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*Article*

## Oxidative Coupling of Methane over YSZ Support Catalysts for Application in C<sub>2</sub> Hydrocarbon Production

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**Abstract.** This paper studies the development of Mn-Na<sub>2</sub>WO<sub>4</sub> catalysts on YSZ support 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<sub>2</sub>WO<sub>4</sub> catalyst on YSZ support was 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<sub>2</sub>WO<sub>4</sub> catalyst on YSZ support. At 1073 K, S-Mn-Na<sub>2</sub>WO<sub>4</sub>/YSZ provided C<sub>2</sub> selectivity of 60.3% and methane conversion of 31.1%, while P-Mn-Na<sub>2</sub>WO<sub>4</sub>/YSZ offered C<sub>2</sub> selectivity of 59.8% and methane conversion of 34.1%. P-Mn-Na<sub>2</sub>WO<sub>4</sub>/YSZ catalyst was selected as anode catalysts for further study in the SOFC reactor. The experiments were carried out using La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (LSM) as the cathode catalyst, 8mol% yttria-stabilized zirconia (YSZ) as the electrolyte. P-Mn-Na<sub>2</sub>WO<sub>4</sub>/YSZ exhibited the best performance, providing C<sub>2</sub>H<sub>4</sub> selectivity of 89.0%, methane conversion of 10.5% and maximum power density of 7.2 W/m<sup>2</sup> at 1123 K. In addition, the stability of the P-Mn-Na<sub>2</sub>WO<sub>4</sub>/YSZ catalyst was tested at 1123 K. Good stability of the reaction system could be observed at least for 29 hours.

**Keywords:** OCM, C<sub>2</sub> hydrocarbon, electro co-generation, YSZ.

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## 1. Introduction

Solid oxide fuel cell is an electrochemical cell that converts chemical energy of a fuel into electrical energy with water and heat as its by-products [1, 2]. It has a number of advantages particularly its high efficiency and low emission of pollutants [3–5]. 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 [6–10]. Various valuable industrial compounds such as ethylene, hydrogen, hydrogen cyanide, nitric oxide, styrene, and formaldehyde have been considered to Alcaide et al [11]. In this study, the focus is on the production of ethylene as it is one of the most important feedstock in the petrochemical industry. 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. 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) [12] investigated anode for solid oxide fuel cells to generate  $C_2$  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% [13]. Thus in this study we studied YSZ support for sodium tungsten manganese catalyst which these supports active and selective with OCM reaction. 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 YSZ support 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.

## 2. Experimental

### 2.1. Catalyst Preparation and Characterization

The 5% $Na_2WO_4$ -2%Mn/YSZ catalysts were prepared by the incipient wetness impregnation method following the method described in literature of Wang et al. [14]. The 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.

The synthesized catalysts were determined their physical properties by various techniques. Surface area and pore size were determined by BET method. The crystalline phases of prepared samples were identified by x-ray diffraction technique using  $Cu-K\alpha$  radiation. The x-ray diffractograms were recorded in range of  $10^\circ$  to  $80^\circ$  ( $2\theta$ ). Scanning Electron Microscopy (SEM) was also used to examine the surface morphology of synthesized catalyst.

### 2.2. Catalytic Activity Testing

#### 2.2.1. Fixed bed reactor

Activity tests were carried out in a quartz fixed-bed microreactor (i.d. 6 mm), using 0.2 g of catalyst as shown in Fig. 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  $ml \cdot min^{-1}$  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  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ , and a 5 Å molecular sieve column for the separation of  $\text{O}_2$ ,  $\text{CH}_4$ , and  $\text{CO}$ .

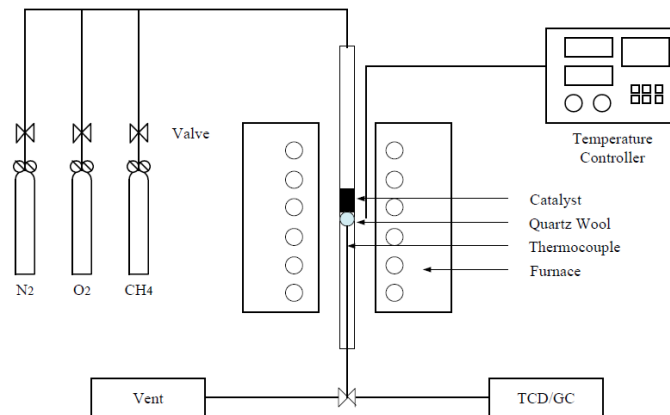


Fig. 1. Schematic diagram of oxidative coupling of methane in fixed bed.

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.

## 2.2.2. SOFC reactor

### 2.2.2.1. Apparatus

The schematic diagram of the SOFC reactor was illustrated in Fig. 2. A tube-type YSZ membrane (8mol%  $\text{Y}_2\text{O}_3$ , thickness = 1.5 mm, inside diameter = 18 mm, outside diameter = 21 mm, length 100 mm, effective surface area is 0.006126  $\text{m}^2$ ) was used as an electrolyte. The anode catalyst on the inner surface of the tube while  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$  (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  $\text{ml}\cdot\text{min}^{-1}$  at anode side and oxygen was allowed to continually flow into the cathode catalyst at a total flow rate 100  $\text{ml}\cdot\text{min}^{-1}$  at 1 atm. At 973 K the argon was transposed to methane continually flow into anode catalyst side at total flow rate 5  $\text{ml}\cdot\text{min}^{-1}$ . 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  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ , and a 5 Å molecular sieve column for the separation of  $\text{O}_2$ ,  $\text{CH}_4$ , and  $\text{CO}$ .

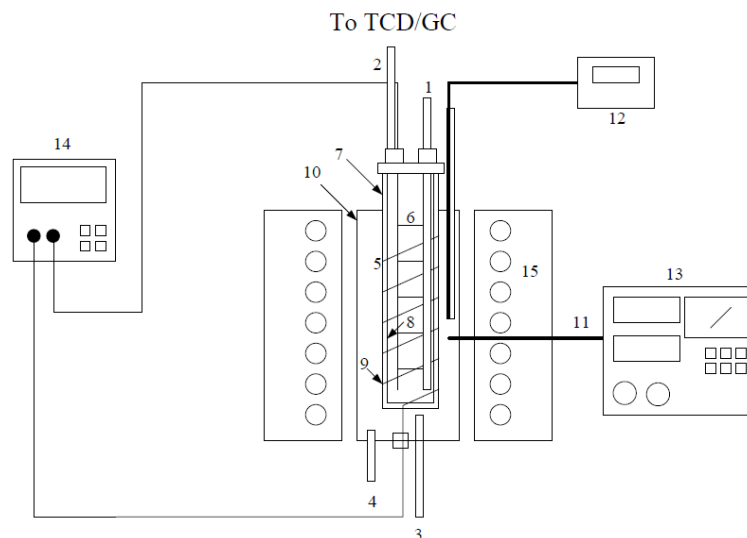


Fig. 2. Schematic diagram of oxidative coupling of methane in SOFC reactor.

#### 2.2.2.2. 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 glycerol and pasted into film on the inside of YSZ tube and heated at 1123 K for about 3 hrs in air.

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

### 3. Result and Discussion

#### 3.1. Catalyst Characteristics

The YSZ support in XRD pattern involve in part metal loading, which did not found active phase such as  $\text{Na}_2\text{WO}_4$  ( $17^\circ$ ),  $\text{Na}_2\text{W}_2\text{O}_7$  ( $15.5^\circ$ ),  $\text{Na}_2\text{SO}_4$  ( $34^\circ$ ,  $49^\circ$ ) but found only  $\text{Mn}_2\text{O}_3$  ( $33^\circ$ ) in catalyst promoted with manganese except S- $\text{Na}_2\text{WO}_4$ -Mn/ $\text{Y}_2\text{O}_3$  and S- $\text{Na}_2\text{WO}_4$ -Mn/YSZ. Figure 3 shows that the diffraction peaks were unexpanded and remained unchanged this cause may be the formation of the composite oxide  $\text{Na}_2\text{WO}_4$ ,  $\text{Na}_2\text{W}_2\text{O}_7$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Mn}_2\text{O}_3$  as an amorphous phase as described by Li and Wang [15].

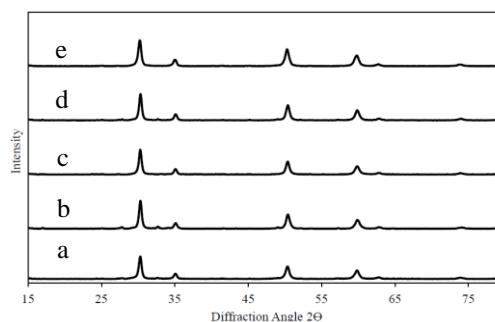


Fig. 3. The XRD pattern a) YSZ, (b)  $\text{Na}_2\text{WO}_4$ -Mn/YSZ, (c) S- $\text{Na}_2\text{WO}_4$ -Mn/YSZ, (d) P- $\text{Na}_2\text{WO}_4$ -Mn/YSZ, (e) Ce- $\text{Na}_2\text{WO}_4$ -Mn/YSZ.

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 approximated 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 Figs. 4–8. However the all SEM micrographs did not show the difference between metal oxide and support.

From mapping of element on YSZ support 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. [16]. They reported high performance of  $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$  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.

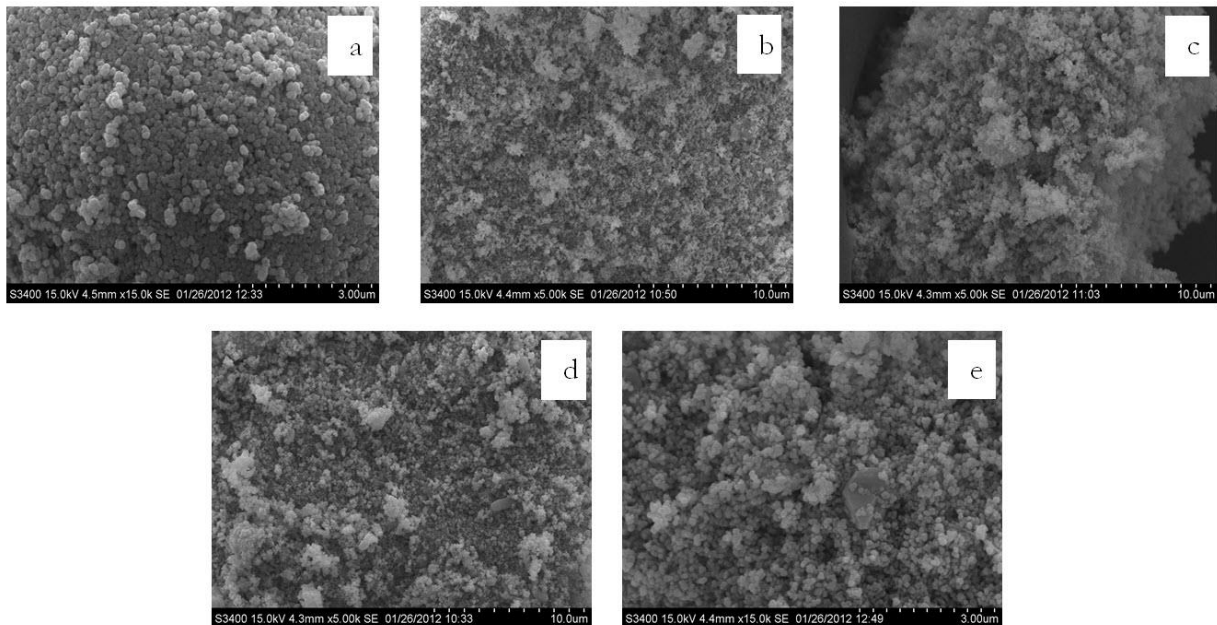


Fig. 4. Surface morphology of catalyst on YSZ support a) YSZ, (b)  $\text{Na}_2\text{WO}_4\text{-Mn/YSZ}$ , (c)  $\text{S-Na}_2\text{WO}_4\text{-Mn/YSZ}$ , (d)  $\text{P-Na}_2\text{WO}_4\text{-Mn/YSZ}$ , (e)  $\text{Ce-Na}_2\text{WO}_4\text{-Mn/YSZ}$ .

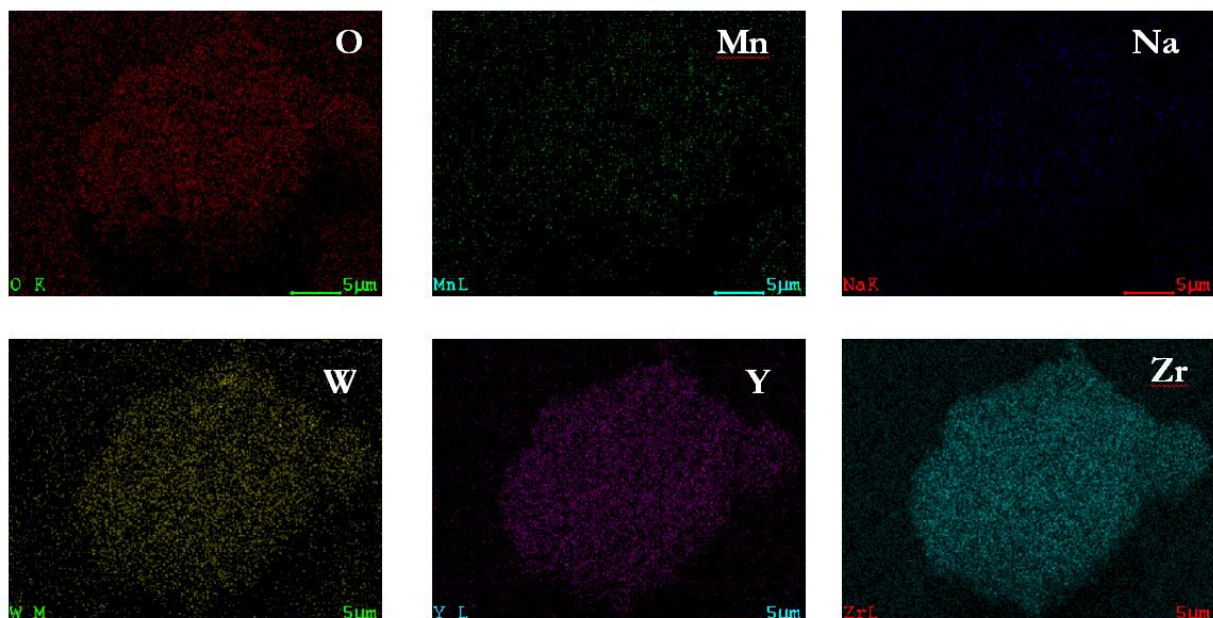


Fig. 5. The SEM-EDS mapping of elements on  $\text{Na}_2\text{WO}_4\text{-Mn/YSZ}$  catalyst.

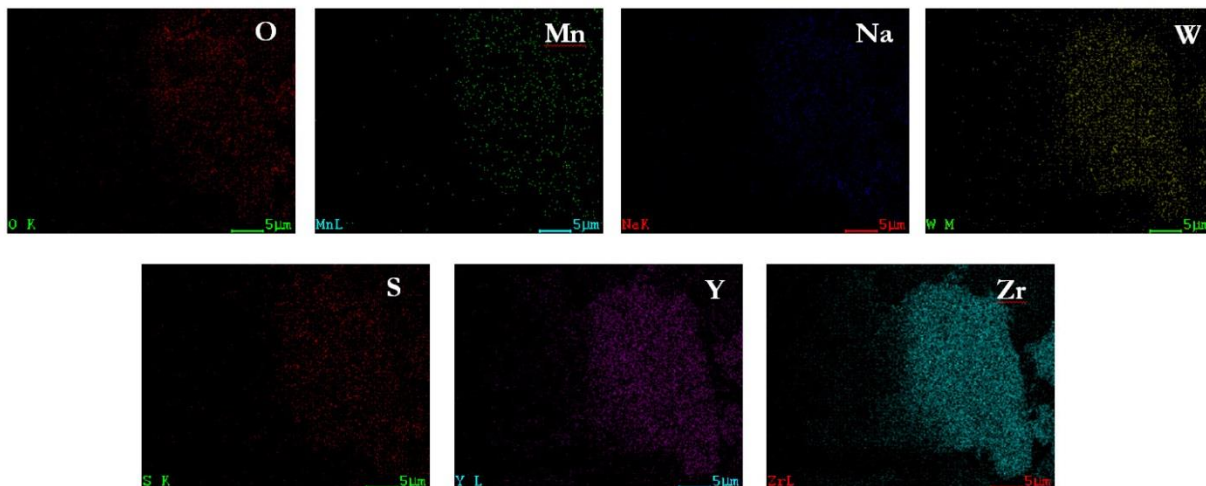


Fig. 6. The SEM-EDS mapping of elements on S- $\text{Na}_2\text{WO}_4$ -Mn/YSZ catalyst.

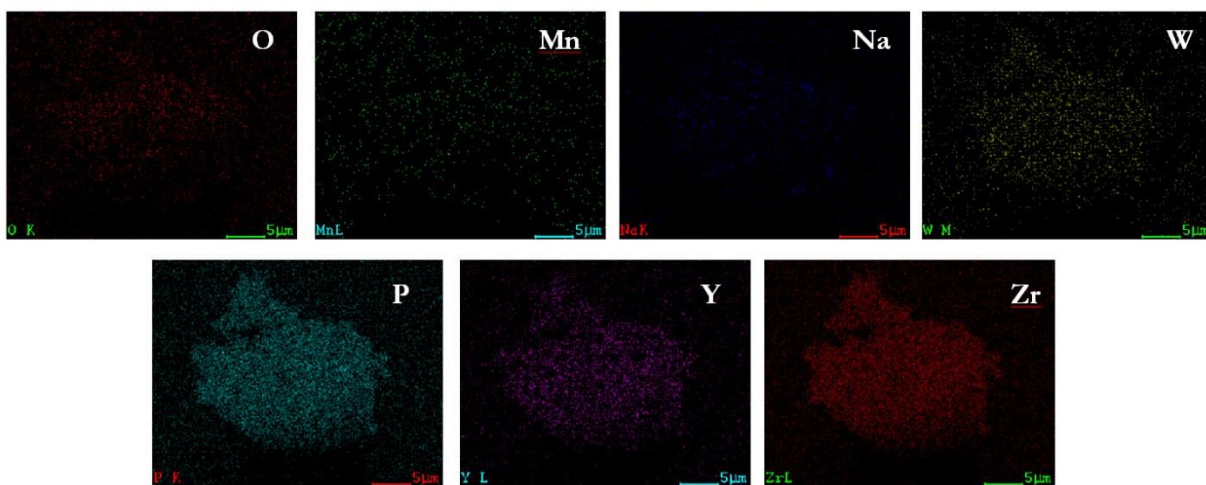


Fig. 7. The SEM-EDS mapping of elements on P- $\text{Na}_2\text{WO}_4$ -Mn/YSZ catalyst.

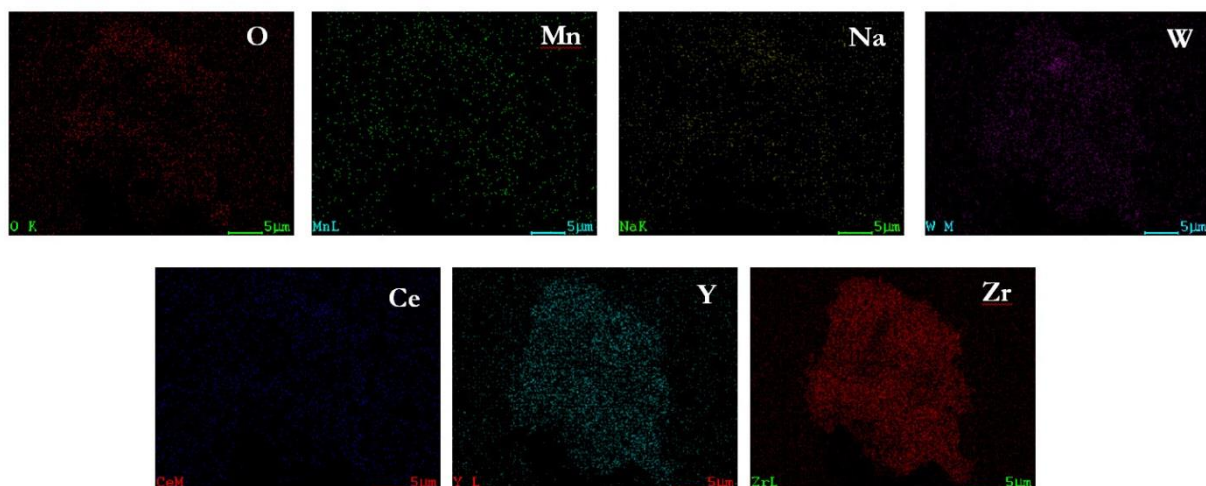


Fig. 8. The SEM-EDS mapping of elements on Ce- $\text{Na}_2\text{WO}_4$ -Mn/YSZ catalyst.

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 YSZ was  $11.263 \text{ m}^2 \text{ g}^{-1}$ . After the YSZ supports were loaded with catalysts precursor, the BET surface area of the catalyst decreased because active catalyst

deposit in YSZ support [17]. Table 1 shows the BET surface area, total pore volume and average pore each catalyst.

Table 1. The results of BET surface area, total pore volume and average pore diameter of YSZ support catalyst.

Catalyst	BET ( $\text{m}^2 \text{g}^{-1}$ )	Total pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Average pore diameter (nm)
YSZ	11.263	0.021	7.534
$\text{Na}_2\text{WO}_4\text{-Mn/YSZ}$	7.483	0.015	7.875
$\text{S- Na}_2\text{WO}_4\text{-Mn/YSZ}$	7.716	0.012	6.171
$\text{P- Na}_2\text{WO}_4\text{-Mn/YSZ}$	5.789	0.009	6.628
$\text{Ce- Na}_2\text{WO}_4\text{-Mn/YSZ}$	6.954	0.009	5.566

### 3.2. Performance of Catalyst for OCM Reaction in Fixed Bed Reactor

YSZ support showed the performance of OCM reaction, which provided methane conversion between 26.8-29.8% and  $\text{C}_2$  selectivity between 17.1-29.7%. The YSZ support exhibited the higher methane conversion when compared with other supports. When a  $\text{Na}_2\text{WO}_4\text{-Mn}$  was added to YSZ support, the catalyst was higher  $\text{C}_2$  selectivity than YSZ support, which showed 27.5-52.1%. for the  $\text{C}_2$  selectivity. However methane conversion was lower than YSZ support. The S-  $\text{Na}_2\text{WO}_4\text{-Mn /YSZ}$  and P-  $\text{Na}_2\text{WO}_4\text{-Mn /YSZ}$  showed the high performance in OCM reaction. The maximum  $\text{C}_2$  yield from P-  $\text{Na}_2\text{WO}_4\text{-Mn /YSZ}$  was 20.3% at 1073 K whereas S- $\text{Na}_2\text{WO}_4\text{-Mn /YSZ}$  catalyst did not differ from P-  $\text{Na}_2\text{WO}_4\text{-Mn /YSZ}$ , which provided 18.7%  $\text{C}_2$  yield at 1073 K. The sulfur helped the active phase such as  $\text{Na}_2\text{SO}_4$  occurred and phosphorus can help manganese to form  $\text{Mn}_2\text{O}_3$  which was the active phase. In case of cerium doped into  $\text{Na}_2\text{WO}_4\text{-Mn/YSZ}$  observed the decreasing of methane conversion and  $\text{C}_2$  selectivity when compared with  $\text{Na}_2\text{WO}_4\text{-Mn/YSZ}$ , as shown in Figs. 9–11.

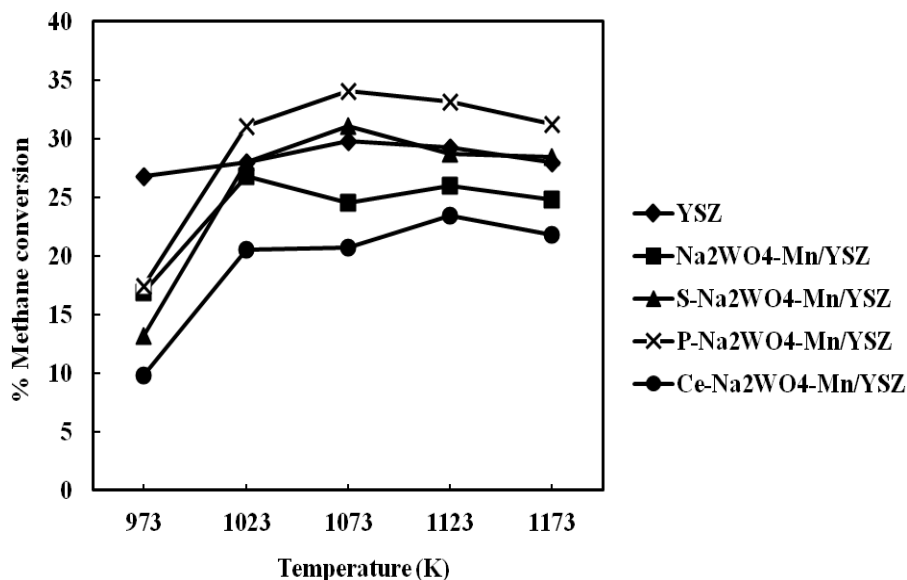


Fig 9. Methane conversion of YSZ support catalyst with WHSV  $15,000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ .

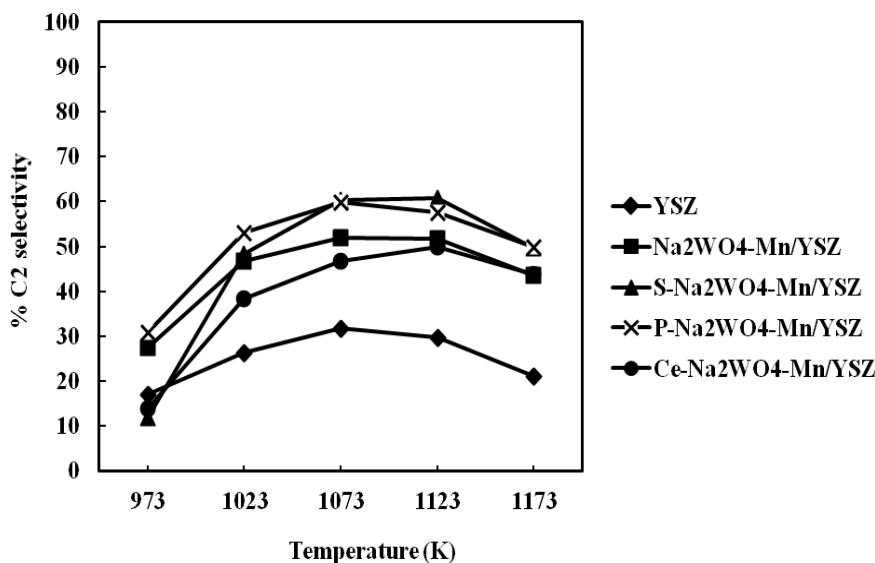


Fig. 10. C<sub>2</sub> selectivity of YSZ support catalyst with WHSV 15,000 cm<sup>3</sup>.g<sup>-1</sup>.h<sup>-1</sup>.

### 3.3. OCM in SOFC Reactor for C<sub>2</sub>H<sub>4</sub> Hydrocarbon and Electricity Co-generation

After experiment in fixed bed reactor the P- Na<sub>2</sub>WO<sub>4</sub>-Mn /YSZ was selected to test in SOFC reactor for investigate the performance to produce C<sub>2</sub> hydrocarbon and electrical current. In addition, the stability of catalyst is interesting in this work, which chooses the best condition to carry out. The performance of catalysts and electrical current showed in Fig. 12 and Table 2 respectively. The highest C<sub>2</sub>H<sub>4</sub> selectivity was approximately 91.2% at 1123 K and could be operated in temperature range between 973-1123 K whereas the C<sub>2</sub>H<sub>4</sub> selectivity did not decreases. The maximum C<sub>2</sub> yield was 10.5% and provided maximum power density about 9.8 W/m<sup>2</sup> at 1123K. The maximum power density was 16.8 W/m<sup>2</sup> at 1273 K and the voltage was similar others. In case OCM in SOFC reactor for C<sub>2</sub>H<sub>4</sub> hydrocarbon and electricity co-generation have a few reports, Tagawa, et. al. [18] used La<sub>1.8</sub>Al<sub>0.2</sub>O<sub>3</sub> as the anode catalyst with a plate-type Ytria Stabilized Zirconia (YSZ) as a solid electrolyte and La<sub>0.85</sub>Sr<sub>0.15</sub>MnO<sub>3</sub> as a cathode the experiment provided 4.0% methane conversion and 96% C<sub>2</sub> selectivity. The electrical current and voltage were 10.1 mA and 0.96 V, respectively or power densities was estimated 13.85 W/m<sup>2</sup>. 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 15% C<sub>2</sub> yield at 1223 K then provided power density about 13.37 W/m<sup>2</sup>. In addition, Lapeña-Rey and Middleton [19] investigated in Na<sub>2</sub>WO<sub>4</sub>-Mn/SiO<sub>2</sub> and K<sub>2</sub>WO<sub>4</sub>-Mn/SiO<sub>2</sub> in co-feed mode and electrochemical mode at 1123K. It found that the best performance was 86% C<sub>2</sub> selectivity, and 4% C<sub>2</sub> yield obtained from potassium tungstate supported catalysts in electrochemical mode. In case of the Na<sub>2</sub>WO<sub>4</sub>-Mn/SiO<sub>2</sub> catalyst from this literature provided lower C<sub>2</sub> selectivity (70.5-87.6%) than the P-Na<sub>2</sub>WO<sub>4</sub>-Mn/YSZ catalyst at 1123 K.



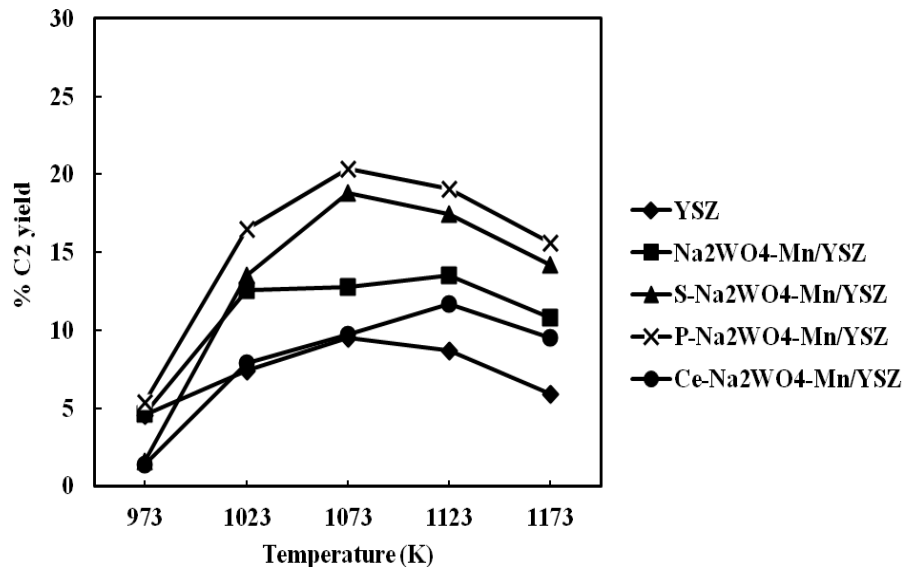


Fig. 11. C<sub>2</sub> yield of YSZ support catalyst with WHSV 15,000 cm<sup>3</sup>.g<sup>-1</sup>.h<sup>-1</sup>

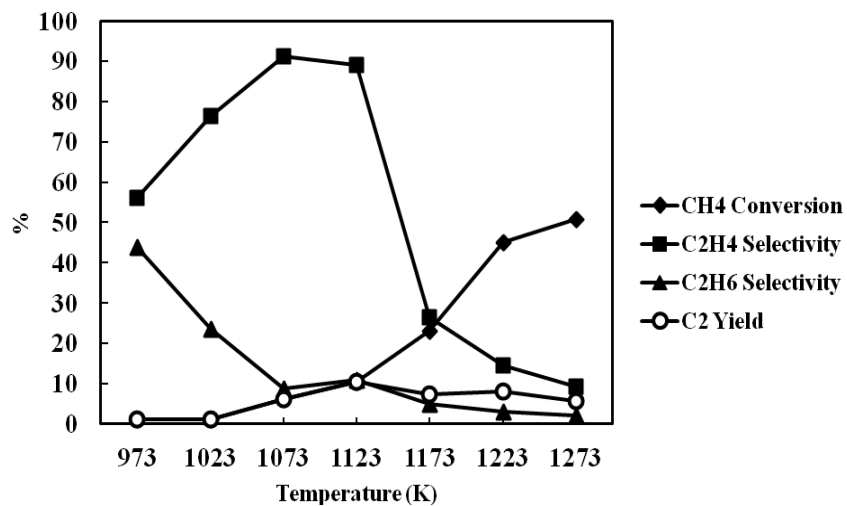


Fig 12. Performance of P-Na<sub>2</sub>WO<sub>4</sub>-Mn/YSZ catalyst in SOFC reactor.

Table 2. The electric power at each temperature for P-Na<sub>2</sub>WO<sub>4</sub>-Mn/YSZ catalyst in SOFC reactor.

Temperature (K)	Current (mA)	Oxygen consumption (mol•s <sup>-1</sup> )
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

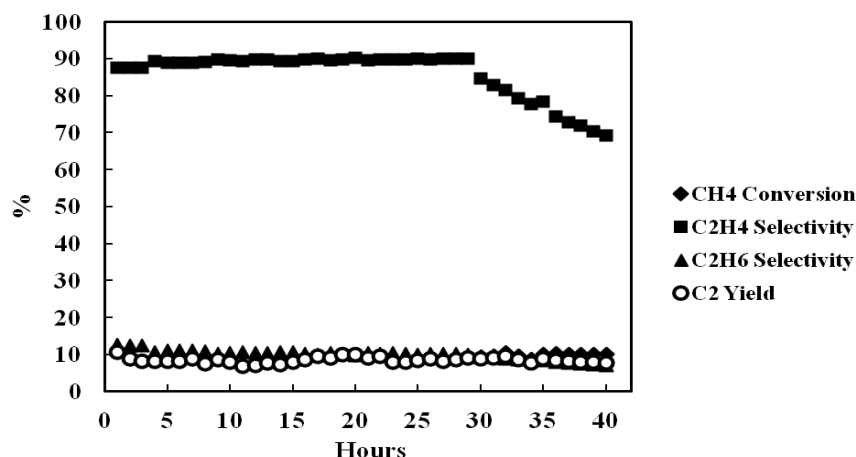


Fig. 13. Stability test of P-Na<sub>2</sub>WO<sub>4</sub>-Mn/YSZ catalyst in SOFC reactor at 1123 K.

Moreover, the P-Na<sub>2</sub>WO<sub>4</sub>-Mn/YSZ catalyst showed the best performance in this work for SOFC reactor provided 10.5% C<sub>2</sub> yield which exhibited higher performance than Lapeña-Rey and Middleton [9]. In addition, the maximum C<sub>2</sub> yield was obtained at 1123 K, which lowers operating temperature than Kiatkittipong [20]. The report showed about 3% C<sub>2</sub> yield at 1173K. However, C<sub>2</sub> 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<sub>2</sub> product. When the oxygen permeated rate greater than rate of consume, The O<sub>2</sub>- may be combined to form O<sub>2</sub>, which reaction with methane to form CO<sub>x</sub>. If the oxygen permeate rate was lower than rate of consume occurred the low C<sub>2</sub> yield. The other reason was the rate of oxygen permeates through YSZ membrane was low lead to methane cracking to generated carbon and hydrogen.

The P-Na<sub>2</sub>WO<sub>4</sub>-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<sub>2</sub> yield. It showed the good performance for 29 hours (Fig. 13), after that the C<sub>2</sub>H<sub>4</sub> selectivity decreased because occurred the carbon deposition on catalysts.

#### 4. Conclusion

The P-Na<sub>2</sub>WO<sub>4</sub>-Mn/YSZ catalyst exhibited the high performance. The stability test exhibited very well because of more than 24 hr. Therefore, P-Na<sub>2</sub>WO<sub>4</sub>-Mn/YSZ catalyst was suitable and can be applied as anode material in solid oxide fuel cell (SOFC) reactor. However, power densities are still low due to the resistance of electrolyte. For the future work, the tape casting method will study in order to reduce the electrolyte thickness and prepare porous ceramic support for the electrode material. The electrode materials will be introduced into porous YSZ support by ion impregnation technique.

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