

## CATALYTIC OXIDATIVE COUPLING OF METHANE – EXPERIMENTAL INVESTIGATION AND OPTIMIZATION OF OPERATIONAL CONDITIONS

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### Abstract

In this research, the effect of operating conditions, such as GHSV, temperature and CH<sub>4</sub>/O<sub>2</sub> ratio was investigated on the catalytic performance of OCM in a Fixed-Bed reactor at pressure of 3 barg. 50 gr of catalyst was loaded in a stainless steel reactor. Heat control in OCM is very important. With attention to this fact series of experiment were designed to investigate the influence of above-mentioned parameters on C<sub>2</sub><sup>+</sup> selectivity, CH<sub>4</sub> conversion and the yield of C<sub>2</sub><sup>+</sup>. The C<sub>2</sub><sup>+</sup> selectivity of 57.3% was obtained at a CH<sub>4</sub> conversion of 20.3% at 840°C, 1620 hr<sup>-1</sup>GHSV and CH<sub>4</sub>/O<sub>2</sub> ratio 4 to 1 and pressure of 3 barg. The OCM reaction is strongly dependent on the operating condition particularly GHSV and the CH<sub>4</sub>/O<sub>2</sub> ratio. The comparison of these results and micro reactor in literature, show that the scale up of fixed bed reactor in OCM reaction without too much change in yield and selectivity of C<sub>2</sub><sup>+</sup>, CH<sub>4</sub> conversion and CO<sub>x</sub> selectivity, with an appropriate GHSV, CH<sub>4</sub>/O<sub>2</sub> ratio is technically feasible and economic.

Key words: OCM, stainless steel, C<sub>2</sub><sup>+</sup> Selectivity, Yield, Ethylene, Natural gas conversion

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### 1. Introduction

Catalytic oxidative coupling of methane (OCM) is a promising catalytic process for direct natural gas conversion to ethylene, which is used as an important raw material in the production of petrochemicals and liquid fuels. A great deal of attention has been focused on this reaction since the early work of Keller and Bhasin in 1982 [1], and several reviews have been written since then [2,3]. Most researchers focused their attention on the OCM at atmospheric pressure, while there have been fewer studies on the OCM at elevated pressures [4-7]. One of the most effective catalysts for the OCM is Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>, which has demonstrated stability for long periods of time under different reaction conditions [7]. Methane is currently available in large quantities from natural gas, anaerobic digestion of organic material, and chemical processing sources. Besides tremendous research work in catalyst development, a lot of investigations dealt with reaction engineering aspect in order to make this process technically feasible and economic, which is the objective of this paper. Various aspects as reaction kinetics, reactor selection and different modes of reactor operation are analyzed with the aim to identify reaction engineering means which can be used to maximize C<sub>2</sub><sup>+</sup> selectivity and yield. Particularly, available kinetic models for reaction engineering applications are revised and the importance of various reaction steps, also pre- and post catalytic reactions is analyzed. Since the OCM is a complex reaction network of parallel and consecutive, heterogeneous and homogeneous reaction steps the selectivity to C<sub>2</sub><sup>+</sup> hydrocarbons strongly depends on the reaction conditions. Reaction conditions such as GHSV, temperature and CH<sub>4</sub>/O<sub>2</sub> ratio play an important role on the catalytic performance of OCM [8]. Central issue in development of OCM process is the choice of the type of reactor. In this work possible design of a fixed bed reactor with ability to control the OCM reaction temperature during catalyst bed, best C<sub>2</sub><sup>+</sup> selectivity and ethylene yield was achieved in

mini pilot scale units. Furthermore, the possibility to improve catalytic performance by applying distributed feed of oxygen is discussed.

## 2. Experimental

### 2.1 Catalyst preparation

A catalyst containing 2 %wt Mn and 5 %wt  $\text{Na}_2\text{WO}_4$  on  $\text{SiO}_2$  ( $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ ) was prepared by incipient wetness impregnation using 20-40 mesh size Davison grade 57 silica gel. Ten ml of aqueous solution containing 0.7 g of  $\text{Mn}(\text{NO}_3)_2$  were added to 5g of silica gel at  $85^\circ\text{C}$ . This material was then dried in air at  $120^\circ\text{C}$  for 5 h. After cooling to  $25^\circ\text{C}$ , 10 ml of solution containing 0.27 g of  $\text{Na}_2\text{WO}_4$  was added to the solid. The catalyst was dried at  $120^\circ\text{C}$  for 24 h and was calcined in air at  $800^\circ\text{C}$  for 8 h.

### 2.2 Reactor system

Reaction was carried out at a total pressure of 3 barg in the differential mode using fixed-bed continuous vertical flow reactor constructed from a stainless steel tube (I.D.=20 mm). A Ni/ Cr-Ni/Al thermocouple was positioned at the hottest part of the reactor, which was heated by a computer-controlled furnace. Another thermocouple was inserted into the center of the reactor for determining the temperature of the catalyst bed. The preheated reactant gas (methane and oxygen without diluents) was co-fed into the reactor. Their flow rates were controlled using mass flow controllers, Brooks (model 5580).

50g of catalysts were loaded into the reactor, and remaining space was filled with ceramic particles (10 mesh). The reactor is heated by furnace and the feed temperature raised up and fed to catalyst bed. When the activation energy of reaction prepared, the reaction takes place, the product passed through to condense water vapors a cold trap. After that the product gas is conducted to an online gas chromatograph (GC) to investigate the catalyst performance Figure 1.

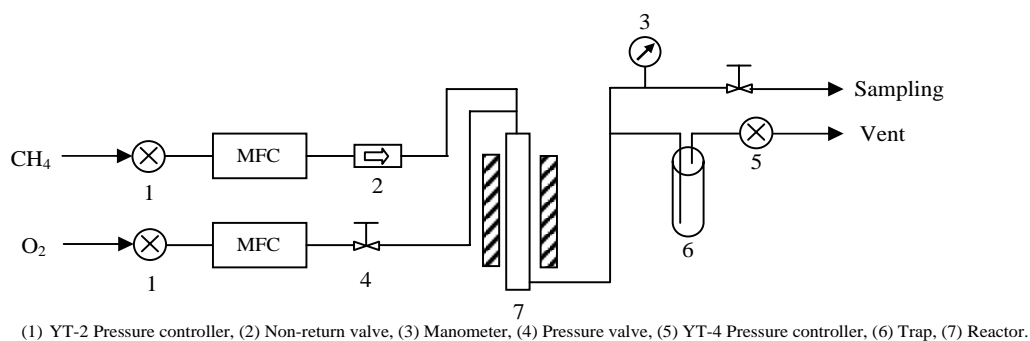


Fig 1. Schematic diagram of the apparatus for the OCM

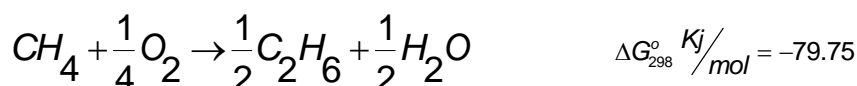
## 3. Result and discussion

The experimental results of a series of GHSV and the ratio of methane to oxygen on the OCM are shown in Table 1. The  $\text{C}_2^+$  selectivity of 57.3% was obtained at a  $\text{CH}_4$  conversion of 20.3% at  $840^\circ\text{C}$ ,  $1620\text{ hr}^{-1}$  GHSV and  $\text{CH}_4/\text{O}_2$  ratio equal 4 (run 2 in table 1). This is one of the few reported examples of favorable oxidative coupling behavior being achieved at such scale of reactor and catalyst loading. Also It shows that the  $\text{Mn}_2\text{O}_3 - \text{Na}_2\text{WO}_4 / \text{SiO}_2$  catalyst is one of the most effective catalysts for the OCM reaction by optimum reaction conditions such as temperature, GHSV and  $\text{CH}_4 / \text{O}_2$  ratio.

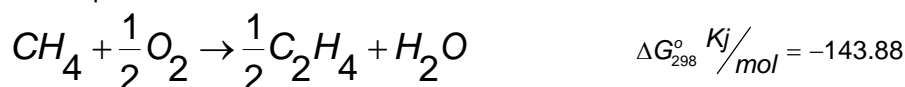
Table 1- Catalytic performance of Mn<sub>2</sub>O<sub>3</sub> - Na<sub>2</sub>WO<sub>4</sub> / SiO<sub>2</sub>, P=3 barg

TEST No.	GHSV (1/hr)	CH <sub>4</sub> /O <sub>2</sub> Ratio	CH <sub>4</sub> con.( % )	C <sub>2</sub> <sup>+</sup> Sel.	Yield C <sub>2</sub> +	CO <sub>x</sub> Sel.	C <sub>2</sub> H <sub>4</sub> Sel.	C <sub>2</sub> H <sub>6</sub> Sel.
1	1320	3	22.90	50.04	11.46	49.96	36.38	13.67
5	1320	4	20.68	54.06	11.18	45.94	36.04	18.02
9	1320	5	4.96	45.75	2.27	54.25	22.61	23.14
13	1320	6	1.94	37.32	0.72	62.68	14.35	22.97
6	1620	3	21.00	53.00	11.13	47.00	39.85	13.14
2	1620	4	20.28	57.31	11.62	42.69	41.32	15.99
14	1620	5	5.30	36.74	1.95	63.26	18.06	18.68
10	1620	6	3.35	25.07	0.84	74.93	15.02	10.05
11	1920	3	16.04	67.07	10.76	32.93	51.10	15.97
15	1920	4	14.90	71.27	10.62	28.73	52.03	19.24
3	1920	5	10.02	57.93	5.79	42.07	39.87	18.07
7	1920	6	7.40	26.96	2.00	73.04	11.64	15.32
16	2220	3	12.59	67.20	8.46	32.80	51.31	15.88
12	2220	4	12.58	72.83	9.16	27.17	53.96	18.87
8	2220	5	8.11	40.12	3.25	59.88	21.84	18.28
4	2220	6	6.12	27.11	1.66	72.89	19.02	8.09

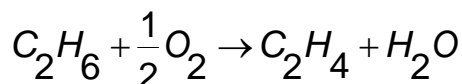
The dependence of the Mn<sub>2</sub>O<sub>3</sub> - Na<sub>2</sub>WO<sub>4</sub> / SiO<sub>2</sub> catalyst's performance on the CH<sub>4</sub>/O<sub>2</sub> ratio is shown in figure 2.1 and 2.2. Increasing the CH<sub>4</sub>/O<sub>2</sub> ratio leads to a decrease in CH<sub>4</sub> conversion and C<sub>2</sub><sup>+</sup> and C<sub>2</sub>H<sub>4</sub> selectivity but an increase in CO<sub>x</sub> selectivity. C<sub>2</sub>H<sub>6</sub> selectivity first increases and then decreases. These results demonstrate that the reaction:



In compare with the reaction:



Has lower activation energy and occurred very faster than another one and consumes a lot of oxygen. So in CH<sub>4</sub>/O<sub>2</sub> ratio from 3-5 the rate of C<sub>2</sub>H<sub>4</sub> production decreases and the rate of C<sub>2</sub>H<sub>6</sub> production increases and no extra oxygen is available for dehydration C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>4</sub> due to following reaction:



At the same time the combustion reaction, which occurs at gas phase and take place before CH<sub>4</sub> and O<sub>2</sub> contact the surface of the catalyst, consumed CH<sub>4</sub> and O<sub>2</sub> to produce CO<sub>x</sub>, These reactions are:



With increasing CH<sub>4</sub>/O<sub>2</sub> ratio from 3-5 and increasing the methane with respect to oxygen, a lot of oxygen is consumed in combustion reaction and the C<sub>2</sub>H<sub>4</sub> selectivity and production rate decreases and selectivity for CO<sub>x</sub> and C<sub>2</sub>H<sub>6</sub> increases. In CH<sub>4</sub>/O<sub>2</sub> ratio from 5-6 the rate and selectivity of C<sub>2</sub>H<sub>6</sub> is decreased due to low concentration of oxygen available for these reactions.

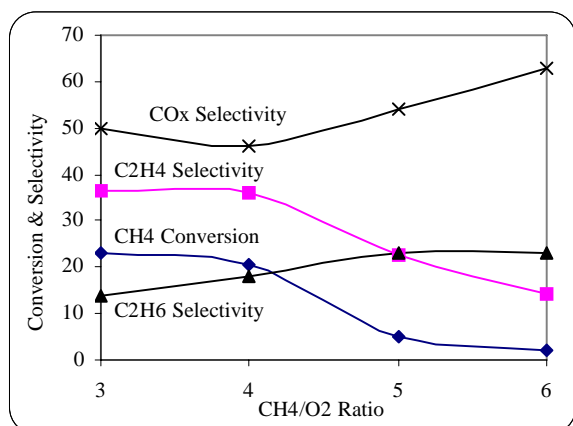


Figure 2.1. Dependence of Selectivity on the  $\text{CH}_4/\text{O}_2$  ratio for the OCM over  $\text{Mn}_2\text{O}_3 - \text{Na}_2\text{WO}_4 / \text{SiO}_2$  catalyst (Reaction condition:  $T=840^\circ\text{C}$ ,  $\text{GHSV}=1320 \text{ hr}^{-1}$ ,  $P=3 \text{ barg}$ )

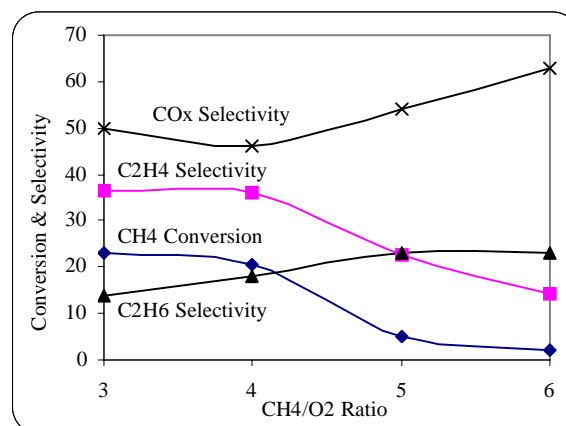


Figure 2.2. Dependence of Yield on the  $\text{CH}_4/\text{O}_2$  ratio for the OCM over  $\text{Mn}_2\text{O}_3 - \text{Na}_2\text{WO}_4 / \text{SiO}_2$  catalyst (Reaction condition:  $T=840^\circ\text{C}$ ,  $\text{GHSV}=1320 \text{ hr}^{-1}$ ,  $P=3 \text{ barg}$ )

The dependence of the  $\text{Mn}_2\text{O}_3 - \text{Na}_2\text{WO}_4 / \text{SiO}_2$  catalyst's performance on the GHSV is shown in figure 3. Increasing the GHSV from  $1320$  to  $1920 \text{ hr}^{-1}$  leads to an increase in  $\text{C}_2^+$  selectivity, a decrease in methane conversion and  $\text{CO}_x$  selectivity. A cause of such result is that the combustion reaction took place before  $\text{CH}_4$  and  $\text{O}_2$  contact the surface of the catalyst at lower GHSV, and the contribution of the combustion reaction to methane conversion is limited under the higher ratio of  $\text{CH}_4$  and  $\text{O}_2$ . When GHSV increases from  $1920$  to  $2220 \text{ hr}^{-1}$ ,  $\text{C}_2^+$  selectivity is decreased abruptly with an obvious increase in  $\text{CO}_x$  selectivity. The observations point out that the homogeneous reaction in the gas phase may occur when the residence time in the catalyst bed is too short for the catalytic reaction on the catalyst surface to take place. One of the manifestations of this role of  $\text{CO}_x$  is the effect of residence time on selectivity. Usually, in oxidation catalysis, the conversion increases, but selectivity to a partial oxidation product decreases as the residence time in the catalyst bed increases. However, in the oxidative coupling of methane it is often found that short residence times result in low  $\text{C}_2^+$  selectivity [2]. As a result of this effect, the fact that the competition between the combustion reaction in the gas phase and the catalytic reaction on the surface of the catalyst is controlled by adjusted reaction conditions.

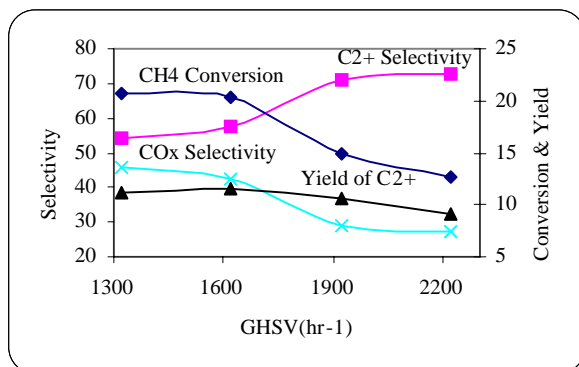


Figure 3. Dependence of catalytic activity, Selectivity and Yield on the GHSV for the OCM reaction over  $\text{Mn}_2\text{O}_3 - \text{Na}_2\text{WO}_4 / \text{SiO}_2$  catalyst (Reaction condition:  $T=840^\circ\text{C}$ ,  $\text{CH}_4/\text{O}_2=4$ ,  $P=3 \text{ barg}$ )

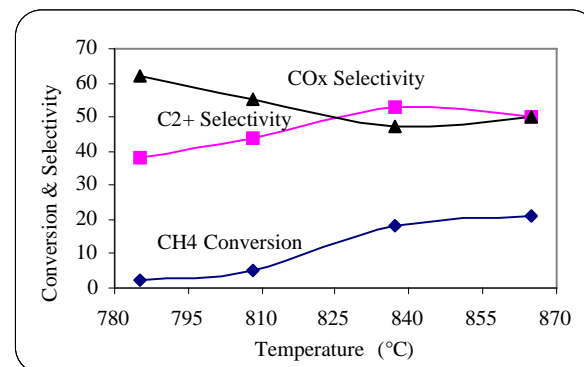


Figure 4. Effect of temperature on the OCM reaction over  $\text{Mn}_2\text{O}_3 - \text{Na}_2\text{WO}_4 / \text{SiO}_2$  catalyst (Reaction condition:  $\text{GHSV}=1320 \text{ hr}^{-1}$ ,  $\text{CH}_4/\text{O}_2=4$ ,  $P=3 \text{ barg}$ )

The effect of temperature on the performance of the  $\text{Mn}_2\text{O}_3 - \text{Na}_2\text{WO}_4 / \text{SiO}_2$  catalyst is shown in figure 4. Elevating the temperature from 780 to 840°C causes  $\text{C}_2^+$  selectivity and  $\text{CH}_4$  conversion to increase, while the  $\text{CO}_x$  selectivity decreases. With elevation of temperature from 840 to 860°C,  $\text{C}_2^+$  selectivity and the variation rate of  $\text{CH}_4$  conversion decreases and it is predicted that with increasing temperature  $\text{CH}_4$  conversion decreases. These observations point out that the gas phase reaction become dominant when the OCM reaction performs at higher temperature.

#### 4. Conclusion

The results here demonstrate that a mini-pilot scale stainless steel reactor system can be successfully utilized for the OCM to produce useful hydrocarbons. The  $\text{Mn}_2\text{O}_3 - \text{Na}_2\text{WO}_4 / \text{SiO}_2$  catalyst exhibits excellent performance for the OCM reaction. A  $\text{C}_2^+$  selectivity of 57.3% was obtained at a  $\text{CH}_4$  conversion of 20.3% at 840°C, 1320  $\text{hr}^{-1}$  GHSV and  $\text{CH}_4/\text{O}_2$  ratio equal 4 and pressure of 3 barg. Comparison of present results and the micro reactor test show that the scale up of fixed bed catalyst system in OCM reaction for converting natural gas to valuable hydrocarbons, without any change in yield and selectivity  $\text{C}_2^+$ ,  $\text{CH}_4$  conversion and  $\text{CO}_x$  selectivity due to combustion reaction, with an appropriate GHSV,  $\text{CH}_4/\text{O}_2$  is technically feasible and economic.

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