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Article

## Synthesis of $\text{Na}_2\text{WO}_4$ -Mn supported YSZ as a potential anode catalyst for oxidative coupling of methane in SOFC reactor

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**Abstract.** The oxidative coupling of methane (OCM) over a 5% $\text{Na}_2\text{WO}_4$ -2%Mn on YSZ, has been investigated in a fixed bed reactor (FBR) and a solid oxide fuel cell reactor (SOFC). A 60% C<sub>2</sub> selectivity and a 26% CH<sub>4</sub> conversion have been obtained in a FBR at 800°C and CH<sub>4</sub>/O<sub>2</sub> of 4:1. Importantly, an addition of  $\text{Na}_2\text{WO}_4$ -Mn to YSZ support can significantly enhance the performance of the catalyst especially C<sub>2</sub> hydrocarbons selectivity and CH<sub>4</sub> conversion. A maximum power density of 7.8 mW cm<sup>-2</sup> was achieved at 800°C with CH<sub>4</sub> in the SOFC reactor having a 50 μm thick YSZ electrolyte. The CH<sub>4</sub> conversion and C<sub>2</sub> selectivity at 800°C were 1.1% and 85.2%, respectively.

**Keywords:** C<sub>2</sub> hydrocarbons, OCM, YSZ,  $\text{Na}_2\text{WO}_4$ -Mn.

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## 1. Introduction

Oxidative coupling of methane (OCM) to C<sub>2</sub>-hydrocarbons has attracted much attention during the past three decades as it is a potential route in utilizing methane, a major component of natural gas and a byproduct of oil refining and chemical processing. Since the pioneering work of Keller and Bhasin [1], there have been many research efforts on a production of C<sub>2</sub> hydrocarbons from OCM reaction. A wide variety of catalysts have been studied. However, the yield of C<sub>2</sub> hydrocarbons achieved in a fixed-bed reactor (FBR) was limited to about 25% due to the presence of undesired partial or complete oxidation in gas phase and on catalyst surface [2–4]. To overcome this limiting problem, selective catalysts for the methane coupling reaction and some reactors have been designed to inhibit the side reactions. A Solid Oxide Fuel Cell (SOFC) reactor is one of the most attractive reactors. It simultaneously co-generates electricity as by product and C<sub>2</sub> hydrocarbons through OCM reaction. Solid oxide membranes were used to control the necessary oxygen for the OCM process. Therefore, an SOFC reactor is potentially more interesting than other conventional reactors due to the achievement of high selectivity and possible use of generated electricity. Many electrochemical studies of OCM reaction over metallic catalyst-electrodes have been reported but the yield of C<sub>2</sub> hydrocarbons was low (~ 10%). Therefore, the development of anode catalysts for OCM in SOFC becomes an important goal to improve the conversion, selectivity and yield of C<sub>2</sub> hydrocarbons.

Among several catalysts, 5wt%Na<sub>2</sub>WO<sub>4</sub>-2wt%Mn/SiO<sub>2</sub> offers a good performance in OCM with 20% of methane conversion and 80% of C<sub>2</sub><sup>+</sup> selectivity [3, 5–7]]. Lunsford and co-workers [8-9] reported that Na-O-Mn species were responsible for an activation of methane, in which Mn was an active component, Na provided selectivity, and W was required to stabilize the catalyst. Afterwards, Lapeña-Rey *et al.* investigated OCM in SOFC using YSZ as a solid electrolyte, 5wt%Na<sub>2</sub>WO<sub>4</sub>-2wt%Mn/SiO<sub>2</sub> was used as an anode catalyst. Very high C<sub>2</sub> hydrocarbon selectivity was obtained while the methane conversion was low. However, the SiO<sub>2</sub> support had low electrical conductivity, thus it was required to be mixed with a conductive component such as silver to increase the electrical conductivity [10]. In addition, the performance-limiting factor in solid oxide fuel cells (SOFC) is often the electrode impedance [11–13] which can be avoided by using low-temperature, infiltration procedures to synthesize the electrodes [14–17]. This procedure involves a preparation of porous YSZ (dense YSZ is the electrolyte) scaffold together with the electrolyte layer, then infiltrating the required precursor salts to form the particle within the scaffold. Because the procedure allows a formation of a long three-phase boundary (TPB), the initial performance of these electrodes can be good.

The main objective of this research was to investigate the new anode catalysts in SOFC. In the present work, 5wt%Na<sub>2</sub>WO<sub>4</sub>-2wt%Mn/YSZ catalysts were examined. The catalysts were characterized by BET, XRD and XPS. The catalytic activity of catalysts for OCM was evaluated using a continuous-flow fixed bed reactor and a solid oxide fuel cell reactor.

## 2. Experimental

### 2.1. Catalyst Preparation and Characterization

5 wt%Na<sub>2</sub>WO<sub>4</sub>-2 wt%Mn/YSZ catalyst (denoted by Na-W-Mn/YSZ) was prepared by a two-step incipient wetness impregnation method. In the first stage, manganese was impregnated onto YSZ support (8 mol% Ytria-Stabilized Zirconia, TZ-8Y, Tosoh, Japan) with Mn(NO<sub>2</sub>)<sub>3</sub>.6H<sub>2</sub>O (Aldrich) dissolved in deionized water. Then the sample was dried at 110 °C overnight. In the second stage, 2% wt of Na<sub>2</sub>WO<sub>4</sub> was added to the support sample using Na<sub>2</sub>WO<sub>4</sub>.4H<sub>2</sub>O (Aldrich) solution. The impregnated particles were dried again and calcined in air at 850 °C for 5 h. For comparison, the 5 wt%Na<sub>2</sub>WO<sub>4</sub>-2 wt%Mn/SiO<sub>2</sub> catalyst (denoted by Na-W-Mn/SiO<sub>2</sub>) was prepared using the same method. Herein, SiO<sub>2</sub> commercial (40-60 mesh, 250 m<sup>2</sup>/g, Sigma Aldrich) were selected as a support.

The synthesized catalysts were determined by various techniques for their physical properties. Surface area and pore size were determined using BET method. The crystalline phases of prepared samples were identified using x-ray diffraction technique with Cu-K $\alpha$  radiation. The x-ray diffractograms were recorded in the range of 10° to 90° (2 $\Theta$ ). A scanning electron microscope (SEM) was used to study the morphology.

## 2.2. Catalytic Activity Testing in Fixed Bed Reactor

The reaction was carried out in a tubular quartz reactor filled with 200 mg of selected sample and small amount of quartz wool. The reactor was vertically mounted inside a furnace. Gas mixture between methane and oxygen diluted in helium were allowed to continually flow into the reaction zone. The catalytic activity was tested at atmospheric pressure and within a temperature range of 700-900°C in a conventional fixed-bed micro-reactor made of quartz (i.d. 6 mm). The reactants, CH<sub>4</sub> (99.9%) and O<sub>2</sub> (99.9%) without any diluents, were co-fed into the reactor with suitable CH<sub>4</sub>/O<sub>2</sub> ratios and gas hourly space velocity (GHSV) at STP of 15000 ml·g<sup>-1</sup>·h<sup>-1</sup>. A cold trap was used to remove water from the exit gas stream at the reactor outlet. The products were analyzed with an on-line GC equipped with a TCD, using a Porapak Q column and a (5Å) molecular sieve column, every 30 min until reaching the steady state condition.

## 2.3. Single Cell Fabrication and Fuel Cell Performance Testing

The cell fabrication of a porous-dense-porous YSZ wafer was carried out using a tape-casting method. As described elsewhere [18] the dense electrolyte layers were approximately 50 μm thick and 2 cm in diameter, while the two porous layers were each 150 μm thick. After synthesizing the three-layer YSZ, La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>3</sub> (LSF) was added to the cathode porous layers using aqueous nitrate solutions until the loading of LSF was 45 wt.% as described by Vohs and Gorte [18]. For the anode side, Mn-Na<sub>2</sub>WO<sub>4</sub> was added after the final 850 °C calcination used to produce the LSF. Ag paste and Ag wire were used to make electrical connections to both electrodes. In the cell testing, both electrodes were exposed to either humidified (3% H<sub>2</sub>O) H<sub>2</sub> or CH<sub>4</sub>. Impedance spectra were measured at open circuit in the galvanostatic mode using a Solartron potentiostat. Products from the anode side were analyzed with an equipped on-line GC.

## 3. Results and Discussion

### 3.1. Catalyst Characteristics

The BET surface area, volume and pore size of all catalysts prepared in this work are summarized in Table 1. After the active phase was loaded with Na<sub>2</sub>WO<sub>4</sub> and Mn precursor, the surface areas, volume and pore sizes of the YSZ and SiO<sub>2</sub> decreased due to a packing effect during the drying and calcination processes. For Na-W-Mn/SiO<sub>2</sub> catalyst, calcinations of the amorphous silica in the presence of an alkali salt like sodium tungstate as a mineralizing agent caused the complete conversion of the silica to the low surface area crystalline phase [19].

Table 1. Surface area, average pore size and pore volume.

Catalysts	surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Mean pore diameter (nm)
SiO <sub>2</sub>	255.0	0.878	10.5
YSZ	14.2	0.0964	26.4
Na-W-Mn/SiO <sub>2</sub>	3.50	0.0043	6.50
Na-W-Mn/YSZ	7.90	0.0405	18.5

The SEM images in Fig. 1 clearly show a congregation of many particles. The Mn distribution determined by EDX spectroscopy (shown in Figs. 1(a-d)) also qualitatively confirm that Mn elements were well dispersed on the YSZ and SiO<sub>2</sub> supports. Malekzadeh et al. [19] have reported that manganese oxide (MnO<sub>x</sub>) promoted catalyst can decrease the band gap of the catalyst. The conductivity of the catalyst depends on the band gap of the metal oxide constituent of the catalyst. MnO<sub>x</sub> shows the high electrical conductivity, which could improve a performance in OCM reaction.

X-ray powder diffraction (XRD) was used to identify bulk phase composition in the catalysts. The XRD patterns of YSZ, Na-W-Mn/SiO<sub>2</sub> and Na-W-Mn/YSZ are displayed in Figs. 2(a-c). For Na-W-Mn/SiO<sub>2</sub> catalyst, the main phase is Na<sub>2</sub>WO<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub> and α-cristobalite [7]. For the XRD spectra of Na-W-

Mn/YSZ, the formation of the  $\text{Na}_2\text{WO}_4$  and  $\text{Mn}_2\text{O}_3$  phase were not detected. However,  $\text{Na}_2\text{WO}_4$  and  $\text{Mn}_2\text{O}_3$  phases on YSZ support were confirmed by using an X-ray photoelectron spectroscopy (XPS).

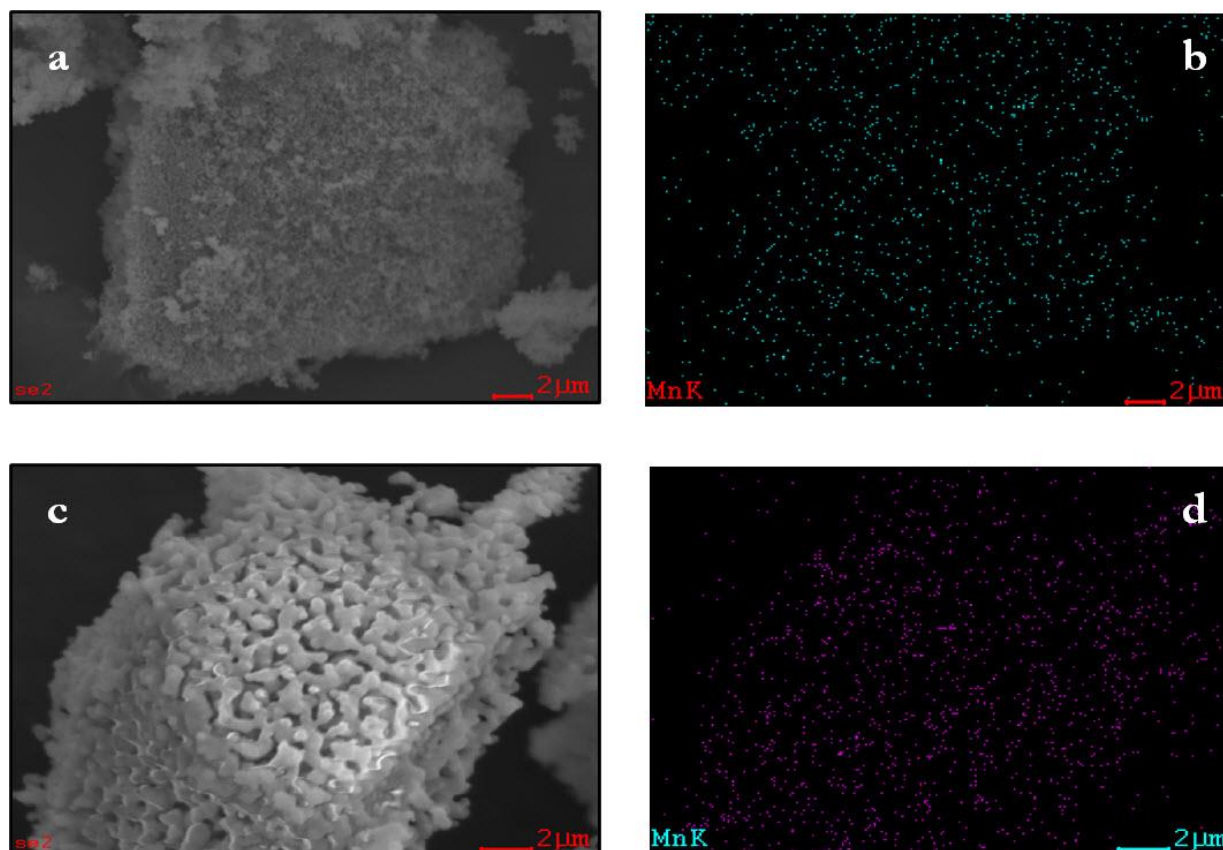


Fig. 1. SEM images and Mn elemental mappings of (a) SEM of Na-W-Mn/YSZ, (b) Mn mapping of Na-W-Mn/YSZ (c) SEM of Na-W-Mn/SiO<sub>2</sub>, (d) Mn mapping of Na-W-Mn/SiO<sub>2</sub>.

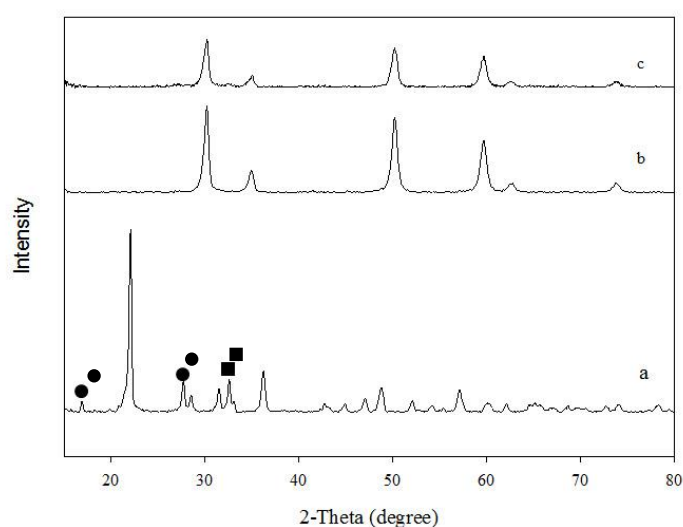


Fig. 2. XRD patterns of (a) Na-W-Mn/SiO<sub>2</sub>, (b) YSZ and (c) Na-W-Mn/YSZ, (●)  $\text{Na}_2\text{WO}_4$ , (■)  $\text{Mn}_2\text{O}_3$ .

Table 2. Surface composition (at%) of the components of fresh catalysts.

Catalysts	Na(1s)	W(4f)	Mn(2p)	O(1s)	O(1s)(MO <sub>x</sub> )	Y(3d)	Zr(3d)
Na-W-Mn/YSZ	12.3	7.2	3.1	24.8	17.8	3.8	31

Table 2 shows the observed elemental concentrations near the surface of the fresh catalysts by XPS characterization. These catalysts show that the surface atomic concentrations of Na, W and Mn are close to those of the bulk compositions, indicating that Na, W and Mn are enriched on the catalysts surface. Moreover, two kinds of surface oxygen on the catalysts were found. Na(1s), W(4f) and Mn(2p) are clearly present on the catalyst surface. This confirms that YSZ surface have the  $\text{Na}_2\text{WO}_4$  and  $\text{Mn}_2\text{O}_3$  active species on the catalyst surface.

### 3.2. Catalytic Performance of Catalysts

Table 3 summarizes the catalytic performances of different catalysts after 90 min of reaction at steady state under GHSV of  $15000 \text{ ml g}^{-1} \text{ h}^{-1}$ ,  $800^\circ\text{C}$  and a molar ratio of  $\text{CH}_4/\text{O}_2$  of 4:1 [6, 20]. For Na-W-Mn/ $\text{SiO}_2$  catalyst, 12.0% CO selectivity, 12.9%  $\text{CO}_2$  selectivity and 69.0% C2 selectivity at 28.5%  $\text{CH}_4$  conversion are obtained, which are in agreement with several reports [21-24]. In a comparison among different supports, YSZ shows greater selectivity to partial oxidation than the complete combustion, as the selectivity to CO is much greater than that to  $\text{CO}_2$ . When  $\text{Na}_2\text{WO}_4$  and Mn are added on YSZ, the promoting effects on  $\text{CH}_4$  conversion from 10.6 to 26.9% and C2 selectivity from 18.9 to 60.6% are obviously observed. It is really interesting to note that the promotion of tri-metallic oxide (Na, W, and Mn) can significantly improve the catalytic performance of YSZ for the selective OCM reaction.

Table 3. Catalytic performance of catalysts<sup>a</sup>.

Catalyst	Conversion (%)		Selectivity (%)					Yield (%)
	$\text{CH}_4$	$\text{H}_2$	CO	$\text{CO}_2$	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_6$	C2	C2
YSZ	10.6	48.5	54.0	27.3	0	18.9	18.9	2.0
Na-W-Mn/ $\text{SiO}_2$	28.5	4.1	12.0	12.9	21.2	47.8	69.0	19.7
Na-W-Mn/YSZ	26.9	2.6	9.9	25.2	22.9	37.7	60.6	16.3

<sup>a</sup>Reaction condition:  $T=1073 \text{ K}$ ;  $\text{CH}_4/\text{O}_2=4$ ;  $\text{WHSV}=15000 \text{ ml g}^{-1} \text{ h}^{-1}$ ; 0.2 g catalyst.

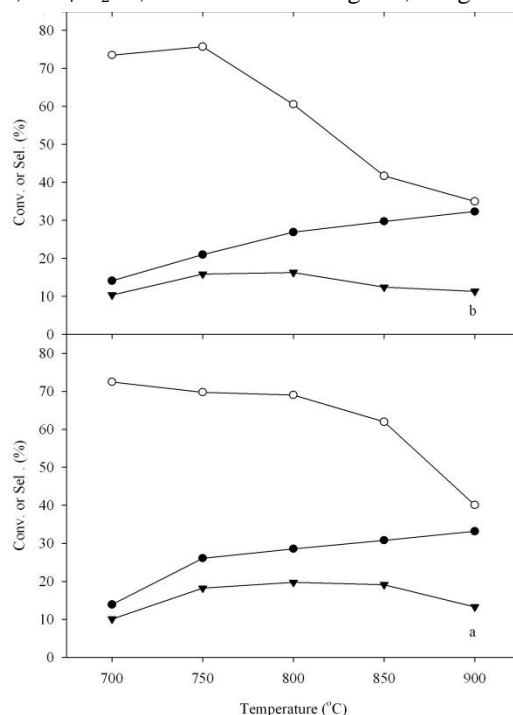


Fig. 3. Catalytic performance of Na-W-Mn/ $\text{SiO}_2$  and Na-W-Mn/YSZ catalysts as related to operating temperatures at GHSV of  $15000 \text{ ml g}^{-1} \text{ h}^{-1}$  and  $\text{CH}_4/\text{O}_2$  of 4. (a) Na-W-Mn/ $\text{SiO}_2$ , (b) Na-W-Mn/YSZ. (●) conversion of  $\text{CH}_4$ , (○) C2 selectivity, (▼) C2 yield.

Effect of temperature for OCM reaction over Na-W-Mn/SiO<sub>2</sub> and Na-W-Mn/YSZ catalysts is shown in Fig. 3. Trends of CH<sub>4</sub> conversion over three catalysts showed a slight increase with rising operating temperature. However, decreases in C<sub>2</sub> selectivity and C<sub>2</sub> hydrocarbons yield are observed in the temperature range of 800-900°C because of kinetic limitations. The upper limit of OCM yield under the conventional fixed bed is considered to be dominated by the enthalpies of hydrogen severance from methane and oxygen dissociative adsorption [20]. The optimum temperature for three catalysts appears to be at 800°C, where C<sub>2</sub> hydrocarbon yields are 19.7% and 16.3% for Na-W-Mn/SiO<sub>2</sub> and Na-W-Mn/YSZ, respectively in which these results are not significantly different while higher C<sub>2</sub> selectivity (61%) is observed over Na-W-Mn/YSZ. Therefore, Na-W-Mn/YSZ is an attractive catalyst for use in an SOFC reactor.

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

After being tested in a fixed bed reactor, the Na-W-Mn/YSZ was tested in an SOFC reactor to investigate the fuel cell performance and performance to produce C<sub>2</sub> hydrocarbons and electric current. Figure 4 shows voltage, current, and power density properties for three tape-cast SOFC cells fabricated by impregnation of Na<sub>2</sub>WO<sub>4</sub> and Mn<sub>2</sub>O<sub>3</sub> with Ag current collectors. The measurements of these cells at 800°C in wet H<sub>2</sub> and wet CH<sub>4</sub> are shown in Figs. 4a and 4b, respectively. For H<sub>2</sub> fuel, their open circuit voltage (OCV) values were 1.07 V, which were very close to the theoretical value calculated from Nernst equation. Such high OCV values indicate that a dense structure is well-formed in the YSZ electrolyte and leakage of the gas is negligible for each sample. As seen in Figs. 4a and 4b, the power density was 13.2 and 7.8 mW.cm<sup>-2</sup>, respectively. The power density of the specimen measured in H<sub>2</sub> was nearly double of that measured in CH<sub>4</sub>. From the experiments at 800°C under load of 0.3 V, the methane conversion was around 2.1% and 85.2% for C<sub>2</sub> hydrocarbons selectivity observed with a significant C<sub>2</sub> hydrocarbons production.

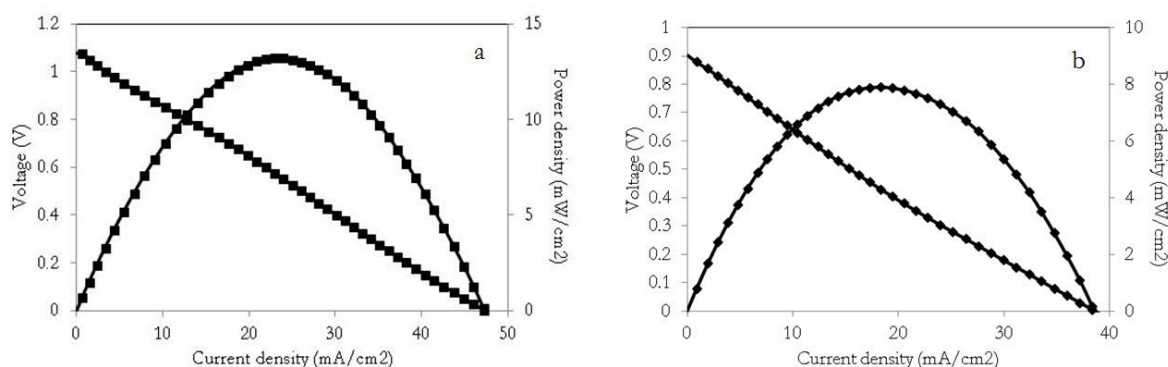


Fig. 4. Voltage current and power density versus current density plots for the cells with each of the four anode compositions at 800°C, under (a) wet H<sub>2</sub> and (b) wet CH<sub>4</sub>.

## Conclusions

Na-W catalysts supported YSZ catalyst was synthesized, characterized and explored as anode catalyst materials for the OCM reaction. The presence of Mn<sup>3+</sup> and W<sup>6+</sup> on YSZ were confirmed while they significantly improve the catalytic activity and C<sub>2</sub> selectivity despite of a very low surface area YSZ. Additionally, using YSZ as a support has reduced the distance and thickness of interface layer between anode and cathode, resulting in a good diffusion and catalytic reaction. Therefore, Na-W-Mn/YSZ is potentially a promising anode catalyst for use in an SOFC reactor for C<sub>2</sub> hydrocarbons production via OCM reaction.

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