ENGINEERING JOURNAL

Article

Oxidative Coupling of Methane over YSZ Support Catalysts for Application in C_2 Hydrocarbon Production

Kridsada Khammona[1], Wisitsree Wiyaratn[2,*], Weerinda Appamana[1], and Suttichai Assabumrungrat[1]

1 Centre of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
2 Faculty of Industrial Education and Technology, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand
*E-mail: Wisitsree.wiy@kmutt.ac.th (Corresponding author)

Abstract. This paper studies the development of Mn-Na_2WO_4 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_2WO_4 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_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 C2 selectivity of 59.8% and methane conversion of 34.1%. P-Mn-Na_2WO_4/YSZ catalyst was 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 maximum power density of 7.2 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 29 hours.

Keywords: OCM, C_2 hydrocarbon, electro co-generation, YSZ.

ENGINEERING JOURNAL Volume 19 Issue 4
Received 25 October 2013
Accepted 7 January 2015
Published 31 July 2015
Online at http://www.engj.org/
DOI:10.4186/ej.2015.19.4.1

DOI:10.4186/ej.2015.19.4.1

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 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% [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 C2 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-Kα radiation. The x-ray diffractograms were recorded in range of 10° to 80° (2Θ). 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 $ml.min^{-1}$ 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.

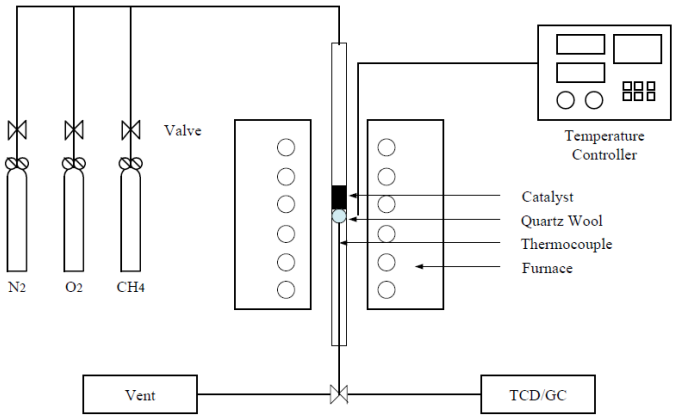

Fig. 1. Schematic diagram of oxidative coupling of methane in fixed bed.

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% 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.

DOI:10.4186/ej.2015.19.4.1

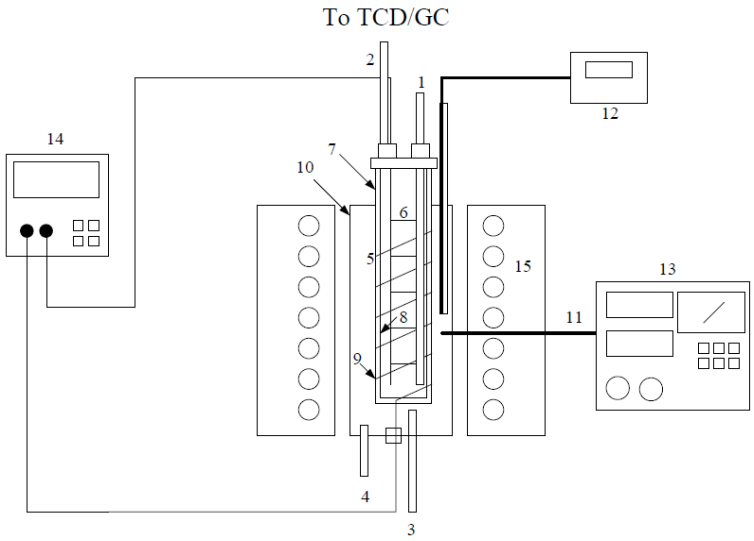

Fig. 2. Schematic diagram of oxidative coupling of methane in SOFC reactor.

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 grycerol 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 grycerol 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 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. Figure 3 shows that 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 as described by Li and Wang [15].

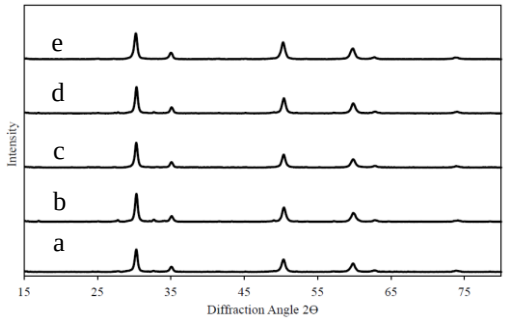

Fig. 3. The XRD pattern a) YSZ, (b) Na_2WO_4-Mn/YSZ, (c) S-Na_2WO_4-Mn/YSZ, (d) P-Na_2WO_4-Mn/YSZ, (e) Ce-Na_2WO_4-Mn/YSZ.

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 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.

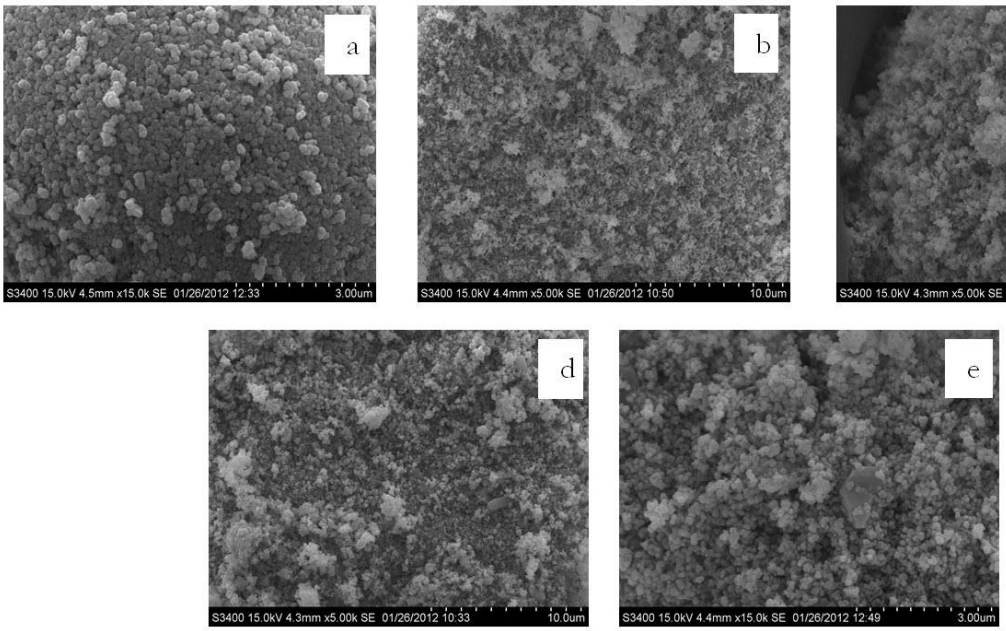

Fig. 4. Surface morphology of catalyst on YSZ support a) YSZ, (b) Na_2WO_4-Mn/YSZ, (c) S-Na_2WO_4-Mn/YSZ, (d) P-Na_2WO_4-Mn/YSZ, (e) Ce-Na_2WO_4-Mn/YSZ.

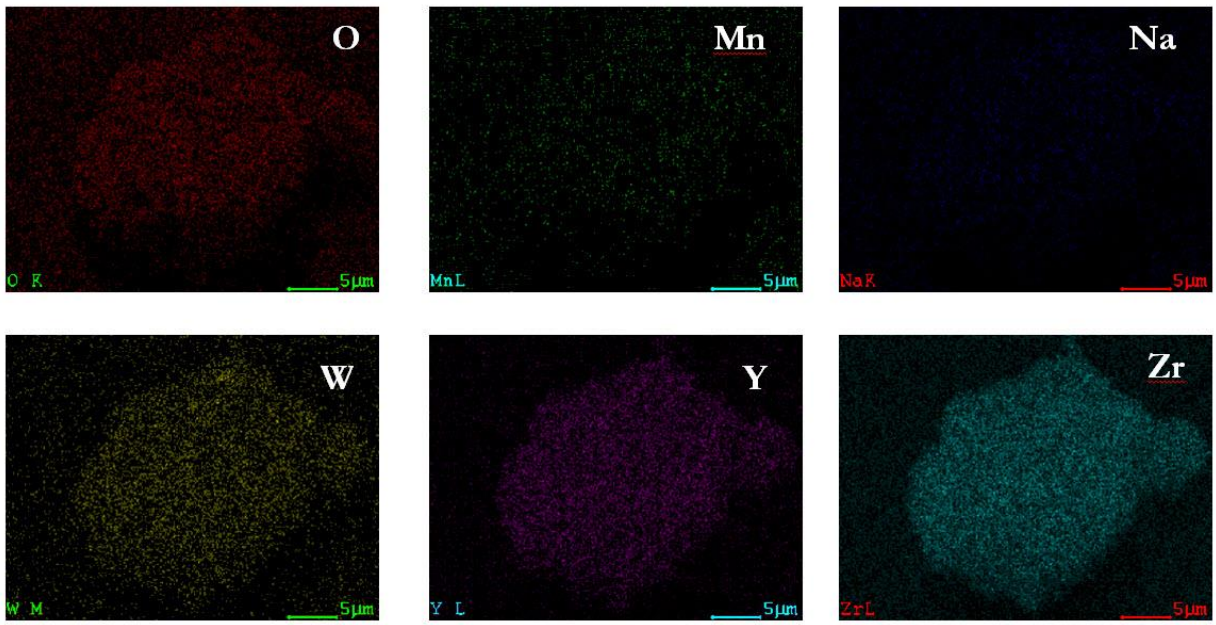

Fig. 5. The SEM-EDS mapping of elements on Na_2WO_4-Mn/YSZ catalyst.

DOI:10.4186/ej.2015.19.4.1

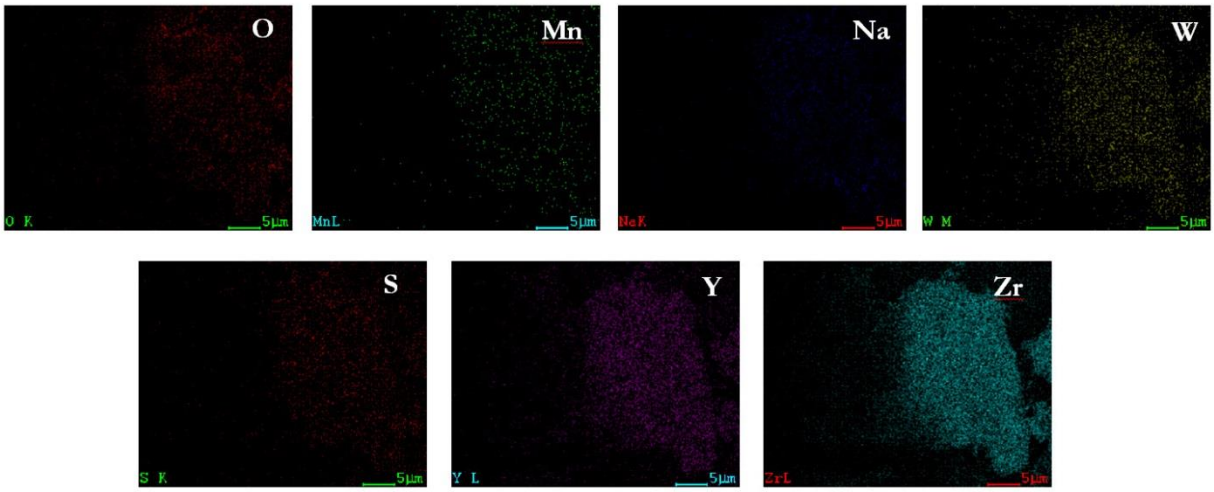

Fig. 6. The SEM-EDS mapping of elements on S-Na_2WO_4-Mn/YSZ catalyst.

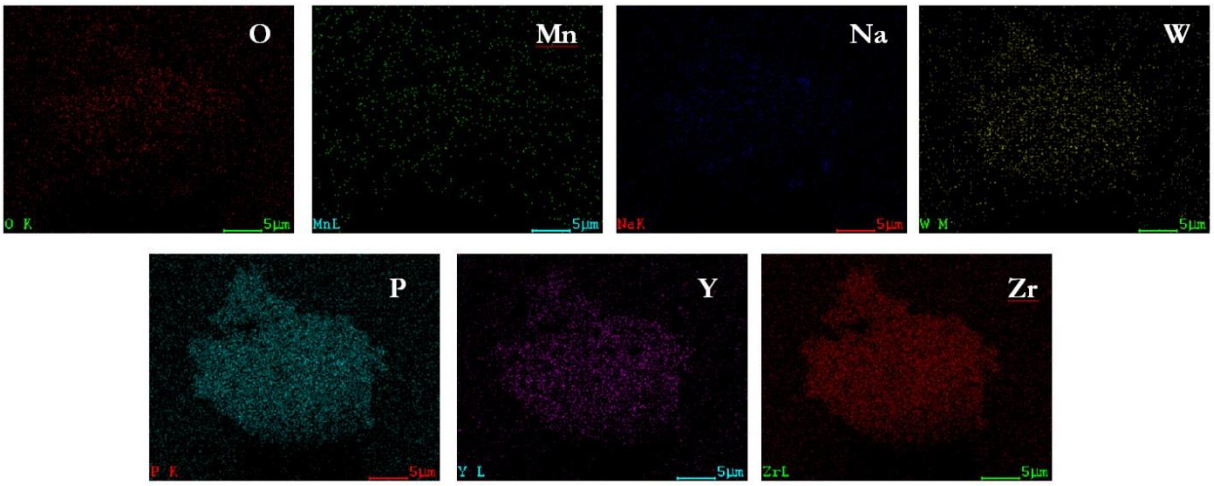

Fig. 7. The SEM-EDS mapping of elements on P-Na_2WO_4-Mn/YSZ catalyst.

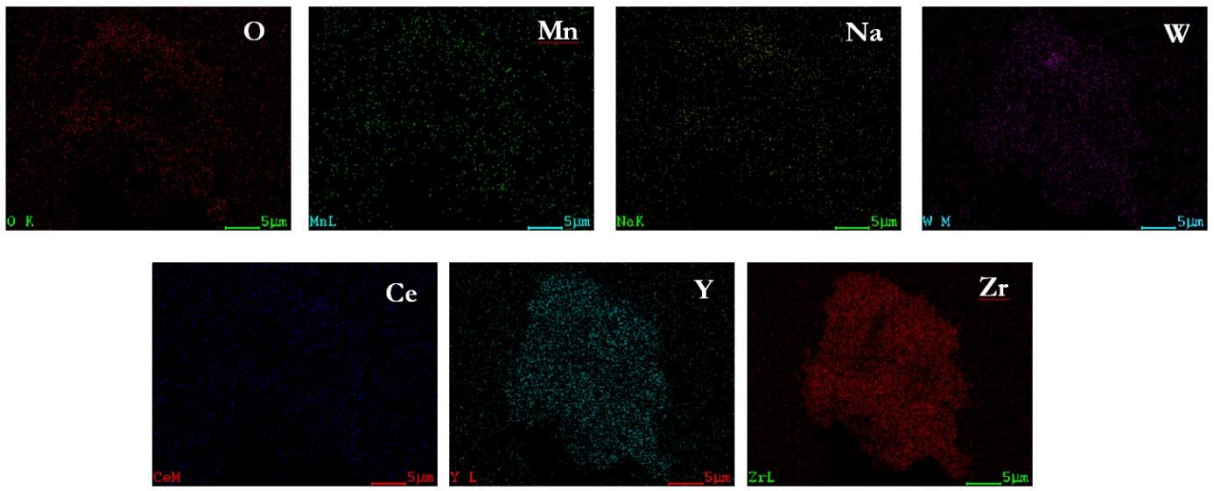

Fig. 8. The SEM-EDS mapping of elements on Ce-Na_2WO_4-Mn/YSZ catalyst.

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 m^2 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 ($m^2 g^{-1}$)	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

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 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 C2 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 Figs. 9–11.

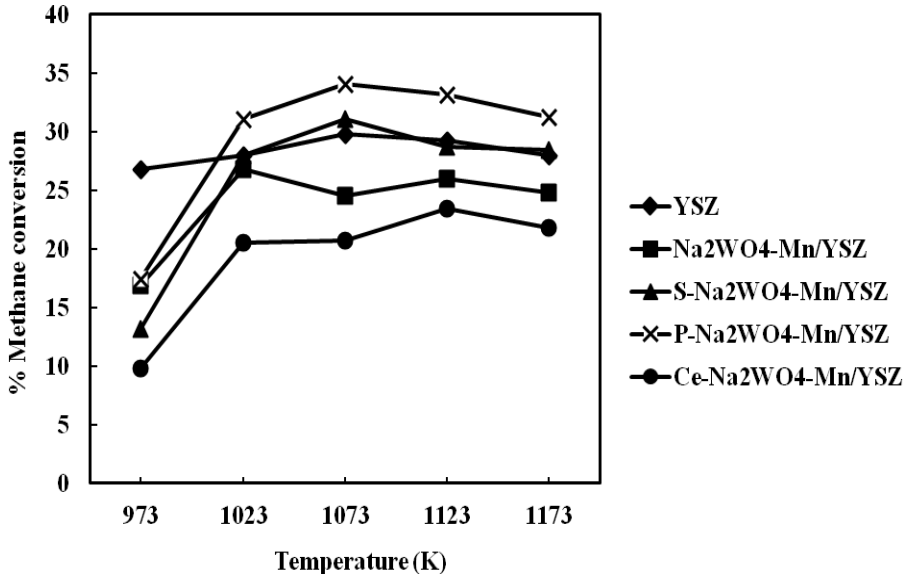

Fig 9. Methane conversion of YSZ support catalyst with WHSV 15,000 $cm^3.g^{-1}.h^{-1}$.

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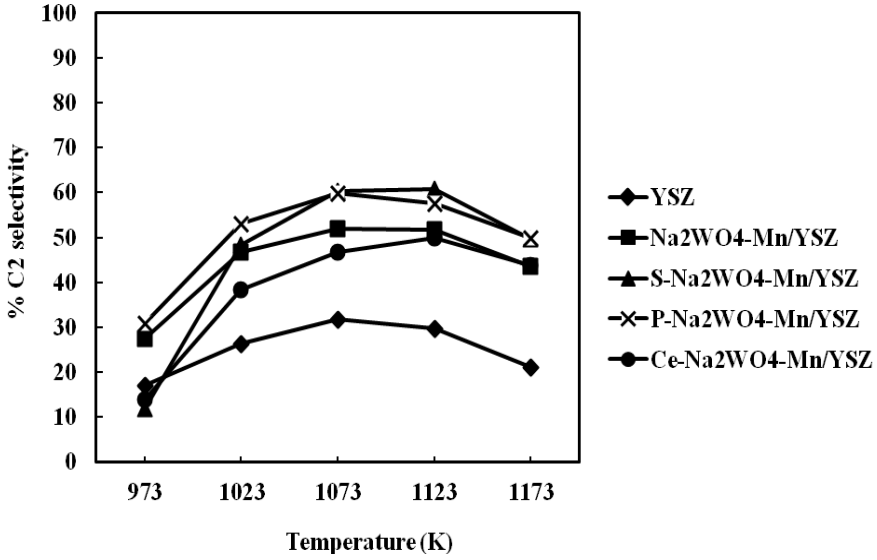

Fig. 10. C_2 selectivity of YSZ support catalyst with WHSV 15,000 $cm^3.g^{-1}.h^{-1}$.

3.3. OCM in SOFC Reactor for C_2H_4 Hydrocarbon and Electricity Co-generation

After experiment in fixed bed reactor the P- Na_2WO_4-Mn /YSZ was selected to test in SOFC reactor for investigate the performance to produce C_2 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_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 maximum power density about 9.8 W/m^2 at 1123K. The maximum power density was 16.8 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. [18] 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 15% C_2 yield at 1223 K then provided power density about 13.37 W/m^2. In addition, Lapeña-Rey and Middleton [19] investigated in Na_2WO_4-Mn/SiO_2 and K_2WO_4-Mn/SiO_2 in co-feed mode and electrochemical mode at 1123K. 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.

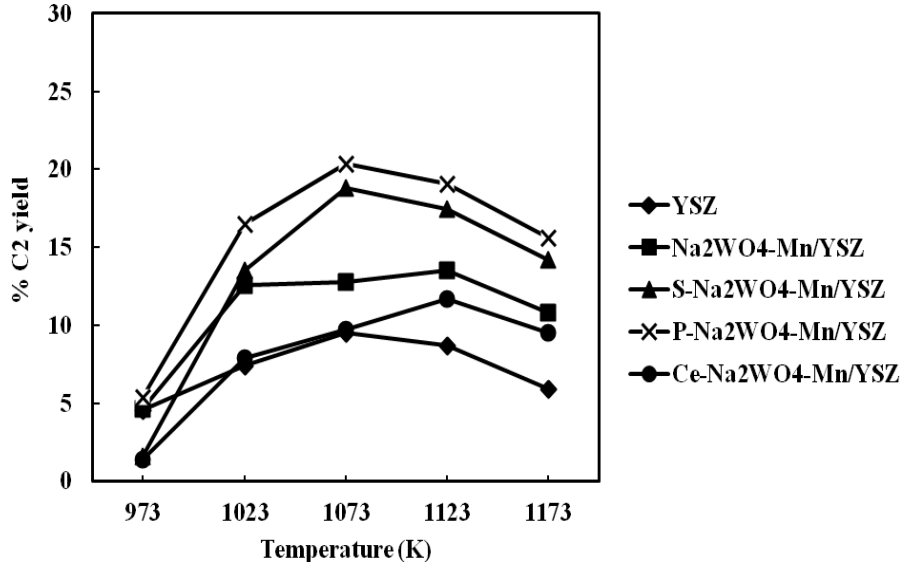

Fig. 11. C_2 yield of YSZ support catalyst with WHSV 15,000 $cm^3.g^{-1}.h^{-1}$

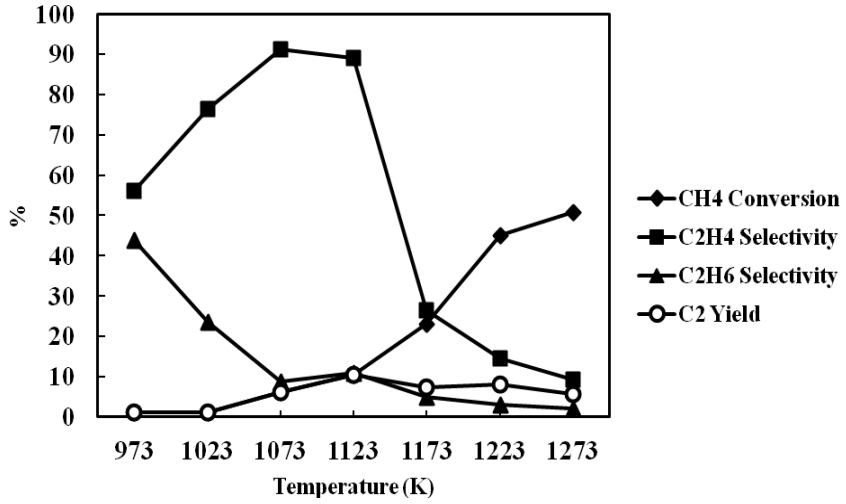

Fig 12. Performance of P-Na_2WO_4-Mn/YSZ catalyst in SOFC reactor.

Table 2. The electric power at each temperature for P-Na_2WO_4-Mn/YSZ catalyst in SOFC reactor.

Temperature (K)	Current (mA)	Oxygen consumption (mol•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

DOI:10.4186/ej.2015.19.4.1

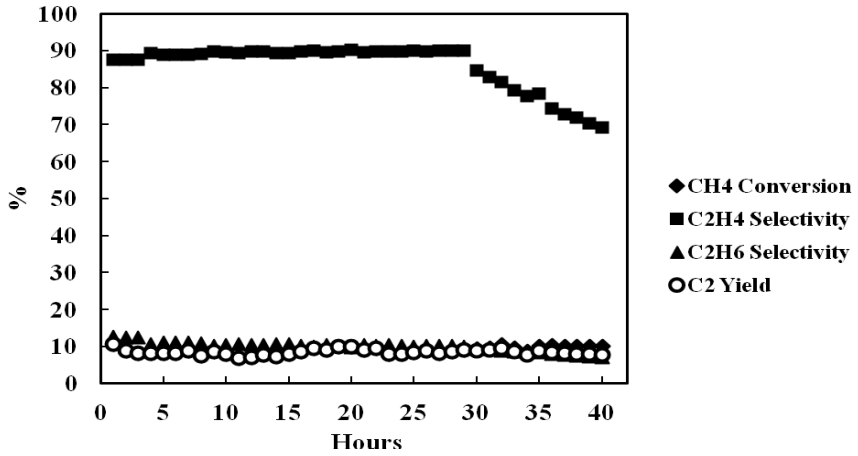

Fig. 13. Stability test of P-Na_2WO_4-Mn/YSZ catalyst in SOFC reactor at 1123 K.

Moreover, the P-Na2WO4-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 [9]. In addition, the maximum C_2 yield was obtained at 1123 K, which lowers operating temperature than Kiatkittipong [20]. The report showed about 3% C2 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 O2- 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 C2 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-Na2WO4-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 (Fig. 13), after that the C_2H_4 selectivity decreased because occurred the carbon deposition on catalysts.

4. Conclusion

The P-Na_2WO_4-Mn/YSZ catalyst exhibited the high performance. The stability test exhibited very well because of more than 24 hr. Therefore, P-Na_2WO_4-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.

Acknowledgements

The authors gratefully acknowledge the Thailand Research Fund, Higher Education Commission and Chulalongkorn University for financial support, as well as Professor Piyasan Praserthdam.

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