catalyst did not found of cerium on the surface which effected to performance of it. Generally, the active catalysts worked together therefore the Y_2O_3 support, which showed the active catalyst near surface it should be provide high activity for OCM reaction.

YSZ support catalyst near surface found sodium between 11.34 to 18.25% and found all elements loading near surface, which differ from other supports. In addition, it still provides higher oxygen on surface of catalyst than other supports that confirm the active components, such as W and Mn, enhances the storage capability of the active oxygen. The methane molecule was activated by oxygen species on the surface of the catalyst to methyl radical in first step (Gao and Ma, 2010) consistent with mapping of element.

Table 5.4 Surface composition (% at) of metal on La_2O_3 support

Catalyst	Na(1s)	W(4f)	Mn(2p)	S(2p)	P(2p)	Ce(3d)	La(3d)	O(1s)	
								La_2O_3	MO_x
La_2O_3	-	-	-	-	-	-	39.71	71.20	-
Na_2WO_4-Mn/La_2O_3	-	3.43	-	-	-	-	52.90	24.46	19.19
S-Na_2WO_4-Mn/La_2O_3	-	5.16	-	-	-	-	73.95	13.74	5.88
P-Na_2WO_4-Mn/La_2O_3	35.39	1.19	-	-	0.88	-	33.01	17.13	12.38
Ce-Na_2WO_4-Mn/La_2O_3	-	3.45	-	-	-	-	57.91	26.61	12.01

Table 5.5 Surface composition (% at) of metal on Y_2O_3 support

Catalyst	**Na(1s)**	**W(4f)**	**Mn(2p)**	**S(2p)**	**P(2p)**	**Ce(3d)**	**Y(3d)**	**O(1s)**	
								Y_2O_3	**MO_x**
Y_2O_3	-	-	-	-	-	-	23.20	53.31	-
Na_2WO_4-Mn/Y_2O_3	24.65	6.64	2.23	-	-	-	31.09	18.34	17.04
S-Na_2WO_4-Mn/Y_2O_3	9.63	6.39	1.20	22.48	-	-	21.22	20.34	18.72
P-Na_2WO_4-Mn/Y_2O_3	46.87	3.08	0.85	-	1.44	-	9.93	22.40	11.94
Ce-Na_2WO_4-Mn/Y_2O_3	26.39	8.48	2.17	-	-	-	27.21	18.78	16.94

Table 5.6 Surface composition (% at) of metal on YSZ support

Catalyst	**Na(1s)**	**W(4f)**	**Mn(2p)**	**S(2p)**	**P(2p)**	**Ce(3d)**	**Y(3d)**	**Zr(3d)**	**O(1s)**	
									YSZ	**MO_x**
YSZ	-	-	-	-	-	-	4.32	-	43.29	-
Na_2WO_4-Mn/YSZ	15.09	7.59	1.71	-	-	-	5.01	29.71	32.09	8.78
S-Na_2WO_4-Mn/YSZ	11.34	6.85	2.11	5.01	-	-	4.84	28.17	26.81	14.83
P-Na_2WO_4-Mn/YSZ	18.25	6.17	1.86	-	0.84	-	2.09	30.26	21.30	19.19
Ce-Na_2WO_4-Mn/YSZ	16.52	7.16	2.06	-	-	3.95	4.31	24.53	24.45	17.00

5.2 Part I: Performance of catalyst for OCM reaction in fixed bed reactor

The catalyst was divided into three categories according support, La_2O_3, Y_2O_3, YSZ. Each support showed the difference performance in OCM reaction.

5.2.1 La_2O_3 support

In normally the La_2O_3 support has a catalytic activity in OCM reaction. In this study La_2O_3 catalyst provided 23.4-27.8% methane conversion, 36.0-52.7% C_2 selectivity and 9.9-13.6% C_2 yield this result agreed with previous researches (Dedov *et al.*, 2003; Long *et al.*, 1995). When loading Na_2WO_4-Mn on La_2O_3 support the methane conversion increased about 3-5% whereas the C_2 selectivity decreased numerous from 30 to 17.7% at 973-1173 K. In S-Na_2WO_4-Mn/La_2O_3, P-Na_2WO_4-Mn/La_2O_3, and Ce-Na_2WO_4-Mn/La_2O_3 catalysts the performances did not differ from La_2O_3 support, which occurred from the near surface. The active phase such as sodium, manganese did not observe. This is main reason to explain La_2O_3 support catalyst provided low performance. In addition, most of all active catalysts loading did not deposit La_2O_3 support it could know from the increasing of surface area after load active catalyst which affect to low activity of catalyst because sodium, tungsten, and manganese work together on support. The performance of catalyst support showed the trend of the same direction when increase temperature from 973 to 1173 K. The methane conversion increased but decreasing of the C_2 selectivity was observed. The maximum C_2 yield was 13.8% of Ce-Na_2WO_4-Mn/La_2O_3 catalyst at 1073 K.

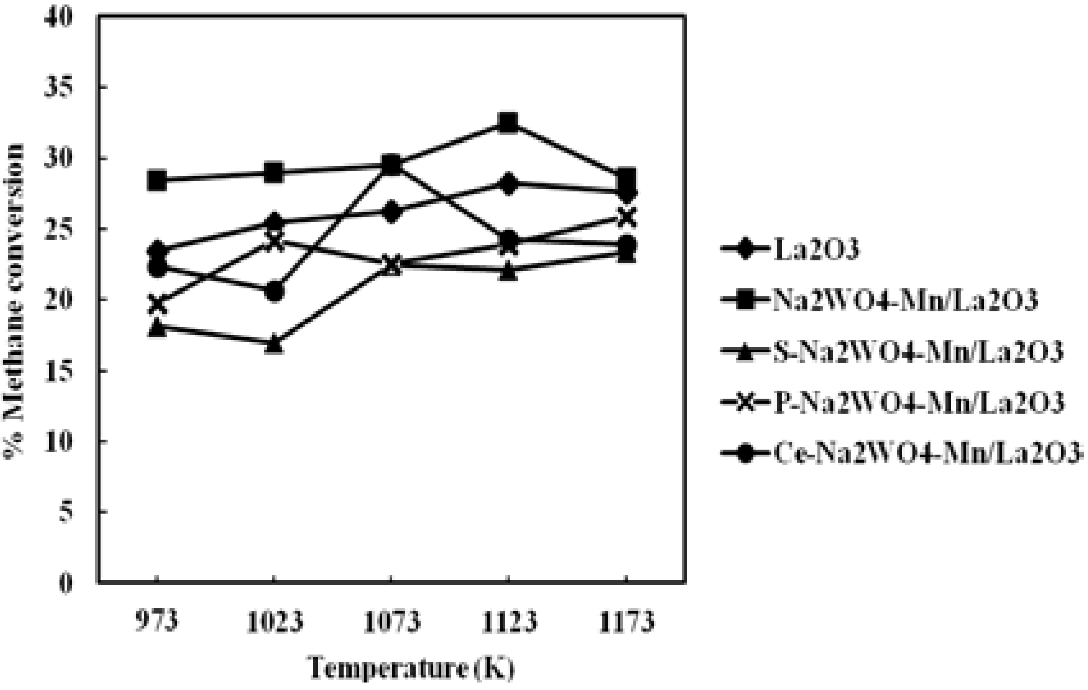


Figure 5.19 Methane conversion of La_2O_3 support catalyst with WHSV 15,000 $cm^3 \cdot g^{-1} \cdot h^{-1}$

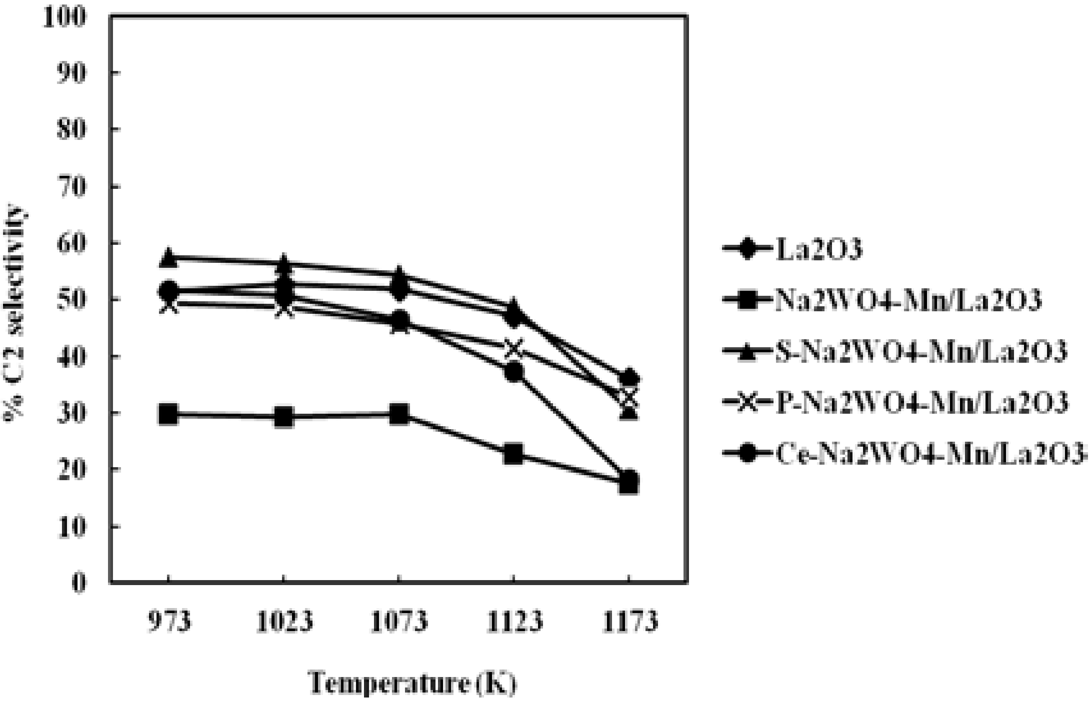


Figure 5.20 C_2 selectivity of La_2O_3 support catalyst with WHSV 15,000 $cm^3 \cdot g^{-1} \cdot h^{-1}$

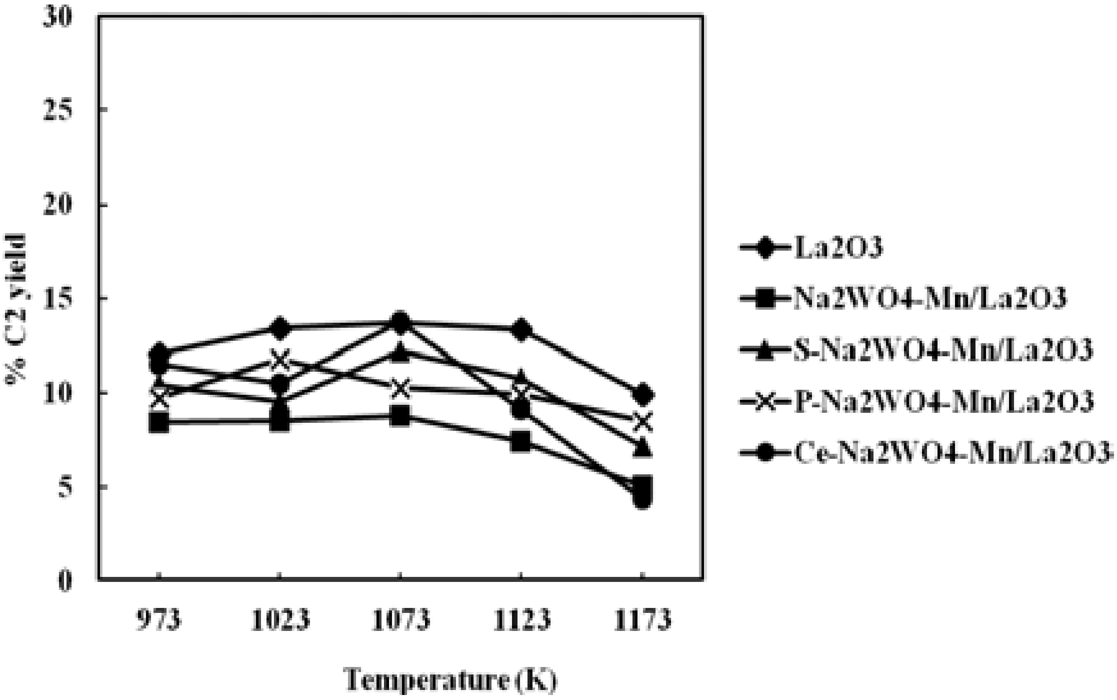


Figure 5.21 C_2 yield of La_2O_3 support catalyst with WHSV 15,000 $cm^3 \cdot g^{-1} \cdot h^{-1}$

5.2.2 Y_2O_3 support

The Y_2O_3 catalyst from previous research showed the performance consisted with this study (Dedov *et al.*, 2003). 21.2-28.8% methane conversion, 33.0-46.6% C_2 selectivity was obtained from only Y_2O_3 support .When added Na_2WO_4-Mn on Y_2O_3 support, the methane conversion unchanged, but provided the lower C_2 selectivity. In S-Na_2WO_4-Mn/Y_2O_3 and P-Na_2WO_4-Mn/Y_2O_3 catalyst at 973 and 1023 K provided methane conversion relatively low not more than 13%, but the highest C_2 selectivity were obtained at 1023 K. The reason was sulfur to help the active phase such as Na_2SO_4 occurred and phosphorus could help manganese to form Mn_2O_3 which was the active phase. After that at high temperature (1073-1173 K) the C_2 selectivity rapidly decreased which was caused by carbon decomposition from methane it knowed from decreasing of surface area and SEM-EDS. Cerium loading in Na_2WO_4-Mn/Y_2O_3 catalyst was significant to the performance of catalyst, which provided the low methane conversion and C_2 selectivity. From XPS result did not find cerium on Ce-Na_2WO_4-Mn/Y_2O_3 catalyst which effected to performance of catalyst. The maximum C_2 yield was 17.0% from P-Na_2WO_4-Mn/Y_2O_3 catalyst at 1123 K.

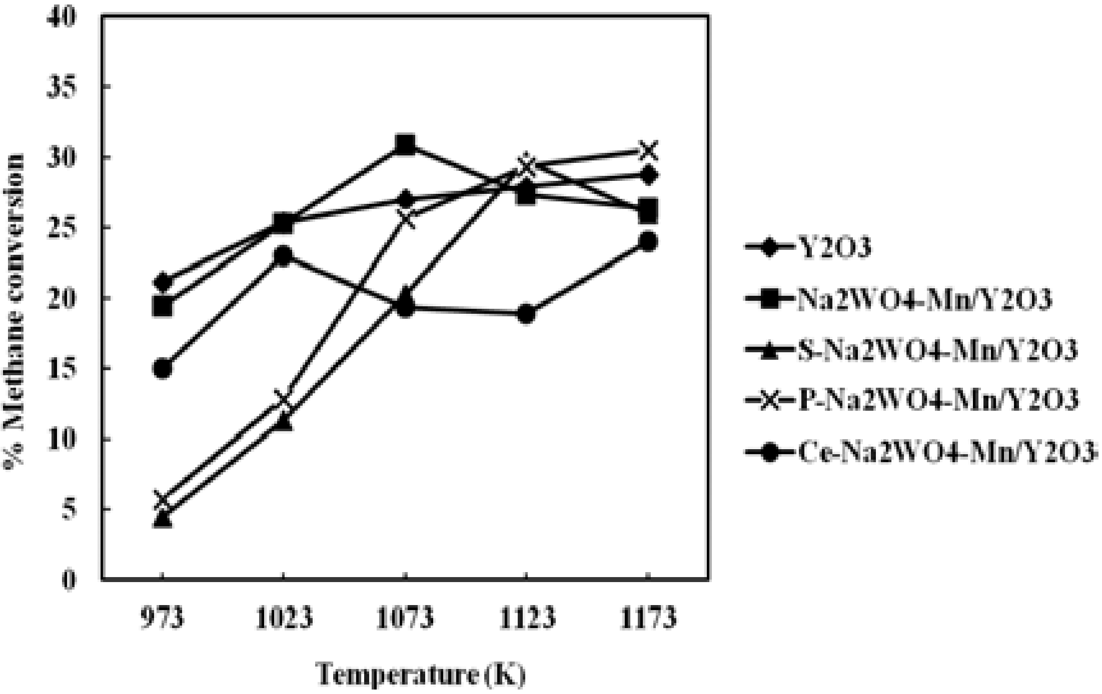


Figure 5.22 Methane conversion of Y_2O_3 support catalyst with WHSV 15,000 $cm^3 \bullet g^{-1} \bullet h^{-1}$

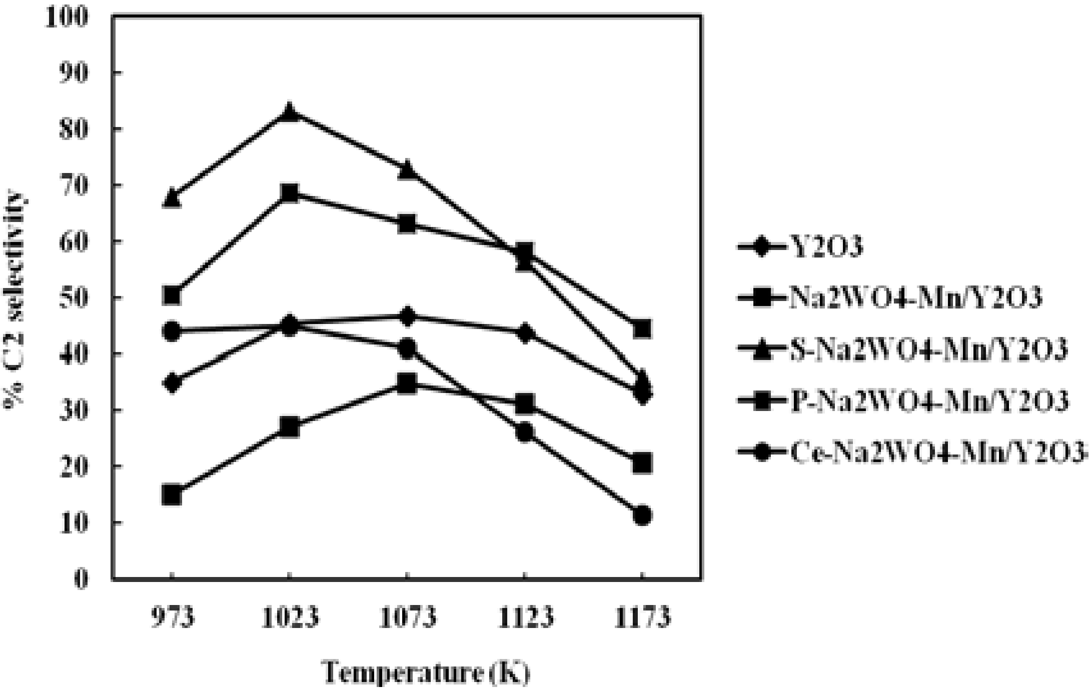


Figure 5.23 C_2 selectivity of Y_2O_3 support catalyst with WHSV 15,000 $cm^3 \bullet g^{-1} \bullet h^{-1}$

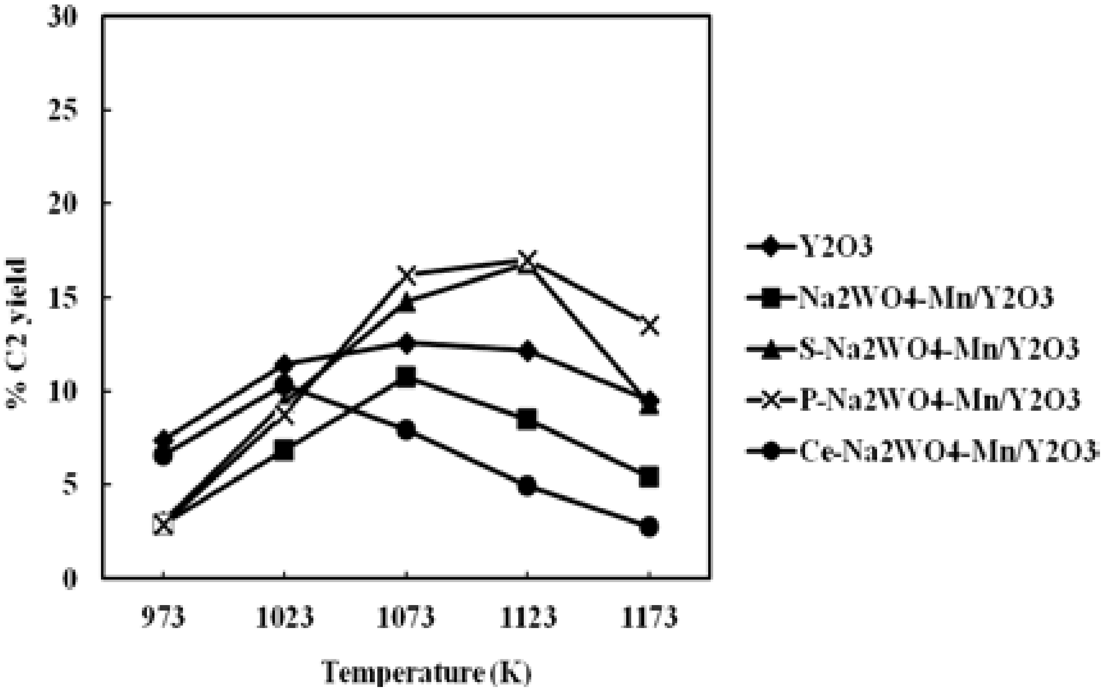


Figure 5.24 C_2 yield of Y_2O_3 support catalyst with WHSV 15,000 $cm^3 \bullet g^{-1} \bullet h^{-1}$

5.2.3 YSZ support

YSZ support showed the performance of OCM reaction, which provided methane conversion between 26.8-29.8% and C_2 selectivity between 17.1-29.7%. The YSZ support exhibited the higher methane conversion when compared with other supports. When a Na_2WO_4-Mn was added to YSZ support, the catalyst was higher C_2 selectivity than YSZ support, which showed 27.5-52.1%. for the C_2 selectivity. However methane conversion was lower than YSZ support. The S-Na_2WO_4-Mn/YSZ and P-Na_2WO_4-Mn/YSZ showed the high performance in OCM reaction. The maximum C_2 yield from P-Na_2WO_4-Mn/YSZ was 20.3% at 1073 K whereas S-Na_2WO_4-Mn/YSZ catalyst did not differ from P-Na_2WO_4-Mn/YSZ, which provided 18.7% C_2 yield at 1073 K. The sulfur helped the active phase such as Na_2SO_4 occurred and phosphorus can help manganese to form Mn_2O_3 which was the active phase. In case of cerium doped into Na_2WO_4-Mn/YSZ observed the decreasing of methane conversion and C_2 selectivity when compared with Na_2WO_4-Mn/YSZ, as shown in figure 5.25-5.27.

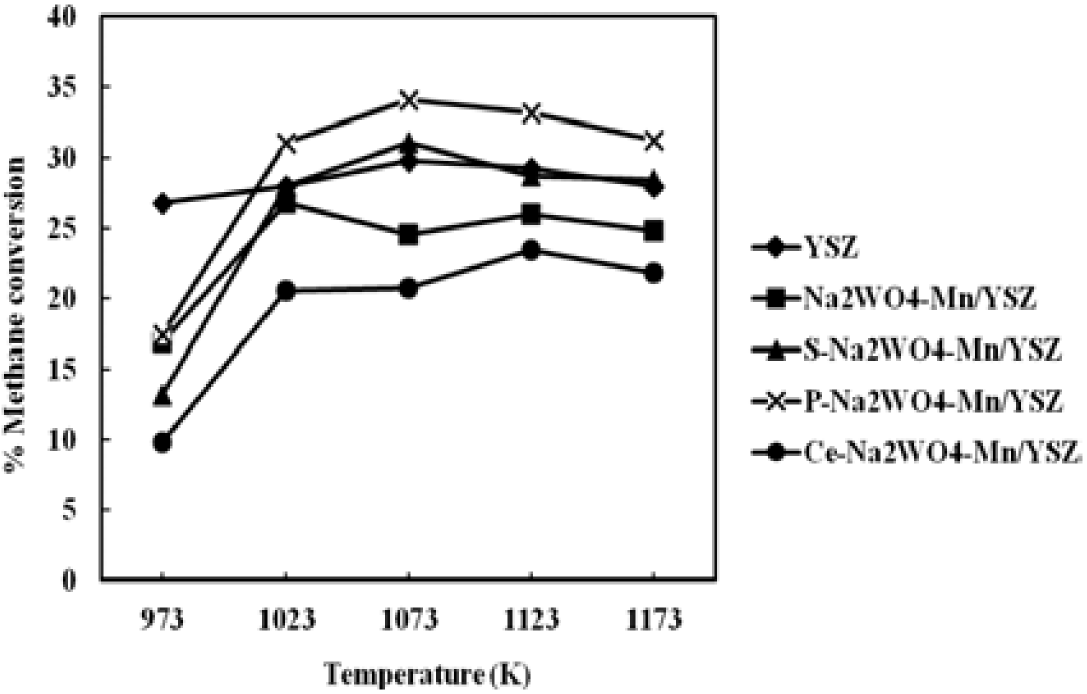


Figure 5.25 Methane conversion of YSZ support catalyst with WHSV 15,000 cm^3•g^{-1}•h^{-1}

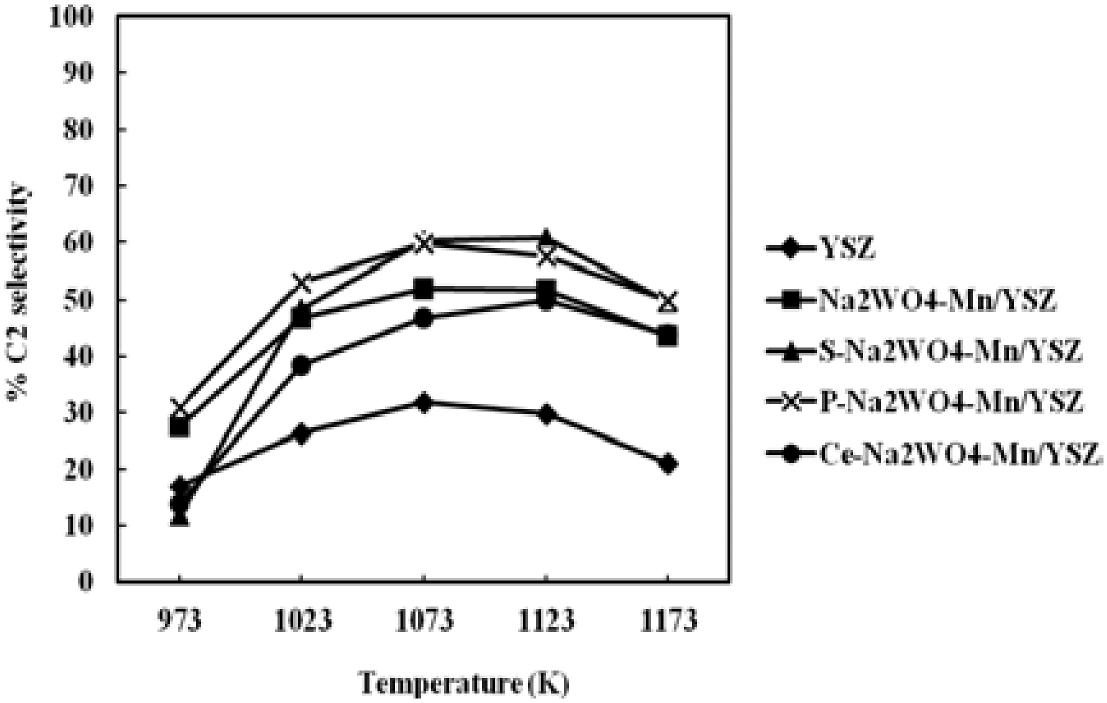


Figure 5.26 C_2 selectivity of YSZ support catalyst with WHSV 15,000 cm^3•g^{-1}•h^{-1}

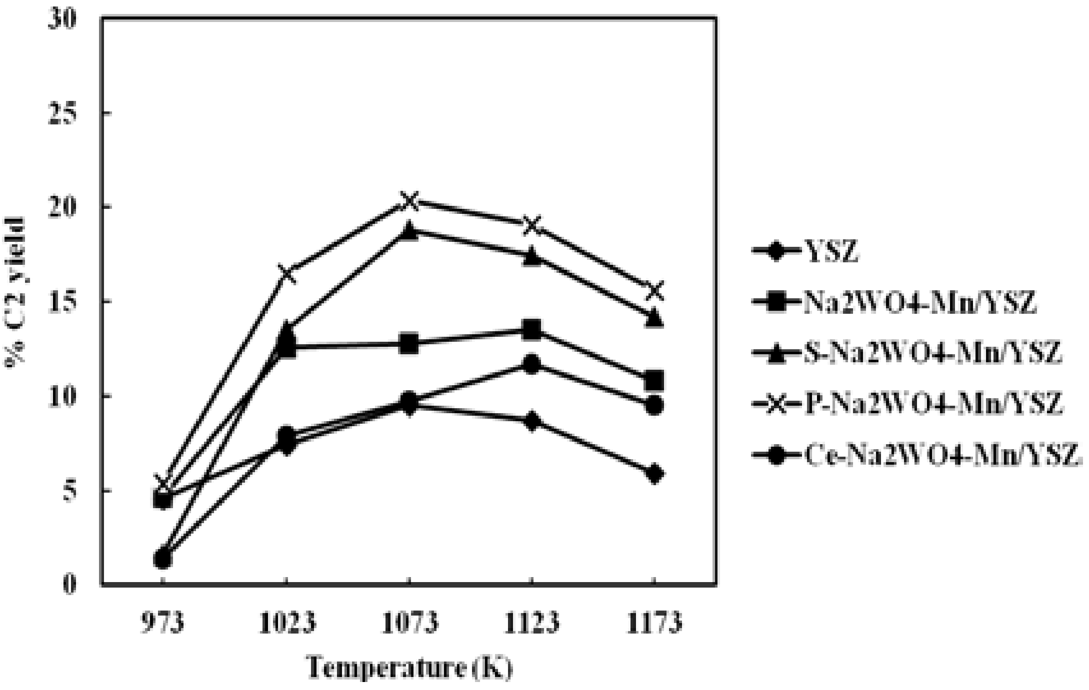


Figure 5.27 C_2 yield of YSZ support catalyst with WHSV 15,000 $cm^3 \cdot g^{-1} \cdot h^{-1}$

5.2.4 Compare the performance of the catalyst in fixed bed reactor

The activity test in fixed bed reactor for OCM reaction from all catalyst it found that the suitable operating temperature in rang 1023-1123 K, which in this interval the catalyst provided the high C_2 yield. However in case of La_2O_3 support catalyst showed the lower performance than other; the maximum C_2 yield only 13.8% C_2 yield at 1073 K obtained from Ce-Na_2WO_4-Mn/La_2O_3 catalyst. The main reason for La_2O_3 support catalyst provided the low performance because it did not found the active phase such as Na, and Mn near surface of catalyst. The catalysts especially sulfur and phosphorous dopped on Y_2O_3 and YSZ support showed the better performance The S-Na_2WO_4-Mn/Y_2O_3, and P-Na_2WO_4-Mn/Y_2O_3 catalysts provided the maximum C_2 yield is 16.82% and 17.02%, respectively at 1123 K. 18.77% and 20.39% C_2 yield at 1073 K obtained from the S-Na_2WO_4-Mn/YSZ, and P-Na_2WO_4-Mn/YSZ catalyst, respectively. In case of Ce promoted Na_2WO_4-Mn/Y_2O_3 catalyst it showed the low performance at 1123 K, which did not consistent with some researchers. (Shahri and Pour, 2010; Zhang *et al.*, 2007) It did not show the cerium near surface of catalyst while in Ce-Na_2WO_4-Mn/YSZ support provided 11.7% C_2 yield at 1123 K not far from literature (15-19% C_2 yield).

There are several reasons for that help the performance of YSZ support catalysts. Yoon and Seo, (1996) studied in sodium salt-promoted zirconia catalysts that the catalyst showed the maximum yield about 16.6% which consistent with Zheng *et al.*, (2010) reported ZrO_2 helps activation of CH_4. Moreover, Murata *et al.*, (1998) investigated in zirconia, and sulfated-zirconia catalyst the experiment result showed zirconia catalyst provided 2% C_2 yield and 4% C_2 yield obtained from sulfated-zirconia catalyst that indicated sulfated could help the performance of catalyst for OCM reaction. In additional, S and P promoted YSZ support from XPS result showed higher oxygen on surface than other supports enhanced the storage capability of the active oxygen. There were significant difference between Y_2O_3 support and YSZ support in term of methane conversion and C_2 selectivity. In Y_2O_3 support exhibited lower methane conversion than YSZ support, because of low surface area.

In normally, Na_2WO_4-Mn/SiO_2 catalyst was reported in several researchers. Ji *et al.*, (2003) reported Na_2WO_4–Mn/SiO_2 catalyst provided 28.9% methane conversion, 66.6% C_2 selectivity and 19.3% C_2 yield. Wang *et al.*, (1995) investigated in this catalyst; the methane conversion and C_2 selectivity were 20% and 80%, respectively. It was not different with S-Na_2WO_4-Mn/YSZ catalyst and P-Na_2WO_4-Mn/YSZ catalyst in this works.

5.3 Part II: OCM in SOFC reactor for C_2H_4 hydrocarbon and electricity co-generation

After experiment in fixed bed reactor the Na_2WO_4-Mn/YSZ, S-Na_2WO_4-Mn/YSZ and, P-Na_2WO_4-Mn/YSZ was selected to test in SOFC reactor for investigate the performance to produce C_2 and electrical current. In addition, the stability of catalyst is interesting in this work, which chooses the best catalyst and condition to carry out. The performance of catalysts and electrical current showed in figure and table below, respectively.

5.3.1 The performance of Na_2WO_4-Mn/YSZ catalyst in SOFC reactor

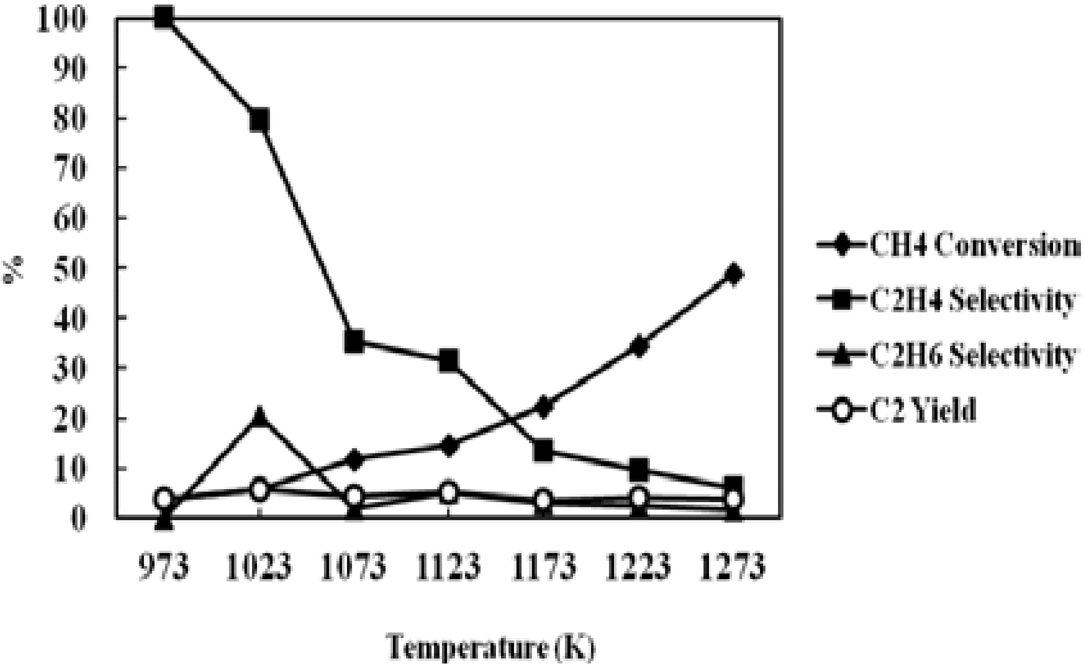


Figure 5.28 Performance of Na_2WO_4-Mn/YSZ catalyst in SOFC reactor

Table 5.7 The electric power at each temperature for Na_2WO_4-Mn/YSZ catalyst in SOFC reactor

Temp (K)	Current (mA)	Oxygen consumption ($mol \cdot s^{-1}$)
973	2.20	1.57E-08
1023	4.50	1.71E-08
1073	11.00	1.91E-08
1123	15.50	2.01E-08
1173	35.00	8.84E-08
1223	90.00	1.26E-07
1273	145.00	1.72E-07

The Na_2WO_4-Mn/YSZ catalyst showed the highest C_2H_4 selectivity at 973 K. It found that increased temperature, the C_2H_4 selectivity decreased because the carbon decomposition of methane covers the active site of catalyst. On the other hand methane conversion increased when increasd temperature; a maximum C_2H_4 yield was 4.59% at 1123 K. The C_2 yield obtained from Na_2WO_4-Mn/YSZ catalyst was low which caused from the preparation of anode catalyst in paste method that was not good dispersion of catalyst on electrolyte. In term of electrical current when increased temperature, the electrical current go up that caused the higher oxygen permeate from cathode side to anode side encouraged to discharge and receive of electron. The maximum current density was 25.58 W/m^2 at 1273 K and the voltages were in rang 1.0-1.1 V.

5.3.2 The performance of S-Na_2WO_4-Mn/YSZ catalyst in SOFC reactor

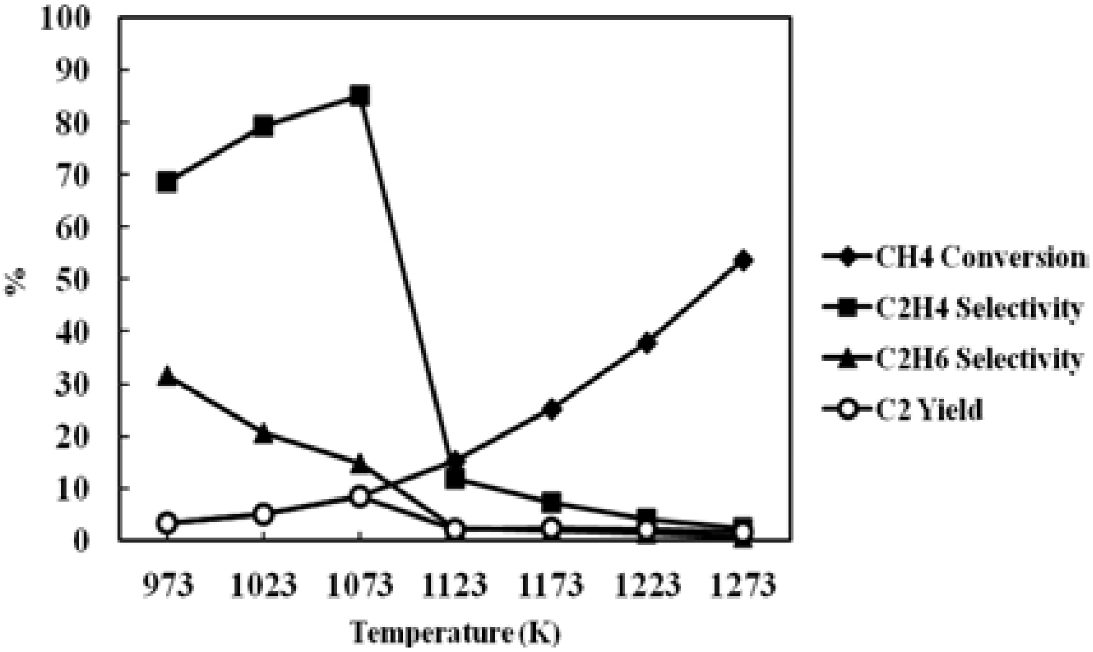


Figure 5.29 Performance of S-Na_2WO_4-Mn/YSZ catalyst in SOFC reactor

Table 5.8 The electric power at each temperature for S-Na_2WO_4-Mn/YSZ catalyst in SOFC reactor

Temp (K)	**Current (mA)**	**Oxygen consumption (mol•s^{-1})**
973	0.10	1.90E-09
1023	0.16	3.11E-09
1073	2.00	2.70E-08
1123	18.10	5.00E-08
1173	40.00	8.00E-08
1223	60.00	1.43E-07
1273	85.00	1.54E-07

In case of The S-Na_2WO_4-Mn/YSZ catalyst, the maximum C_2H_4 yield was 7.21% at 1073 K, which was higher than Na_2WO_4-Mn/YSZ catalyst. The maximum current density of S-Na_2WO_4-Mn/YSZ catalyst was 15.0 W/m^2, which was lowers than Na_2WO_4-Mn/YSZ catalyst and the voltages was similar to Na_2WO_4-Mn/YSZ catalyst. At high temperature the catalyst actived with partial oxidation than OCM.

5.3.3 The performance of P-Na_2WO_4-Mn/YSZ catalyst in SOFC reactor

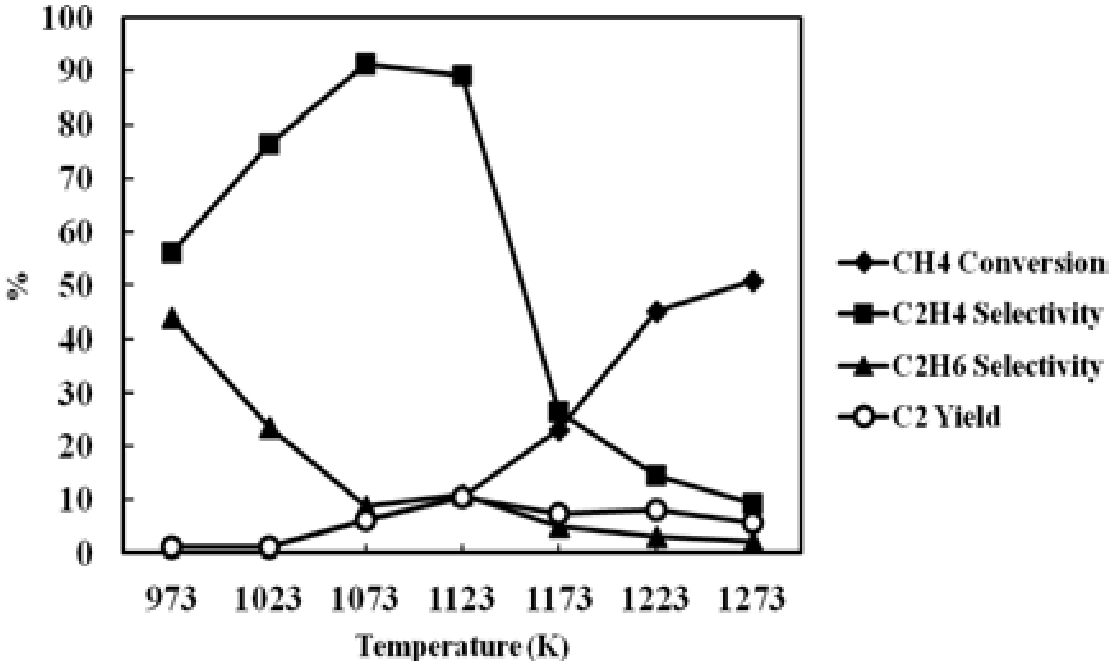


Figure 5.30 Performance of P-Na_2WO_4-Mn/YSZ catalyst in SOFC reactor

Table 5.9 The electric power at each temperature for P-Na_2WO_4-Mn/YSZ catalyst in SOFC reactor

Temperature (K)	**Current (mA)**	**Oxygen consumption ($mol \bullet s^{-1}$)**
973	12.00	1.68E-08
1023	17.50	1.74E-08
1073	35.00	3.40E-08
1123	75.00	5.14E-08
1173	95.00	1.69E-07
1223	145.00	2.09E-07
1273	185.00	3.39E-07

The P-Na_2WO_4-Mn/YSZ catalyst exhibited the best performance in SOFC. The highest C_2H_4 selectivity was approximately 91.2% at 1123 K and could be operated in temperature range between 973-1123 K whereas the C_2H_4 selectivity did not decreases. The maximum C_2 yield was 10.5% and provided current density about 13.2 W/m^2 at 1123 K. The maximum current density was 32.6 W/m^2 at 1273 K and the voltage was similar others. In case OCM in SOFC reactor for C_2H_4 hydrocarbon and electricity co-generation have a few reports , Tagawa *et al*., (1998) used $La_{1.8}Al_{0.2}O_3$ as the anode catalyst with a plate-type Yttria Stabilized Zirconia (YSZ) as a solid electrolyte and $La_{0.85}Sr_{0.15}MnO_3$ as a cathode the experiment provided 4.0% methane conversion and 96% C_2 selectivity. The electrical current and voltage were 10.1 mA and 0.96 V, respectively or power densities was estimated 13.85 W/m^2. After that they carried out in SOFC co-generation, which used the same anode and cathode catalyst but using the YSZ tube was electrolyte. It was high effective area the experiment result showed higher methane conversion about 13% and 5% C_2 yield at 1223 K then provided power density about 13.37 W/m^2. In addition, Lapeña-Rey and

Middleton, (2003) investigated in Na_2WO_4-Mn/SiO_2 and K_2WO_4-Mn/SiO_2 in co-feed mode and electrochemical mode at 1123 K. It found that the best performance was 86% C_2 selectivity, and 4% C_2 yield obtained from potassium tungstate supported catalysts in electrochemical mode. In case of the Na_2WO_4-Mn/SiO_2 catalyst from this literature provided lower C_2 selectivity (70.5-87.6%) than the P-Na_2WO_4-Mn/YSZ catalyst at 1123 K.

Moreover, the P-Na_2WO_4-Mn/YSZ catalyst showed the best performance in this work for SOFC reactor provided 10.5% C_2 yield which exhibited higher performance than Lapeña-Rey and Middleton, (2003). In addition, the maximum C_2 yield was obtained at 1123K which lowers operating temperature than Worapon, (2004) he reported about 3% C_2 yield at 1173K. However, C_2 yield were still low that caused the rate of oxygen permeates through YSZ membrane to form oxygen species did not match with methane consume oxygen species to produce methyl radical, which methyl radical coupling occurred to C_2 product. When the oxygen permeated rate greater than rate of consume, The O^{2-} may be combined to form O_2, which reaction with methane to form CO_x. If the oxygen permeate rate was lower than rate of consume occurred the low C_2 yield. The other reason was the rate of oxygen permeates through YSZ membrane was low lead to methane cracking to generated carbon and hydrogen.

5.4 Stability test for P-Na_2WO_4-Mn/YSZ catalyst

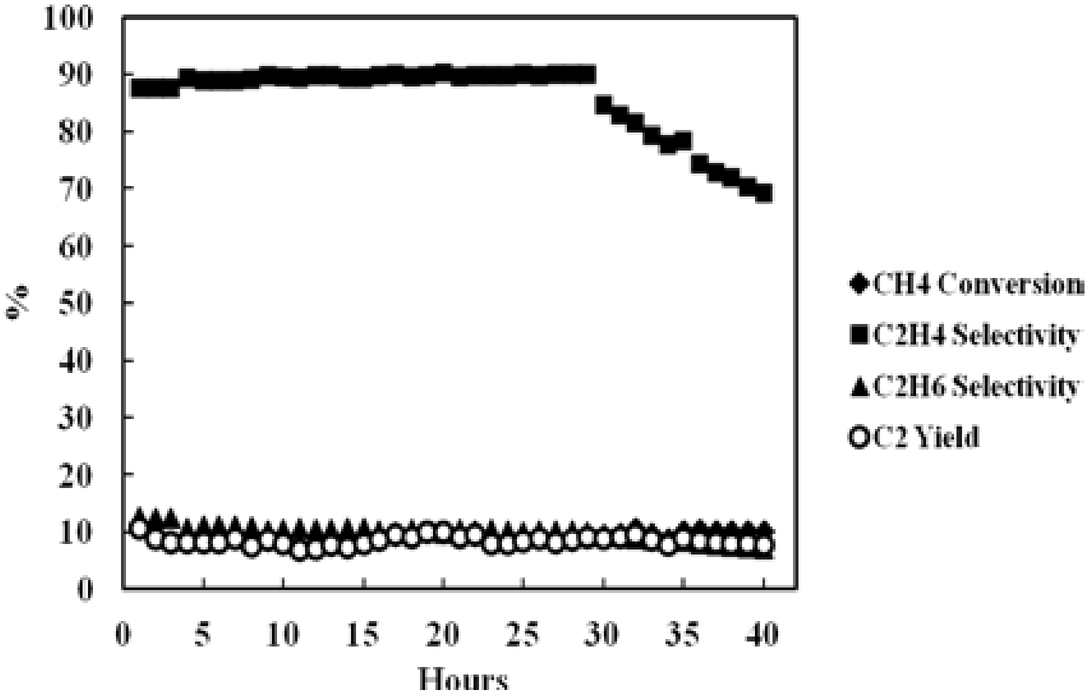


Figure 5.31 Stability test of P-Na_2WO_4-Mn/YSZ catalyst in SOFC reactor at 1123 K

The P-Na_2WO_4-Mn/YSZ catalyst was examined in SOFC reactor. The catalyst exhibited the activity and stability at 1123 K. The catalyst provided about 8.9% methane conversion and 8.0% C_2 yield. It showed the good performance for 29 hours, after that the C_2H_4 selectivity was decrease because occurred the carbon deposition on catalysts. These results coincided with BET results as shown in table 5.10. The catalyst showed lower surface area, and total pore volume than before operated.

Table 5.10 The surface area of catalyst after operated in SOFC reactor for P-Na_2WO_4-Mn/YSZ stability test at 1123 K

Catalyst	**BET** **(m^2 g^{-1})**
P-Na_2WO_4-Mn/YSZ	5.789
Stability test	1.909*

*After operated in SOFC reactor

CHAPTER VI
CONCLUSION

6.1 Conclusion

Oxidative coupling of methane (OCM) reaction was studied in this research for find suitable catalyst and electrical conductivity and applied as anode material in solid oxide fuel cell (SOFC) reactor. The catalyst support (La_2O_3, Y_2O_3, and YSZ) is the semi-conductor material was used in this study. The active phase of catalyst is Na_2WO_4, Mn. It was doped in each support for compare performance of catalyst. The experiment results were divided into two parts. Part I: Performance of catalyst for OCM reaction in fixed bed reactor and Part II: OCM in SOFC reactor for C_2 hydrocarbon and electricity co-generation.

6.1.1 Part I: Performance of catalyst for OCM reaction in fixed bed reactor

The Na_2WO_4-Mn catalyst in three supports (La_2O_3, Y_2O_3, and YSZ) was prepared by incipient wetness impregnation method. It found that the catalyst in La_2O_3 support showed lower performance than others, which caused in XPS characterization to analyst near surface of catalyst. It did not found active phases such as Na_2WO_4, $Na_2W_2O_7$, Na_2SO_4, Mn_2O_3. In La_2O_3 support the Ce-Na_2WO_4-Mn/La_2O_3 catalyst showed the best performance provided 29.6% methane conversion, 46.6% C_2 selectivity, and 13.8% C_2 yield. In Y_2O_3, and YSZ support the catalyst showed the active phase near surface of catalyst. The catalyst in Y_2O_3, and YSZ support exhibited the high performance especially S-Na_2WO_4-Mn/Y_2O_3, P-Na_2WO_4-Mn/Y_2O_3, S-Na_2WO_4-Mn/YSZ, and P-Na_2WO_4-Mn/YSZ. The best performance 34.1% methane conversion, 59.8% C_2 selectivity, and 20.4% C_2 yield were obtained from P-Na_2WO_4-Mn/YSZ.

6.1.2 Part II: OCM in SOFC reactor for C_2H_4 hydrocarbon and electricity co-generation

The Na_2WO_4-Mn/YSZ, S-Na_2WO_4-Mn/YSZ, and P-Na_2WO_4-Mn/YSZ catalyst were selected to operate in SOFC reactor to generated C_2H_4 hydrocarbon and electricity co-generation. The experiment result showed the methane conversion increased with increased operating temperature of all catalysts. In case of P-Na_2WO_4-Mn/YSZ catalyst, C_2H_4 selectivity decreased after operating temperature over 1123 K. In case of Na_2WO_4-Mn/YSZ, the C_2H_4 selectivity of S-Na_2WO_4-Mn/YSZ catalyst decreased after 1073 K. The P-Na_2WO_4-Mn/YSZ catalysts showed the best performance in SOFC (10.5% of C_2 yield, 89% C_2H_4 selectivity at 1123 K) and provided current density, 13.2 W/m^2 at 1123 K. When comparing with Lapeña-Rey and Middleton, (2003) K_2WO_4-Mn/SiO_2 catalyst provided 4% C_2 yield at 1123 K. The P-Na_2WO_4-Mn/YSZ catalysts in this work provided higher C_2 yield (10.5% C_2 yield) at 1123 K. In addition, the maximum C_2 yield was obtained at 1123 K ,which was lowers operating temperature than Worapon, (2004), that reported about 3% C_2 yield at 1173K. The stability test exhibited at least 29 hours in P-Na_2WO_4-Mn/YSZ catalysts and the catalyst deactivated because of carbon decomposition from methane cracking.

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APPENDICES

APPENDIX A

DATA FOR CATALYTIC PERFORMANCE EVALUATION

Table A.1: Response factor for calculating the gas concentration.

Gas Composition	Response Factor
CH_4	3.00E-11
O_2	5.88E-11
C_2H_4	4.00E-11
C_2H_6	4.00E-11
CO	7.00E-11
CO_2	1.00E-10
H_2	6.00E-09

APPENDIX B

THE DATA FOR CATALYTIC PERFORMANCE IN FIXED BED AND SOFC REACTOR

I Fixed bed reactor

La_2O_3 support

Table B.1 La_2O_3 catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	23.5	51.5	12.1
1023	25.4	52.8	13.4
1073	26.3	52.0	13.7
1123	28.2	47.2	13.3
1173	27.6	36.0	10.0

Table B.2 Na_2WO_4-Mn/La_2O_3 catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	28.4	29.8	8.5
1023	29.0	29.4	8.5
1073	29.5	29.8	8.8
1123	32.5	22.8	7.4
1173	28.6	17.7	5.1

Table B.3 S-Na_2WO_4-Mn/La_2O_3 catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	18.1	57.55	10.4
1023	16.9	56.4	9.5
1073	22.5	54.3	12.2
1123	22.1	48.7	10.7
1173	23.4	30.6	7.2

Table B.4 P-Na_2WO_4-Mn/La_2O_3 catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	19.7	49.5	9.8
1023	24.2	48.8	11.8
1073	22.5	45.8	10.31
1123	23.9	41.6	9.9
1173	25.9	32.9	8.5

Table B.5 Ce-Na_2WO_4-Mn/La_2O_3 catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	22.3	51.6	11.5
1023	20.7	50.9	10.5
1073	29.6	46.6	13.8
1123	24.3	37.5	9.1
1173	23.9	18.2	4.4

Y_2O_3 support

Table B.6 Y_2O_3 catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	21.2	35.1	7.4
1023	25.3	45.3	11.5
1073	27.0	46.7	12.6
1123	27.9	43.7	12.2
1173	28.8	33.1	9.5

Table B.7 Na_2WO_4-Mn/Y_2O_3 catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	19.4	15.1	2.9
1023	25.3	27.2	6.9
1073	30.9	34.8	10.8
1123	27.4	31.2	8.5
1173	26.4	20.7	5.5

Table B.8 S-Na_2WO_4-Mn/Y_2O_3 catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	4.5	67.8	3.1
1023	11.3	83.1	9.4
1073	20.3	72.9	14.8
1123	29.8	56.5	16.8
1173	26.0	35.8	9.3

Table B.9 P-Na_2WO_4-Mn/Y_2O_3 catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	5.7	50.5	2.9
1023	12.8	68.5	8.8
1073	25.6	63.2	16.2
1123	29.4	58.0	17.0
1173	30.6	44.4	13.6

Table B.10 Ce-Na_2WO_4-Mn/Y_2O_3 catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	15.0	43.9	6.6
1023	23.0	44.9	10.3
1073	19.4	41.1	8.0
1123	18.9	26.2	5.0
1173	24.0	11.6	2.8

YSZ support

Table B.11 YSZ catalyst

Temperature (K)	**CH_4 conversion**	**C_2 selectivity**	**C_2 yield**
973	26.8	17.1	4.6
1023	27.9	26.4	7.4
1073	29.8	31.8	9.5
1123	29.3	29.7	8.7
1173	28.0	21.2	5.9

Table B.12 Na_2WO_4-Mn/YSZ catalyst

Temperature (K)	**CH_4 conversion**	**C_2 selectivity**	**C_2 yield**
973	16.9	27.5	4.6
1023	26.8	46.9	12.6
1073	24.6	52.1	12.8
1123	26.0	51.8	13.5
1173	24.8	43.7	10.8

Table B.13 S-Na_2WO_4-Mn/YSZ catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	13.2	11.9	1.6
1023	28.0	48.4	13.5
1073	31.1	60.3	18.8
1123	28.7	60.8	17.4
1173	28.5	49.8	14.2

Table B.14 P-Na_2WO_4-Mn/YSZ catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	17.4	30.9	5.4
1023	31.1	53.2	16.5
1073	34.1	59.8	20.4
1123	33.2	57.5	19.1
1173	31.2	50.0	15.6

Table B.15 Ce-Na_2WO_4-Mn/YSZ catalyst

Temperature (K)	CH_4 conversion	C_2 selectivity	C_2 yield
973	9.8	13.9	1.4
1023	20.6	38.4	7.9
1073	20.7	46.8	9.7
1123	23.5	49.9	11.7
1173	21.8	43.7	9.5

II SOFC reactor

Table B.16 Na_2WO_4-Mn/YSZ catalyst

Temperature (K)	CH_4 conversion	C_2H_6 selectivity	C_2H_4 selectivity	C_2 yield
973	3.9	0.0	100	3.9
1023	5.7	20.4	79.6	5.7
1073	12.0	1.8	35.4	4.5
1123	14.6	5.2	31.4	5.4
1173	22.4	2.9	13.5	3.7
1223	34.6	2.4	9.6	4.1
1273	48.9	1.6	6.0	3.7

Table B.17 S-Na_2WO_4-Mn/YSZ catalyst

Temperature (K)	CH_4 conversion	C_2H_6 selectivity	C_2H_4 selectivity	C_2 yield
973	3.3	31.5	68.5	3.3
1023	5.2	20.7	79.3	5.2
1073	8.5	14.9	85.2	8.5
1123	15.3	2.4	12.0	2.2
1173	25.4	2.0	7.2	2.3
1223	38.0	1.4	4.2	2.1
1273	53.8	0.8	2.51	1.8

Table B.18 P-Na_2WO_4-Mn/YSZ catalyst

Temperature (K)	CH_4 conversion	C_2H_6 selectivity	C_2H_4 selectivity	C_2 yield
973	1.0	43.9	56.1	1.0
1023	1.1	23.7	76.3	1.1
1073	6.1	8.84	91.2	6.1
1123	10.5	11.0	89.0	10.5
1173	23.1	5.0	26.6	7.3
1223	45.1	3.2	14.6	8.0
1273	50.9	2.1	9.2	5.8

APPENDIX C
PRODUCT DISTRIBUTION

Product distribution in fixed bed reactor for OCM reaction

La_2O_3 support

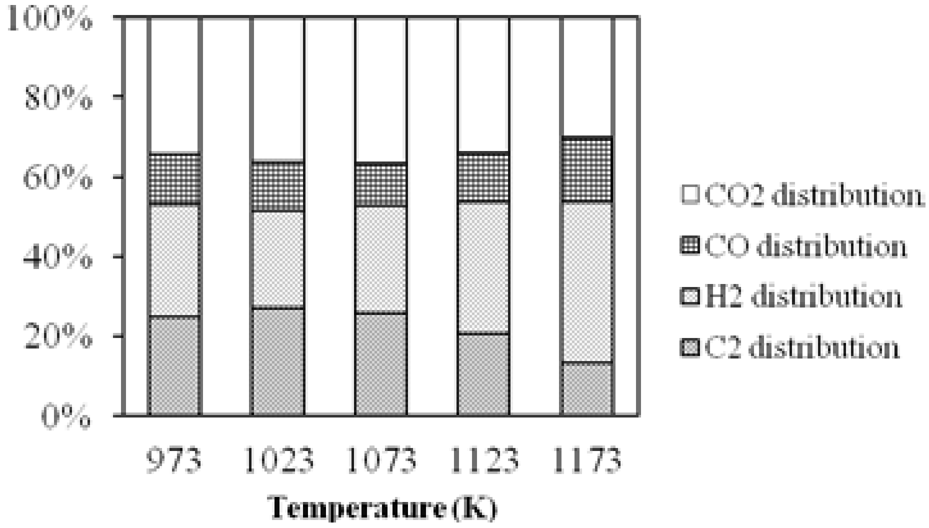

Figure C.1 Product distribution of La_2O_3 catalyst

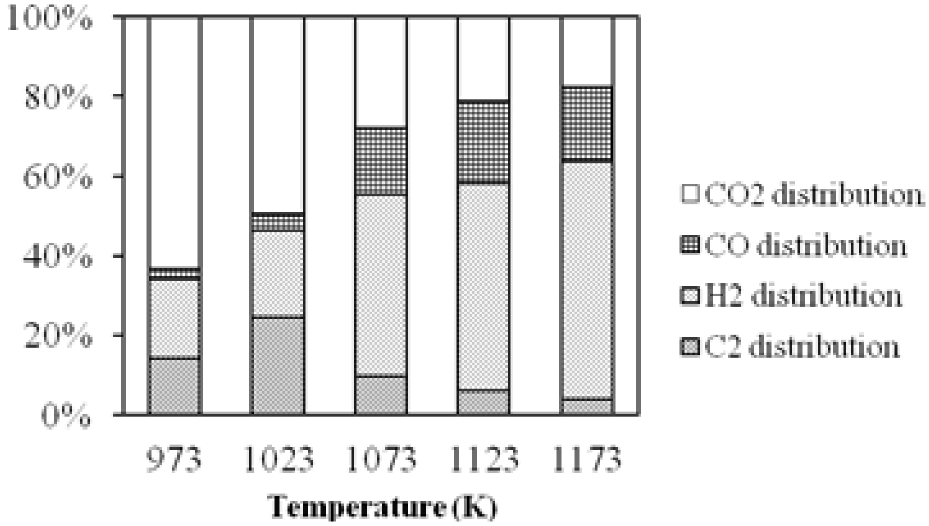

Figure C.2 Product distribution of Na_2WO_4-Mn/La_2O_3 catalyst

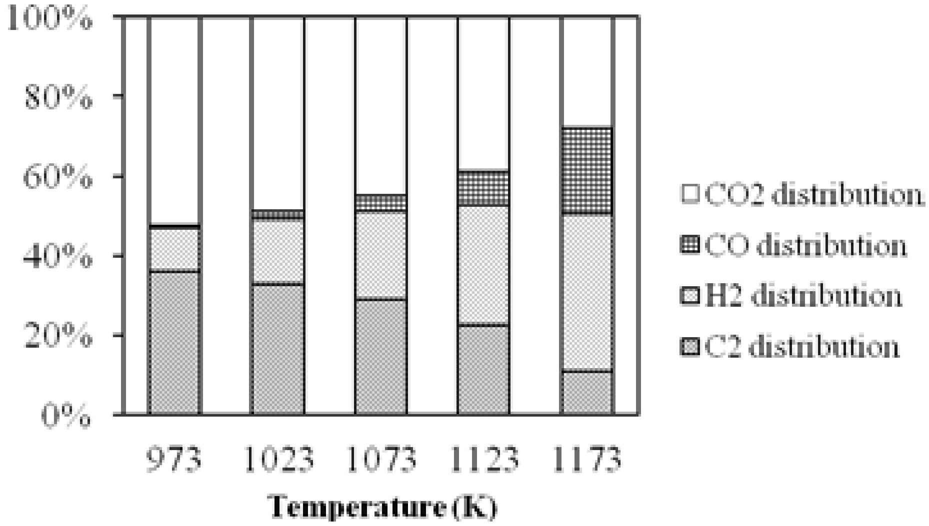

Figure C.3 Product distribution of S-Na_2WO_4-Mn/La_2O_3 catalyst

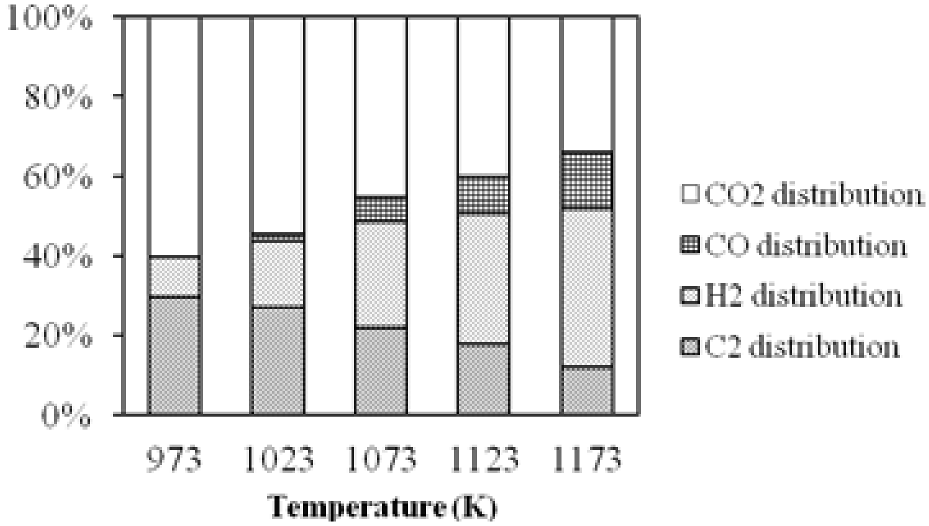

Figure C.4 Product distribution of P-Na_2WO_4-Mn/La_2O_3 catalyst

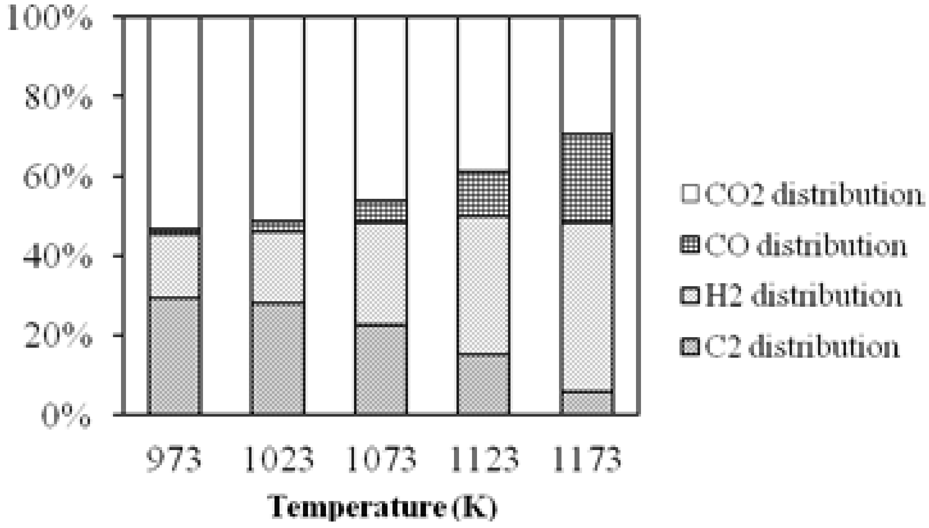

Figure C.5 Product distribution of Ce-Na_2WO_4-Mn/La_2O_3 catalyst

Y_2O_3 Support

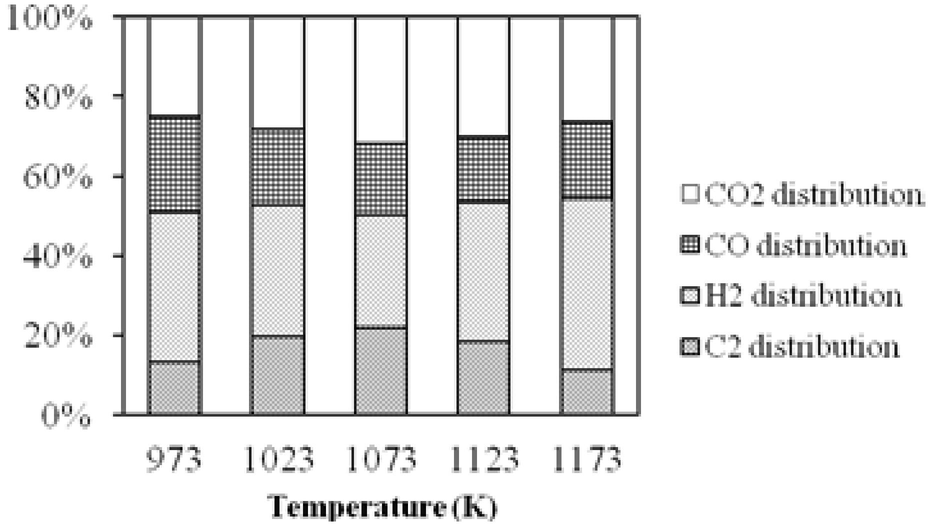

Figure C.6 Product distribution of Y_2O_3 catalyst

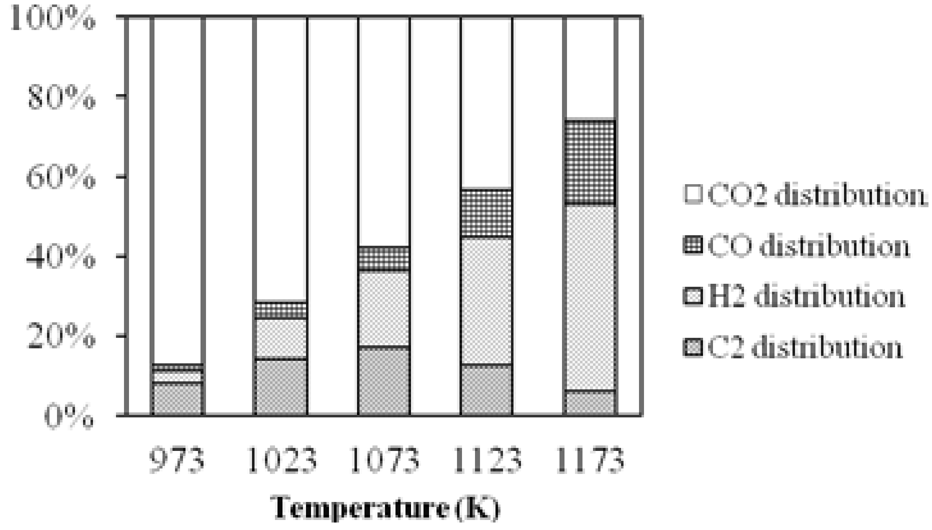

Figure C.7 Product distribution of Na_2WO_4-Mn/Y_2O_3 catalyst

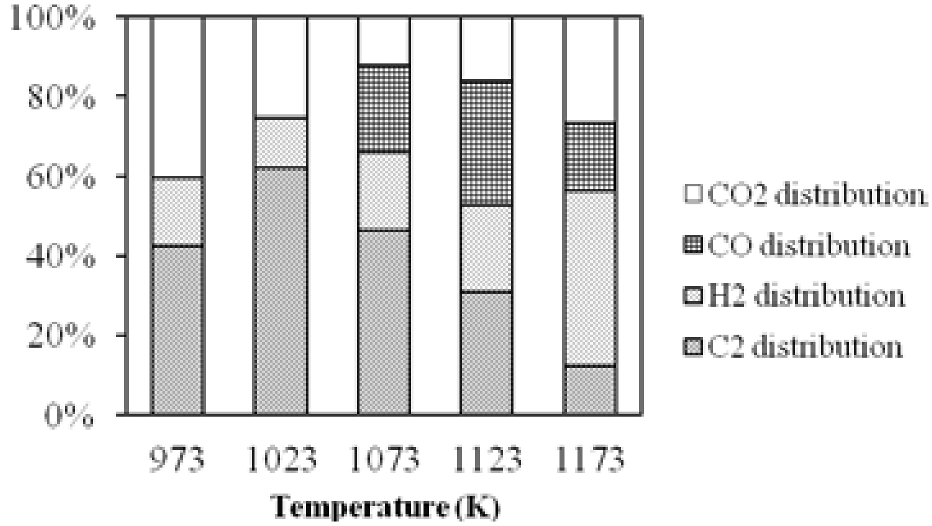

Figure C.8 Product distribution of S-Na_2WO_4-Mn/Y_2O_3 catalyst

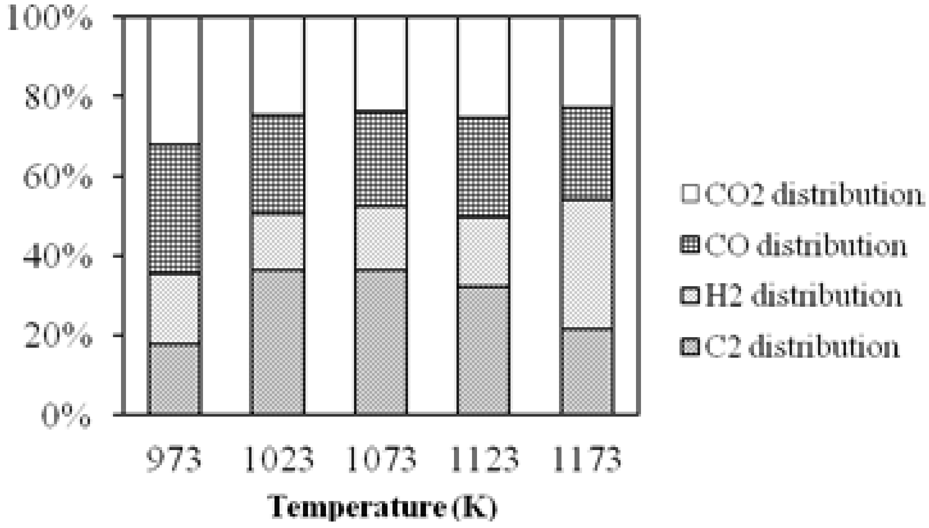

Figure C.9 Product distribution of P-Na_2WO_4-Mn/Y_2O_3 catalyst

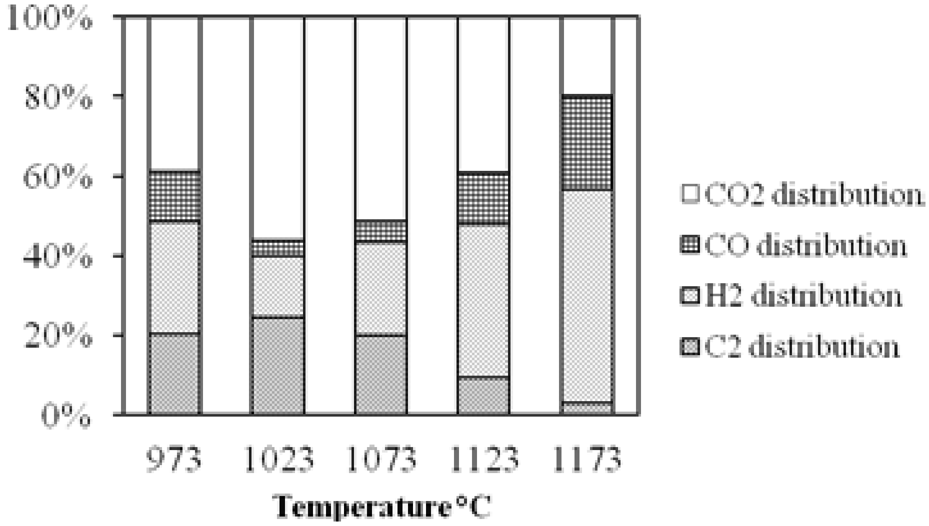

Figure C.10 Product distribution of Ce-Na_2WO_4-Mn/Y_2O_3 catalyst

YSZ support

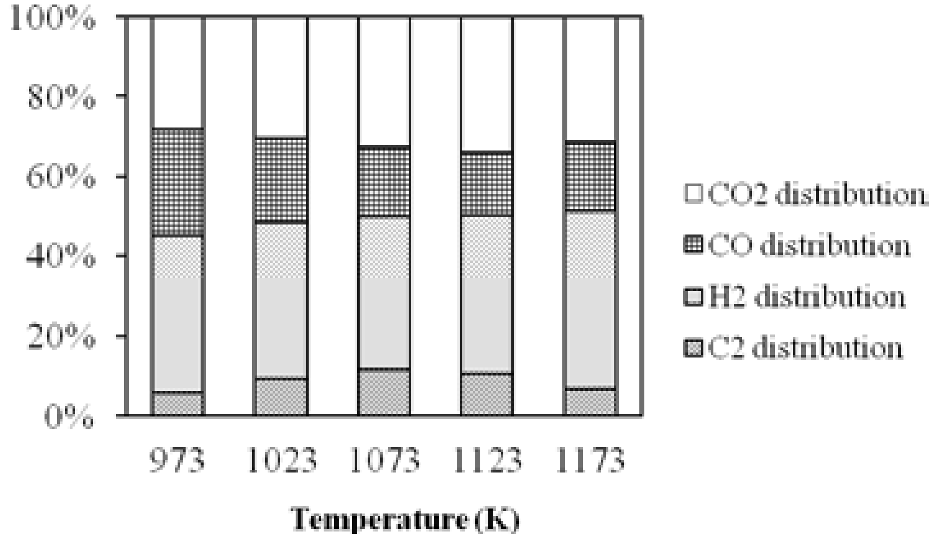

Figure C.11 Product distribution of YSZ catalyst

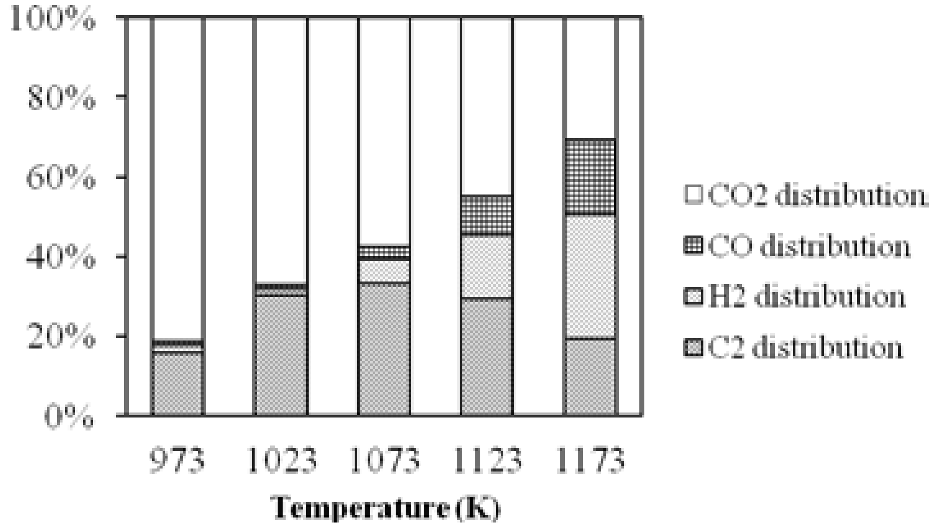

Figure C.12 Product distribution of Na_2WO_4-Mn/YSZ catalyst

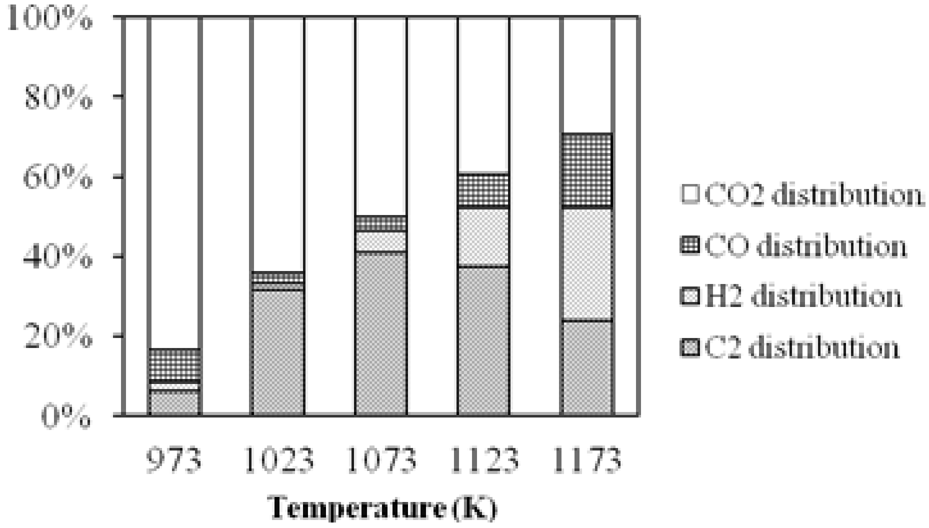

Figure C.13 Product distribution of S-Na_2WO_4-Mn/YSZ catalyst

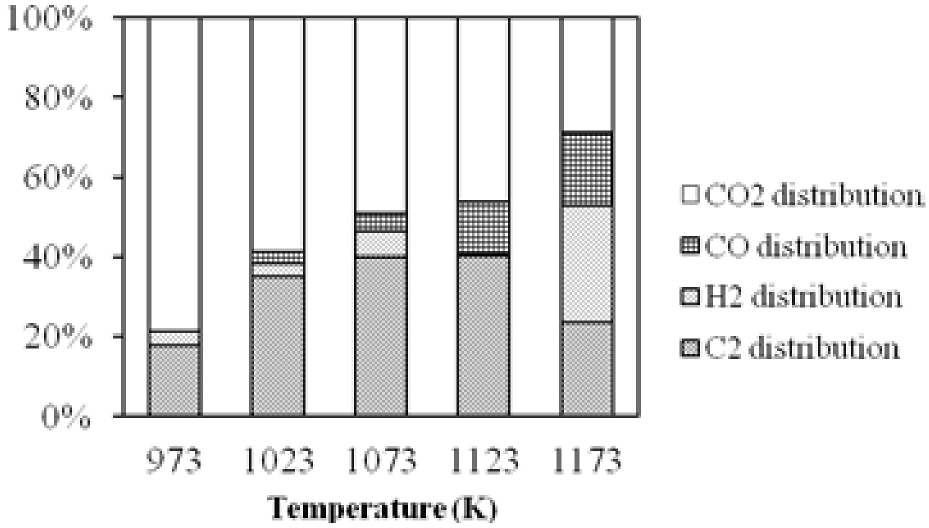

Figure C.14 Product distribution of P-Na_2WO_4-Mn/YSZ catalyst

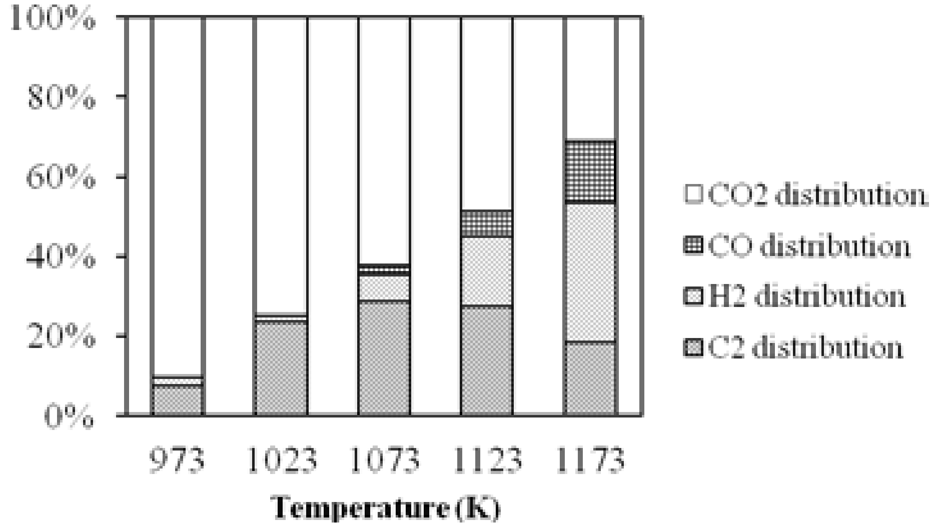

Figure C.15 Product distribution of Ce-Na_2WO_4-Mn/YSZ catalyst

Product distribution in SOFC reactor for OCM reaction

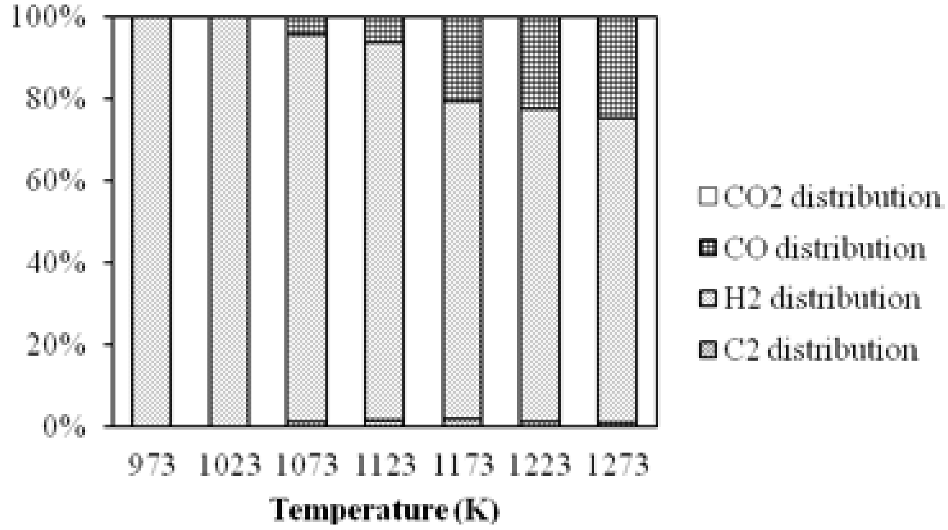

Figure C.16 Product distribution of Na_2WO_4-Mn/YSZ catalyst

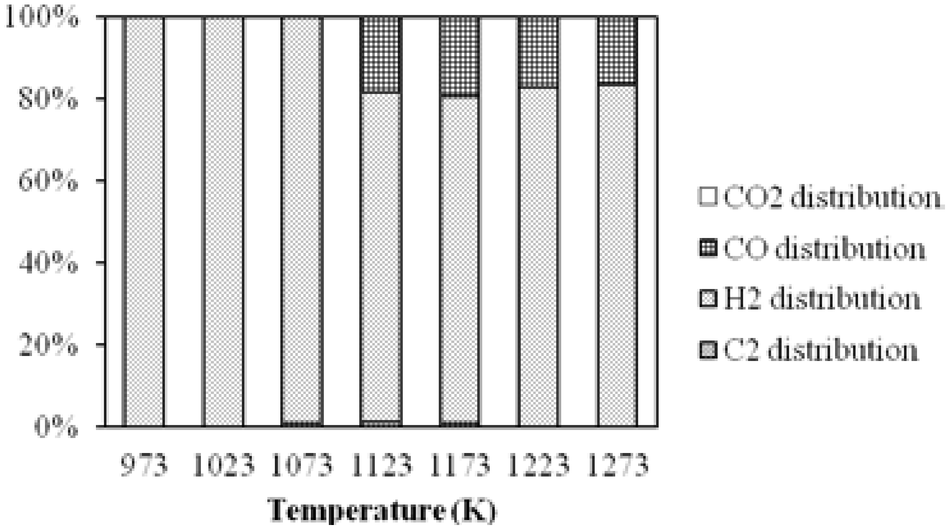

Figure C.17 Product distribution of S-Na_2WO_4-Mn/YSZ catalyst

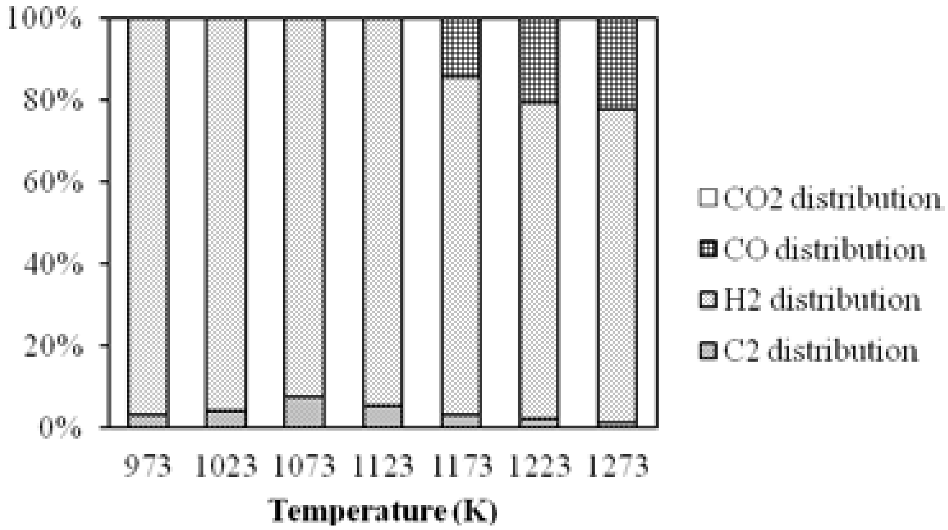

Figure C.18 Product distribution of P-Na_2WO_4-Mn/YSZ catalyst

APPENDIX D
CALCULATION OF EFFECTIVE MEMBRANE AREA

The effective membrane area was calculated from log mean diameter of a tube-type YSZ membrane and coating length of LSM cathode catalyst. The dimension of YSZ tube is; thickness = 1.5 mm, inside diameter (D_i) = 18 mm, outside diameter (D_o) = 21 mm, total length = 500 mm, LSM coating length = 100 mm. The log mean diameter was calculated from Eq. (C.1)

$$D_{\ln\ \mathrm{mean}} = \frac{D_\mathrm{o} - D_\mathrm{i}}{\ln\left(D_\mathrm{o}/D_\mathrm{i}\right)} \tag{C.1}$$

$$D_{\ln\ \mathrm{mean}} = \frac{21 - 18}{\ln\left(21/18\right)} = 19.5\ \mathrm{mm}$$

The effective membrane area = π x 19.5 x 100 = 6126.10 mm^2

= 0.006126 m^2

APPENDIX E

THE SURFACE AREA OF CATALYST

Table E.1 The surface area of catalyst after operated in SOFC reactor

Catalyst	BET ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Average pore diameter (nm)
Na_2WO_4-Mn/YSZ	7.483	0.015	7.875
	6.756*	0.010*	6.072*
S-Na_2WO_4-Mn/YSZ	7.716	0.012	6.171
	5.232*	0.008*	6.421*
P-Na_2WO_4-Mn/YSZ	5.789	0.009	6.628
	2.965*	0.005*	6.339*

*After operated in SOFC reactor

APPENDIX F

THE CHEMICAL COMPOSITION VALUES FROM SEM-EDS MEASUREMENTS

Table F.1 The chemical composition values obtained from SEM-EDS measurements on La_2O_3 support catalyst

Element	**Percentage weight of element (%)**				
	Theoretical values	**Na_2WO_4 -Mn/La_2O_3**	**S-Na_2WO_4 -Mn/La_2O_3**	**P-Na_2WO_4 -Mn/La_2O_3**	**Ce-Na_2WO_4 -Mn/La_2O_3**
Na		1.08	1.52	3.65	1.04
W		4.92	3.29	4.43	3.37
Mn	2.00	5.69	4.33	4.22	2.00
S	2.00	-	1.11	-	-
P	2.00	-	-	2.54	-
Ce	2.00	-	-	-	6.00
La		71.21	75.52	72.39	71.7
O		17.11	14.22	12.77	15.89

Table F.2 The chemical composition values obtained from SEM-EDS measurements on Y_2O_3 support catalyst

Element	**Percentage weight of element (%)**				
	Theoretical values	**Na_2WO_4 -Mn/Y_2O_3**	**S-Na_2WO_4 -Mn/Y_2O_3**	**P-Na_2WO_4 -Mn/Y_2O_3**	**Ce-Na_2WO_4 -Mn/Y_2O_3**
Na		0.68	1.92	2.78	0.51
W		3.76	4.99	5.05	6.68
Mn	2.00	2.43	1.55	3.67	2.75
S	2.00	-	1.75	-	-
P	2.00	-	-	2.12	-
Ce	2.00	-	-	-	1.54
Y		78.22	75.55	75.21	72.16
O		14.91	14.24	11.17	16.36

Table F.3 The chemical composition values obtained from SEM-EDS measurements on YSZ support catalyst

Element	**Percentage weight of element (%)**				
	Theoretical values	**Na_2WO_4 -Mn/YSZ**	**S-Na_2WO_4 -Mn/YSZ**	**P-Na_2WO_4 -Mn/YSZ**	**Ce-Na_2WO_4 -Mn/YSZ**
Na		0.73	1.82	2.16	0.91
W		6.76	9.02	6.81	3.15
Mn	2.00	2.94	2.61	2.34	4.50
S	2.00	-	1.99	-	-
P	2.00	-	-	3.04	-
Ce	2.00	-	-	-	3.64
Y	8.00	10.52	10.57	7.15	9.08
Zr		59.67	56.55	57.73	59.93
O		19.39	17.43	20.77	18.79

Table F.4 The chemical composition values obtained from SEM-EDS measurements on YSZ support catalyst after operate in SOFC reactor

Element	**Percentage weight of element (%)**			
	Theoretical values	**Na_2WO_4 -Mn/YSZ**	**S-Na_2WO_4 -Mn/YSZ**	**P-Na_2WO_4 -Mn/YSZ**
Na		0.40	0.39	0.47
W		5.32	1.83	2.09
Mn	2.00	1.75	1.81	1.66
S	2.00	-	1.37	-
P	2.00	-	-	0.33
C		58.62	85.35	52.88
Y	8.00	3.86	1.06	2.89
Zr		24.63	5.48	26.55
O		5.41	2.71	13.13

VITA

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