

Reviews on Coupling of Methane over Catalysts for Application in C₂ Hydrocarbon Production

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Abstract: This study presents a review of Oxidative Coupling of Methane (OCM) reactions over different catalysts for fixed bed reactor and SOFC reactor. The catalysts have much promise role methane conversion, C₂ selectivity and C₂ yield. The review contains the elementary operating principles of OCM and the catalysts. In addition, some of the most important recent advance catalysts in electro co-generation process in SOFC reactor to produce C₂ hydrocarbon along with electricity have been reviewed. Although, OCM recognized as an attractive reaction by many researchers because ethylene product is important base chemical in the petrochemical industries but OCM has a limitation. Commercial application of OCM reaction however requires further improvements in their performance, stability and the development of cheaper catalyst materials.

Key words: OCM, C₂ hydrocarbon, electro co-generation, catalyst, stability

INTRODUCTION

OCM reaction: During the past 2 decades, there has been a global interest in the conversion of methane to high value chemical products, especially ethane and ethylene because ethylene is a base chemical in the petrochemical industries such as Polyethylene (PE), Polyvinyl Chloride (PVC), Polyethylene Terephthalate (PET), etc. Oxidative Coupling of Methane (OCM) is a promising way to convert methane into ethylene and ethane which is valuable product. As shown in Fig. 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 and this reaction is highly exothermic.

Worldwide efforts have been investigated 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 in order to increase C₂ hydrocarbons production. Many investigators caught the catalytic performance can be significantly improved by halides. Long *et al.* (1995) studied alkaline

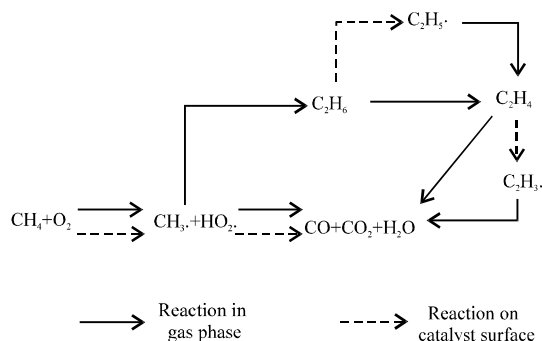


Fig. 1: A general scheme of the reaction network in OCM (Sun *et al.*, 2008)

earth metal fluoride by promoting F⁻ on Sr/La oxide catalysts for OCM in packed bed reactor that the maximum C₂ yields of 18-20% were achieved over the LaF₃/SrO and SrF₂/La₂O₃ catalysts at 650-750°C. In some cases, halides especially chlorides and bromides were added to the oxides in order to improve the catalytic activity and selectivity. Au *et al.* (1998a) proposed that BaF₂, BaCl₂ or BaBr₂ can significantly improve the catalytic performance of Gd₂O₃. Moreover, Fakhroueian *et al.* (2008) studied the XBaSrTiO₃ (X = Li, Na, Mg) perovskite in OCM it was

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found the NaBST showed the maximum catalytic effect providing 42% methane conversion and 51% ethylene selectivity at the temperature of 800°C. Au *et al.* (1997) reported that performance of LaOCl was promoted by BaCO₃ in OCM reaction. When 10 mol% BaCO₃ was added, there was slightly change in CH₄ conversion while C₂ selectivity was increased from 37-66%. Hong and Yoon (2001) studied on CaCl₂ promoted calcium chlorophosphate catalysts and with partial substitution of the calcium with transition metals such as zinc, lead and nickel for OCM at 750°C, the highest C₂ yield of around 22% was obtained with the C₂ selectivity of 56-59%. Although, there are many researches on OCM reaction it has remained not to be successful. The researchers have been still interested on a new approach for improve performance of reaction, i.e., membrane brought into use or applied in SOFC.

Various types of reactors such as fixed bed reactor, membrane reactor and Solid Oxide Fuel Cell (SOFC) 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 C₂ 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.

The application of OCM reaction to SOFC for multifunctional reactor to produce chemical and electrical production is very attractive because SOFC is energy source in the future. In generally, SOFC produce electrical power from hydrogen fuel but hydrogen fuel still high price. In this research showed a development of catalyst in OCM reaction in fixed bed and SOFC reactor from past to present.

PRINCIPLE FOR OCM AND SOFC

The mechanism which 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 CO₂) are usually considered to be formed due to oxidation of methane, C₂ hydrocarbon molecules and hydrocarbon radicals. The reactions are shown as Gao and Ma (2010):

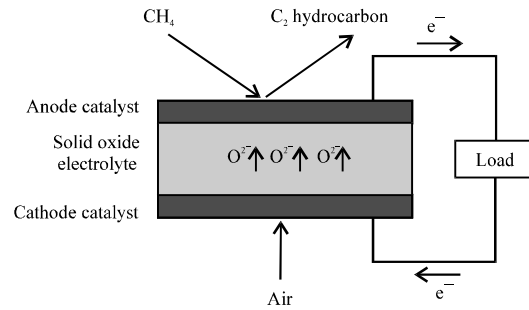
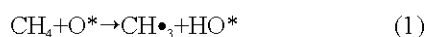
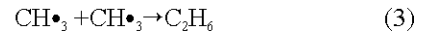
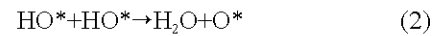
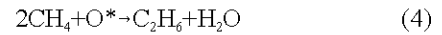


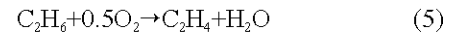
Fig. 2: Scheme of the OCM reaction for SOFC reactor (Tagawa *et al.*, 1999)



Overall reaction of the three steps above is shown in Eq. 4:

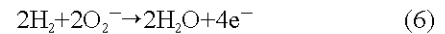


Ethylene is a secondary product formed from dehydrogenation as:



CH₃• is methyl radical and O* is surface active oxygen species. Fuel cell is electrochemical cell similar battery usually used as a power generator but difference between SOFC and battery is lifetime. In SOFC reactant (fuel, 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 600-1000°C.

Briefly, the reduction of O₂ to O²⁻ anions occur at the cathode, the anions transfer through an electrolyte and the oxidation of the fuel with O²⁻ anions at the anode. Effectively, the chemical energy produced when the fuel is oxidized and the electrons are produced at the anode. The schemes of the OCM reaction for SOFC reactor are shown in Fig. 2. The overall reactions are shown in Eq. 6-8:



DEVELOPMENT OF CATALYST IN OCM

OCM reaction can be used in different reactors such as fixed bed reactor, SOFC reactor and the details have

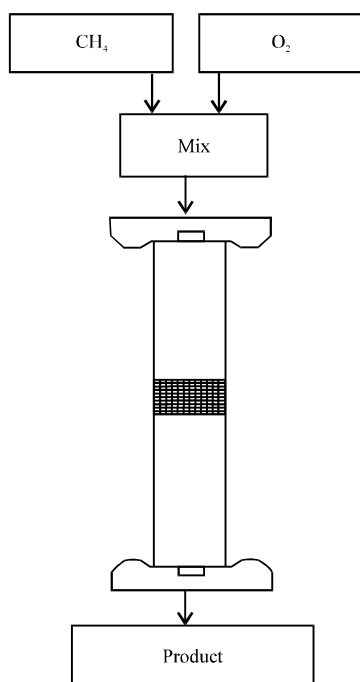


Fig. 3: Configuration of FBR (Chua *et al.*, 2008)

been considered in this review. In addition, the catalysts can be divided into two categories; mixed and perovskite oxide.

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 600-1000°C. The configuration of fixed bed reactor is shown in Fig. 3.

Mixed oxide catalyst: Most researches about OCM process emphasized development of the catalyst performance for increase simultaneously the methane conversion and C₂ selectivity. A large number of catalyst systems have been found to be effective in OCM. Rare earth oxide catalysts (La₂O₃, CeO₂, Sm₂O₃) provide a high performance in this reaction. Murata *et al.* (1998) investigated Li-doped sulfated-zirconia catalysts which these catalysts were effective for OCM. In addition, alkaline earth metal fluoride (SrF₂-La₂O₃, SrO-LaF₃, BaF₂-CeO₂) showed a good catalytic performance in OCM. Chao *et al.* (1995) studied BaF₂/LaOF in fixed bed reactor at 770°C. CH₄ conversion of 33.08% and a C₂ selectivity of 62.47% was achieved at CH₄:O₂ = 3:1. Moreover, the performance of OCM reaction results was obtained over BaF₂/LaOF with BaF₂ content in 10-18

mol%. In addition, Papa *et al.* (2010) proposed the relationship between the surface basicity and catalytic activity for C₂ formation over equimolecular mixtures of alkaline-earth oxides (BeO, MgO, CaO and SrO) and Nd₂O₃. The better was the (MgO, CaO and SrO) and Nd₂O₃. The better was the efficiency for selectively converting methane to C₂ over basicity catalyst which consistent with Rane *et al.* (2008) studied influence of alkali metal (Li, Na, K, Rb and Cs) dope CaO catalysts in OCM. The result of addition alkali metal showed a decreasing in the surface area but a increasing in the surface basicity and the C₂ selectivity and yield in the OCM reaction. The Na-CaO catalyst showed good catalytic performance, C₂ selectivity of 68.8 with 24.7% methane conversion in the OCM. Au *et al.* (1998b) reported OCM reaction over BaX₂/Gd₂O₃ (X = F, Cl, Br) catalysts. The BaCl₂/Gd₂O₃ was effective to increase the C₂ yield (21.1% of C₂ yield with a CH₄ conversion of 36.6% and C₂ selectivity of 57.6%). Therefore, the halides presence can improve performance in BaX₂/Gd₂O₃. Au *et al.* (1997) studied OCM over BaCO₃/LaOCl catalysts at 800°C. The addition of BaCO₃ over LaOCl provided the good performance was 40% methane conversion, 56% C₂ selectivity and 22% C₂ yield. Research on the OCM to C₂ hydrocarbons has been shown that alkali, alkaline earth, rare earth, rare earth oxide/alkaline earth oxide mixed catalysts and transition metal oxides were catalytically active materials. After that Au proposed BaF₂/Y₂O₃ catalyst for OCM reaction. It found that quantity composition of BaF₂ have affected to performance of catalyst when the CH₄:O₂:N₂ = 2.47:1:11.4 and a total flow rate of 50 mL min⁻¹, after 4 h at 750°C, the CH₄ conversion and C₂ selectivity over Y₂O₃ were 29.9 and 26.2%, respectively, giving a C₂ yield of 7.8%. When 30 mol% of BaF₂ was added, the CH₄ conversion, C₂ selectivity and C₂ yield were enhanced to 35.3, 55.4 and 19.5%, respectively. With a 95 mol% BaF₂/Y₂O₃ catalyst, the performance could be achieved a 22.4% C₂ yield with 36.1% CH₄ conversion and 62.1% C₂ selectivity (Au *et al.*, 1998a). Zeng *et al.* (2001) studied catalytic properties of dense fluorite structured Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-δ} (BYS) pellets in a packed bed reactor. C₂ yields of 20-27%, C₂ selectivity of 50-62% were obtain and CH₄/O₂ ratio and He/(CH₄+O₂) ratio had significant effects on OCM performance over BYS catalyst. Another interesting discovers that were a few transition metal oxides to contain group IA ions or transition metal based catalyst for example Mn/Na₂WO₄/SiO₂. 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. The same catalyst was

studied by Ji *et al.* (2002) have great attention in the $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ catalyst system because of its excellent catalytic performance. They are proposed the relationship between structure and the performance of Na-W-Mn/SiO₂ 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%. The addition of sodium to the catalyst is believed to help about the migration of Mn and W to the catalyst surface, therefore improves performance of catalyst. After that, Ji *et al.* (2003) reported performance of M-W-Mn/SiO₂ catalysts (M = Li, Na, K, Ba, Ca, Fe, Co, Ni and Al) in OCM. In the trimetallic catalysts studied, there was evidence for WO₄ tetrahedron on the surface in the Li-, Na- and K-W-Mn/SiO₂ catalysts. The WO₄ tetrahedron on the catalyst surface appears to an essential role in achieving high CH₄ conversion and high C₂ hydrocarbon selectivity in the OCM reaction. Recently, Liu *et al.* (2008) scaled up and tested stability for OCM over Na₂WO₄-Mn/SiO₂ catalyst that the highest C₂ (ethylene and ethane) yield of 25% was achieved. When increased temperature from 640-800°C the C₂ yield decreased and the CO_x certainly increased. The catalyst showed excellent catalytic activity and stability at 800°C. In addition, it found that the GHSV and CH₄/O₂ ratio effect to performance of catalyst. When increased the GHSV whereas C₂ selectivity decreased and the suitable CH₄/O₂ ratio is 5. Several studies proposed a surface W species containing W = O and 3 W-O-Si bonds as the OCM active site as same as Chua *et al.* (2008). Zhang *et al.* (2007) studied on CeO₂-W-Mn/SiO₂ catalyst for OCM at 800°C in fixed bed reactor. Modified W-Mn/SiO₂ catalysts with CeO₂ provided the reaction stable for 500 h and obtained 22% of C₂H₄ yields which these results coincided with Shahri and Pour (2010). Moreover, the difference of dilution gas was significant to performance of reaction. Zheng *et al.* (2010) reported catalytic performance of S and P promoted Na-W-Mn-Zr/SiO₂ catalyst for OCM at 750°C. The XRD result showed addition of S and P to the Na-W-Mn-Zr/SiO₂ catalyst helped the formation of active phases such as α-cristobalite, Na₂WO₄, ZrO₂ and Na₂SO₄ and increased the surface active oxygen species. Improvements of catalyst by add S and P led to increase the performance of catalyst with the maximum C₂ yield of 16%.

Table 1 comparison the performance of several catalysts, the Na-W-Mn/SiO₂ showed better performance than overall and it was interesting. Both Na-O-Mn and Na-O-W act as the active centers of the catalysts for OCM. Although, Na-W-Mn/SiO₂ exhibited good performance in fixed bed reactor but the problem in fixed bed reactor have been still appear:

- The oxygen species is a one of main problem to study because in co-feed the partial oxidation to CO and H₂ can be generated lead to low C₂ selectivity
- Low selectivity at higher conversion on the other hand good selectivity and conversion extremely difficult

Traditional OCM process used this reactor in their studies because it was easiest to design and base on catalytic activity of catalyst.

From the literatures reported showed two behaviors when higher methane conversion but the C₂ selectivity must be lower on the other hand when higher C₂ 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 provided higher selectivity and yields because the oxygen ion more selective than gas phase oxygen in the reaction.

Perovskite oxide catalyst: Perovskite materials can be categorized by their compounds such as oxides, carbides, nitrides, halides and hydrides which crystallize in the structure. Perovskite-type oxide (ABO₃) is the most interesting perovskite and has attracted in many application such as solid state chemistry, advanced materials and catalysis. Moreover, perovskite oxide is interested for development of new materials for OCM.

Perovskite type oxides there are interesting features such as surface oxygen atoms lead to catalytic promoter effects. Elliott *et al.* (1988) studied in perovskite oxide (LaMnO_{3.0}, LaMnO_{3.1}, La_{0.9}K_{0.1}MnO₃, La_{0.9}Na_{0.1}MnO₃, La_{0.8}Na_{0.2}MnO₃) the result indicate catalyst for OCM must have surface oxygen sites with sufficient binding energy and a minimal number of weakly bonded oxygen sites because for deep oxidation, weakly bonded oxygen is considered to be effective. After that Shamsi and Zahir (1989) investigated in La_{0.9}Na_{0.1}MnO₃ perovskite oxide catalyst in term of temperature and pressure. It found that when the pressure was raised to 3.6 atm and temperature <780°C, higher methane and oxygen conversions and higher selectivity to C₂, hydrocarbons were observed compared to those at 1 atm.

In recent year, Ba_{0.5}Sr_{0.5}TiO₃ (BST) was another perovskite oxide that was studied the reactivity of OCM. This research was studied by Fakhroueian *et al.* (2008) BST and Li, Na and Mg doped BST catalysts were determined their properties and found that NaBST exhibited the most conduction and basicity which is

Table 1: Literature reported performance data on various catalysts in fixed-bed configuration at atmospheric pressure (Olivier *et al.*, 2008)

Catalysts	Support	T (°C)	S ₂ (%)	Y ₂ (%)	References
5% (Na ₂ WO ₄)-2% Mn (imp)	SiO ₂	820	70.0	20.0	
5% (Na ₂ WO ₄)-2% Mn (slurry)	-	820	70.0	-	
5% (Na ₂ WO ₄)-2% Mn (sol-gel)	-	820	70.0	-	
20% SrF ₂ La ₂ O ₃	-	650	56.9	19.9	Long <i>et al.</i> (1995)
30 mol% BaCl ₂ /Gd ₂ O ₃	-	750	57.6	21.1	Au <i>et al.</i> (1998)
NaBaSrTiO ₃	-	800	51.0	24.0	Fakhroueian <i>et al.</i> (2008)
BaCO ₃ /LaOCl	-	800	55.0	22.0	Au <i>et al.</i> (1997)
5wt% Na ₂ WO ₄ -1.9 wt% Mn	SiO ₂	800	61.0-66.0	24.2-25.4	Liu <i>et al.</i> (2008)
CeO ₂ -W-Mn	SiO ₂	800	61.8	29.6	Zhang <i>et al.</i> (2007)
S-P-Na-W-Mn-Zr	SiO ₂	750	54.0	22.0	Zheng <i>et al.</i> (2010)
LaMnO _{3,0} perovskite	-	820	11.0	1.1	Elliott <i>et al.</i> (1988)
LaMnO _{3,1} perovskite	-	820	37.2	5.0	Elliott <i>et al.</i> (1988)
La _{0,9} K _{0,1} MnO ₃ perovskite	-	820	41.8	8.0	Elliott <i>et al.</i> (1988)
La _{0,9} Na _{0,1} MnO ₃ perovskite	-	820	63.4	13.3	Elliott <i>et al.</i> (1988)
La _{0,8} Na _{0,2} MnO ₃ perovskite	-	820	71.6	10.1	Elliott <i>et al.</i> (1988)
Ba _{1,4} TiCe _{0,1} O ₃ perovskite	-	775	43.0	20.4	Khodadadian <i>et al.</i> (2011)
SrTi _{0,9} Li _{0,1} O ₃ perovskite	-	800	48.7	13.1	Pang <i>et al.</i> (2008)
30% mol Y ₂ O ₃	Bi ₂ O ₃	800	46.0	18.0	
NaCl-ZrO ₂	ZrO ₂	800	67.0	24.6	
5% Li	MgO	<800	57.0	19.3	
LaF ₃	SrO	650	57.0	18.0	
SrF ₂	La ₂ O ₃	750	58.0	20.0	
NaZr ₂ (PO ₄) ₃	-	750	70.0	30.0	
Na ₂ Zr(PO ₄) ₂	-	750	70.0	30.0	
SrF ₂	La ₂ O ₃	750	57.3	19.6	
-	Nd ₂ O ₃	750	57.1	19.6	
-	Sm ₂ O ₃	800	55.8	19.0	
-	Gd ₂ O ₃	750	54.6	18.8	
-	Y ₂ O ₃	750	56.6	19.0	
-	Eu ₂ O ₃	750	52.9	17.5	
-	Dy ₂ O ₃	750	51.5	16.8	
-	Nd ₂ O ₃	750	57.0	9.0	
5% Ni	-	650	69.0	11.5	
8% Mn	-	720	69.0	12.3	
5% Zr	-	750	74.0	13.0	
BaF ₂	Pr ₂ O ₁₁	800	57.5	19.3	
-	CeO ₂	800	54.6	17.6	
-	Tb ₄ O ₇	800	56.1	18.6	
0.8% MnO ₂	MgO	750	46.0	17.0	
0.35% CoO	MgO	750	35.0	12.0	
MgO	BaCO ₃	780	68.0	16.3	
La ₂ O ₃	BaCO ₃	800	50.0	18.3	
LiCl	NiO	750	71.8	18.6	
LiBr	-	750	46.3	16.2	
Li-La ₂ O ₃	MgO	700	97.8	23.0	
Li-Ce ₂ O ₃	-	700	98.4	24.6	
Li-Pr ₂ O ₃	-	700	43.9	19.6	
Li-Nd ₂ O ₃	-	700	95.6	23.4	
Li-Sm ₂ O ₃	-	700	86.6	20.9	
MnCl ₂	SiO ₂	750	90.0	13.0	
Li-La-Mn-W	TiO ₂	770	61.7	25.6	
La-Mn-W	-	770	47.2	14.2	
Mn-W	-	770	78.2	5.8	
Na	La ₂ O ₃	750	75.2	12.0	

suitable for OCM catalysis. The exhibited catalytic activity of BST at temperature of 800°C were 47% CH₄ conversion, 29.5% C₂₊ selectivity and 14% C₂₊ yield. In case of NaBST catalyst which presented good properties for OCM, it showed 47% CH₄ conversion, 51% C₂₊ selectivity and 24% C₂₊ yield that was the maximum catalytic effect for this research. The overall catalytic performance were found to be NaBST >MgBST>LiBST>BST. Therefore, it can be concluded that these studied

doping metal can increase the catalytic performance of BST perovskite. Moreover, this catalyst was studied by Khodadadian *et al.* (2011) BaTiPO₃ (P:Sn or Ce) found that Ba_{1,4}Ti Ce_{0,1}O₃ which prepared by barium propionate and cerium oxide exhibited the best performance; 47.5% conversion, 43% C₂ selectivity and 20.4% C₂ yield were obtain. In addition, CO₂-TPD analysis exhibited that based on increase in basicity, the anions can be ranked as hydroxide>carbonate>propionate therefore the basic site

perhaps not significant to improve performance of catalyst. Sr Ti_{1-x}Li_xO₃ perovskite oxide showed a good catalytic performance in OCM and can use in anode for SOFC (Pena-Martinez *et al.*, 2006). Liu *et al.* (2008) investigated in SrTi_{0.9}Li_{0.1}O₃ perovskite oxide catalyst by compare between ultrasonic spray pyrolysis technique and sol gel method, the experiment result showed ultrasonic spray pyrolysis technique provided a higher C₂ selectivity and C₂ yield than sol gel method, 26.89% methane conversion, 48.69% C₂ selectivity, 13.09% C₂ yield were obtained.

It seems perovskite oxide catalyst is alternative catalyst but a performance is still low because an old problem such as a formation of CO_x and water, limitation on C₂ yield and methane conversion although when high methane conversion but C₂ selectivity is low.

SOFC reactor: Solid Oxide Fuel Cell (SOFC) is a type of fuel cell. It is currently interest device to convert chemical energy directly into electrical energy. It is the choice of a new energy source that is also continuing education and development. A key component of fuel cells include electrodes are cathode, anode, punctuate by electrolyte with the addition of fuel to the anode while the oxygen from the air pass into the cathode. Oxygen ions (O₂⁻) can move from the cathode through electrolyte to anode combines with the protons occur water. This concept is applied to OCM process for C₂ hydrocarbon production. The OCM reaction can be used to generate electricity which is by-product while the main product is chemical product.

SOFC can be divided into two categories; SOFC operating at elevated temperatures (~700-1000°C) and SOFC operating at intermediate temperatures (~500-650°C).

SOFC for chemical and electrical co-generation: The past 2 decade, new application for fuel cell reactors have been developed for more efficiency many research proposed chemicals and energy co-generation. This application converts of fuel (i.e., H₂, CO, CH₄) 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. Figure 2 shows scheme of OCM reaction in SOFC. This system include 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 simultaneously occurred.

Electricity is supplied to an external load and useful chemical produced is collected. In addition, chemicals and energy co generation provides a benefit over a conventional reactor fuel cell which just produces electricity and pure water as a by-product. Alcaide *et al.* (2006) reported the co-generation technology as:

- 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 co-generation method provide advantages over the conventional catalytic as:

- Co-generation 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 electrochemical devices can operate at temperatures much lower than many conventional catalytic processes
- The selectivity of the process can be controlled by changing the external load (which can vary the electrode potential) or the electrode catalyst
- Co-generation of electricity and chemical products is efficient which improve the potential of industries

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 (H₂) but pure hydrogen is expensive and gives only water as by-product. The most interesting fuel for SOFC is methane (CH₄) because almost of methane are used as fuel for heat and electricity generation. Oxidative Coupling of Methane (OCM) is the promising way to increase value of methane to C₂ 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 co-generation 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 Eq. 9-11, respectively:

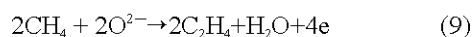
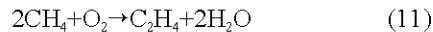
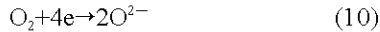


Table 2: Literature reported performance data on various anode catalysts in SOFC reactor

Catalyst	T (°C)	S ₂ (%)	Y ₂ (%)	References
Bi ₂ O ₃ -Au	800	76.9	<2	Pujare and Sammells (1988)
BaCO ₃ -Au	800	86.1	<2	Pujare and Sammells (1988)
La _{1.8} Al _{0.2} O ₃	700	96.5	3.8	Otsuka <i>et al.</i> (1990)
Mn/K ₂ WO ₄ /SiO ₂ -Ag	500-1000	86.0	4.0	White <i>et al.</i> (1992)
Mn/Na ₂ WO ₄ /SiO ₂ -Ag	500-1000	-	4.0	White <i>et al.</i> (1992)
Ni/ZrO ₂	950	95.0	4.5	Kiatkittipong <i>et al.</i> (2004)
LaSrMnO/LaAlO	1000	-	4.0	Olivier <i>et al.</i> (2008)
Au-SrCeO ₃	700-850	-	3.1	Tagawa <i>et al.</i> (1999)

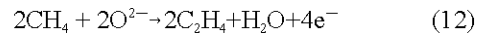


Anode catalyst: The anode layer must be stability for high temperature and chemical reaction as well as high catalytic activity. Anode is important for catalytic properties to oxidation. Generally, the anode is active catalyst to change CH₄ to C₂ hydrocarbon. Keller and Bhasin (1982) proposed the most active catalysts for C₂ formation that 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 was interested in fixed bed reactor there were a few researches to propose anode in SOFC. Pujare and Sammells (1988) studied OCM reaction in SOFC reactor for C₂ hydrocarbon production. Using the SOFC cell was CH₄, Pt/Sm₂O₃/La_{0.89}Sr_{0.10}MnO₃/YSZ/La_{0.89}Sr_{0.10}MnO₃/Pt, O₂ (air). High C₂ 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, BaCO₃, NaCl/MnO₂, Sm Q₂) deposited on Au-electrode. The result showed that BaCO₃ on Au was the most active and selective catalyst. Tagawa *et al.* (1998) proposed the anode catalyst was La_{1.8}Al_{0.2}O₃ in SOFC System (air/La_{0.85}Sr_{0.15}MnO₃/YSZ/La_{1.8}Al_{0.2}O₃/methane). The experiment result showed that C₂ composition and electrical were obtained. In addition, comparing between Ni-Zr cermet and Ag anode showed the Ni-Zr anode to exhibit high current value but the conversion trends to the complete oxidation. Moreover, White *et al.* (1992) investigated perovskite as anode electrocatalysts in SOFC system (anode) electrocatalyst/YSZ/La_{0.9}Sr_{0.1}MnO₃O₂ (air) in which showed to possess activity towards promoting the electrochemical OCM to C₂ hydrocarbons. Lapena-Rey and Middleton (2003) investigated the trimetallic catalysts formulations such as Mn/Na₂WO₄/SiO₂ and Mn/K₂WO₄/SiO₂WO₄ for OCM reaction. Kiatkittipong *et al.* (2004) proposed SOFC reactor using La_{0.85}Sr_{0.15}MnO₃/8 mol%Y₂O₃-ZrO₂/La_{1.8}Al_{0.2}O₃ for C₂ hydrocarbon production. The influence of increasing methane flow rate effected to the decreasing methane conversion while C₂ selectivity slightly increased. In

addition, Carrillo *et al.* (2001) presented mist pyrolysis method to preparation of Ni/ZrO₂ anode catalyst for SOFC type reactor compare with paste method. Ni/ZrO₂ from mist pyrolysis method powders was spherical, well dispersed and homogeneous. The paste method was active for OCM to CO and CO₂. Presently, investigators try to find the appropriate properties of anode electrode in OCM reaction. The good properties of anode are:

- High oxygen ion capacity on surface area
- High physical and chemical stability
- High electrical conductivity and activity

Table 2 shows performance data on various anode catalysts in SOFC reactor. Anode side reaction:



PROSPECT

OCM reaction is the currently interesting. Presently, Na-W-Mn/SiO₂ is the interesting catalyst in conventional reactors. It showed the good performance such as catalyst activity, catalyst stability for OCM but the major problem in this reactor is oxygen gaseous which is not selective with OCM reaction and the formation of CO₂ and H₂O during OCM lead to limit on C₂ yield. OCM is not yet go to commercial scale because this process operated at high temperature about 700-1000°C. Therefore, requires stability for catalyst increasing catalysts activity. In addition at high temperature bring about to catalyst deactivate; C₂ more reactive than methane high selectivity in the process can only be obtained at low methane conversion.

In the future, the IT-SOFC is interesting because IT-SOFCs possess better long-term stability and lower cost of operating and materials in comparison with high temperature SOFCs.

CONCLUSION

The application of OCM reaction to SOFC for multifunctional reactor to produce chemical and electrical production is very attractive because SOFC is energy

source in the future. In generally, SOFC produce electrical power from hydrogen fuel but hydrogen fuel still high price. This research showed a development of catalyst in OCM reaction in fixed bed and SOFC reactor from past to present.

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REFERENCES

- Alcaide, F., P.L. Cabot and E. Brillas, 2006. Fuel cells for chemicals and energy co-generation. *J. Power Sources*, 153: 47-60.
- Au, C.T., H. He, S.Y. Lai and C.F. Ng, 1997. The oxidative coupling of methane over Ba/CO₃LaOCl catalysts. *Applied Catal.*, 159: 133-145.
- Au, C.T., K.D. Chen, C.F. Ng, 1998a. Characterization of BaX₂/Gd₂O₃ (X = F, Cl, Br) catalysts for the oxidative coupling of methane. *Applied Catal.*, 171: 283-291.
- Au, C.T., X.P. Zhou, Y.W. Liu, W.J. Ji and C.F. Ng, 1998b. The characterization of BaF₂/Y₂O₃ catalysts for the OCM reaction. *J. Catal.*, 174: 153-163.
- Carrillo, A.S., T. Tagawa and S. Goto, 2001. Application of mist pyrolysis method to preparation of Ni/ZrO₂ anode catalyst for SOFC type reactor. *Mat. Res. Bull.*, 36: 1017-1027.
- Chao, Z.S., X.P. Zhou, H.L. Wan and K.R. Tsai, 1995. Methane oxidative coupling on BaF₂/LaOF catalyst. *Applied Catal.*, 130: 127-133.
- Chua, Y.T., A.R. Mohamed and S. Bhatia, 2008. Oxidative coupling of methane for the production of ethylene over sodium-tungsten-manganese-supported-silica catalyst (Na-W-Mn/SiO₂). *Applied Catal.*, 343: 142-148.
- Elliott, D.C., E.G. Baker, J. Piskorz, D.S. Scott, Y. Solantausta, 1988. Production of liquid hydrocarbon fuels from peat. *Energy Fuels*, 2: 234-235.
- Fakhroueian, Z., F. Farzaneh and N. Afrookhteh, 2008. Oxidative coupling of methane catalyzed by Li, Na and Mg doped BaSrTiO₃. *Fuel*, 87: 2512-2516.
- Gao, Z. and Y. Ma, 2010. Direct oxidation of methyl radicals in OCM process deduced from correlation of product selectivities. *J. Nat. Gas Chem.*, 19: 534-538.
- Hong, J.H. and K.J. Yoon, 2001. Oxidative coupling of methane over calcium chloride-promoted calcium chlorophosphate. *Applied Catal.*, 205: 253-262.
- Ji, S.F., T.C. Xiao, S.B. Li, C.Z. Xua, R.L. Hou, K.S. Coleman and M.L.H. Green, 2002. The relationship between the structure and the performance of Na-W-Mn/SiO₂ catalysts for the oxidative coupling of methane. *Applied Catal.*, 225: 271-284.
- Ji, S., T. Xiao, S. Li, L. Chou and B. Zhang *et al.*, 2003. Surface WO₄ tetrahedron: The essence of the oxidative coupling of methane over M-W-Mn/SiO₂ catalysts. *J. Catal.*, 220: 47-56.
- Keller, G.E. and M.M. Bhasin, 1982. Synthesis of ethylene via oxidative coupling of methane: I. Determination of active catalysts. *J. Catal.*, 73: 9-19.
- Khodadadian, M., M. Taghizadeh and M. Hamidzadeh, 2011. Effects of various barium precursors and promoters on catalytic activity of Ba-Ti perovskite catalysts for oxidative coupling of methane. *Fuel Process. Technol.*, 92: 1164-1168.
- Kiatkittipong, W., T. Tagawa, S. Goto, S. Assabumrungrat and P. Praserttham, 2004. TPD study in LSM/YSZ/LaAlO system for the use of fuel cell type reactor. *Solid State Ionics*, 166: 127-136.
- Lapena-Rey, N. and P.H. Middleton, 2003. The selective oxidation of methane to ethane and ethylene in a solid oxide electrolyte reactor. *Applied Catal.*, 240: 207-222.
- Liu, H., X. Wang, D. Yang, R. Gao, Z. Wang and J. Yang, 2008. Scale up and stability test for oxidative coupling of methane over Na₂WO₄-Mn/SiO₂ catalyst in a 200 mL fixed-bed reactor. *J. Nat. Gas Chem.*, 17: 59-63.
- Long, R.Q., S.Q. Zhou, Y.P. Huang, W.Z. Weng, H.L. Wan and K.R. Tsai, 1995. Promoting effect of F⁻ on Sr/La oxide catalysts for the oxidative coupling of methane. *Applied Catal.*, 133: 269-280.
- Murata, K., T. Hayakawa, S. Hamakawa and K. Suzuki, 1998. Lithium-doped sulfated-zirconia catalysts for oxidative coupling of methane to give ethylene and ethane. *Catal. Today*, 45: 41-45.
- Olivier, L., S. Haag, H. Pennemann, C. Hofmann, C. Mirodatos, A.C. Van Veen, 2008. High-temperature parallel screening of catalysts for the oxidative coupling of methane. *Catal. Today*, 137: 80-89.
- Otsuka, K., K. Suga and I. Yamanaka, 1990. Oxidative coupling of methane applying a solid oxide fuel cell system. *Catal. Today*, 6: 587-592.
- Pang, Z., X. Tan, R. Ding, Z. Gu and S. Liu, 2008. Preparation, characterization and catalytic performance of SrTi_{0.9}Li_{0.1}O₃ ultrafine powders. *Ceramics Int.*, 34: 1805-1810.
- Papa, F., D. Ginguas, L. Patron, A. Miyazaki and I. Balint, 2010. On the nature of active sites and catalytic activity for OCM reaction of alkaline-earth oxides-neodymia catalytic systems. *Applied Catal.*, 375: 172-178.

- Pena-Martinez, J., D. Marrero-Lopez, J.C. Ruiz-Morales, B.E. Buegler, P. Nunez and L.J. Gauckler, 2006. Fuel cell studies of perovskite-type materials for IT-SOFC. *J. Power Sour.*, 159: 914-921.
- Pujare, N.U. and A.F. Sammells, 1988. Methane activation to C₂ hydrocarbon species in solid oxide fuel cell. *J. Electrochem. Soc.*, 135: 2544-2545.
- Rane, V.H., S.T. Chaudhari, V.R. Choudhary, 2008. Influence of alkali metal doping on surface properties and catalytic activity/selectivity of CaO catalysts in oxidative coupling of methane. *J. Nat. Gas Chem.*, 17: 313-320.
- Shahri, S.M.K. and A.N. Pour, 2010. Ce-promoted Mn/Na₂WO₄/SiO₂ catalyst for oxidative coupling of methane at atmospheric pressure. *J. Nat. Gas Chem.*, 19: 47-53.
- Shamsi, A. and K. Zahir, 1989. Oxidative coupling of methane over perovskite-type oxides and correlation of T_{max} for oxygen desorption with C₂ selectivity. *Energy Fuels*, 3: 727-730.
- Sun, J., J.W. Thybaut and G.B. Marin, 2008. Microkinetics of methane oxidative coupling. *Catal. Today*, 137: 90-102.
- Tagawa, T., K.K. Moe, M. Ito and S. Goto, 1999. Fuel cell type reactor for Chemicals-energy co-generation. *Chem. Eng. Sci.*, 54: 1553-1557.
- Tagawa, T., K.K. Moe, T. Hiramatsu and S. Goto, 1998. Design of electrode for solid oxide fuel cells reactor. *Solid State Ionics*, 106: 227-235.
- Wang, D.J., M.P. Rosynek and J.H. Lunsford, 1995. Oxidative coupling of methane over oxide-supported sodium-manganese catalysts. *J. Catal.*, 155: 390-402.
- White, J.H., E.A. Needham, R.L. Cook and A.F. Sammells, 1992. The electrochemical oxidative dimerization of methane. *Solid State Ionics*, 53-56: 149-161.
- Zeng, Y., F.T. Akin and Y.S. Lin, 2001. Oxidative coupling of methane on fluorite-structured samarium-yttrium-bismuth oxide. *Applied Catal.*, 213: 33-45.
- Zhang, B., J. Wang, L. Chou, H. Song, J. Zhao, J. Yang and S. Li, 2007. Effective and Stable CeO₂-W-Mn/SiO₂ Catalyst for Methane Oxidation to Ethylene and Ethane. In: *Natural Gas Conversion VIII*, Noronha, F.B., M. Schmal and E.F. Sousa-Aguiar, (Eds.). Vol. 167, Elsevier B.V., Amsterdam, The Netherland, ISBN: 978-0-444-53078-3, pp: 237-242.
- Zheng, W., D. Cheng, N. Zhu, F. Chen and X. Zhan, 2010. Studies on the structure and catalytic performance of S and P promoted Na-W-Mn-Zr/SiO₂ catalyst for oxidative coupling of methane. *J. Nat. Gas Chem.*, 19: 15-20.