

## OXIDATIVE COUPLING OF METHANE OVER DIFFERENT SUPPORTED MN/Na<sub>2</sub>WO<sub>4</sub> CATALYSTS

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### Abstract

Different supported Na-W-Mn/S catalysts (S= SiO<sub>2</sub>, different SiO<sub>2</sub>/MgO ratio) were prepared using the impregnation and characterized by XRD, BET, AAS and SEM methods. The catalysts performance was evaluated for the oxidative coupling of methane (OCM) reaction; also influence of different supports was evaluated on the selectivity and yield. Methane conversion studies were performed at different temperatures in a constant GHSV of  $6 \times 10^3 \text{ h}^{-1}$ , CH<sub>4</sub>:O<sub>2</sub> ratio of 4:1, over the Mn /Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> (Powder) (Impo1), Mn /Na<sub>2</sub>WO<sub>4</sub>/ SiO<sub>2</sub> (Spray-dried) (Impo2) and Mn /Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> (mesh-30-35) (Impo3), Mn/Na<sub>2</sub>WO<sub>4</sub>/1SiO<sub>2</sub>/1MgO (Impo4), and Mn /Na<sub>2</sub>WO<sub>4</sub>/1SiO<sub>2</sub>/3MgO (Impo5) catalysts. The XRD patterns of the catalysts revealed the presence of cristoballites, Mn<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>WO<sub>4</sub> phases respectively; the OCM activators of which were not the same. The Impo 2 catalyst, prepared by the impregnation of the active elements on spray-dried support, showed promising result for the OCM reaction at 825 °C (C<sub>2</sub>-selectivity 75.7 % by 37% methane conversion). The yield of different catalysts increased dramatically by increasing the temperature from 750 °C to 800 °C.

**Keyword:** Oxidative coupling of methane; Supported Mn / Na<sub>2</sub>WO<sub>4</sub> catalyst; Impregnation method.

### 1. Introduction

Methane can be converted directly or indirectly to active and more valuable chemicals through different methods. One of the most promising routes for the direct conversion of methane to ethane and ethylene is the so-called oxidative coupling of methane (OCM) [1-3], which was introduced by Keller and Bhasin in 1982, and has been used to produce C<sub>2</sub> hydrocarbons ever since [1].

In 1992, a catalyst with a composition of 1.9% Mn/ 5% Na<sub>2</sub>WO<sub>4</sub> / SiO<sub>2</sub> was prepared and the studies showed that it was a very active catalyst for the OCM reaction [4]. Later, it was proposed that the Mn oxide present in the catalyst plays a catalytic role through electron transfer from methane to oxygen. [5]. The oxide also increases the oxygen exchange between the gaseous and catalyst phases leading to higher catalyst activities. Also tetrahedral WO<sub>4</sub> surface species was proposed as the OCM active site [5, 6].

Lunsford and co-workers achieved a 20% conversion of methane and an 80% selectivity of C<sub>2</sub><sup>+</sup> over Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> and Mn/Na<sub>2</sub>WO<sub>4</sub>/MgO catalysts at 800 °C [7]. The OCM catalysts reported have been based on the application of Li, Bi, Rb, Cs, Ca, and most importantly on Mn and W as active metals [8].

Shengfu Ji et al. studied a series of metals including Li, Na, K, Ba, Ca, Fe, Co, Ni, and Al for the oxidative coupling of methane and their results revealed that the presence of the WO<sub>4</sub> tetrahedron on the catalyst surface appears to play an essential role in achieving high CH<sub>4</sub> conversion and high C<sub>2</sub> hydrocarbon selectivity in the OCM reaction [9].

Different methods have been used for the preparation of these catalysts, including precipitation, in which Control parameters, such as pH, temperature and components flow rate are however difficult. Furthermore, it is time consuming and does not give reproducible results readily.

Another method namely impregnation, is easier to control and handle, has fewer procedure steps, and leads to more reproducible results. The aim of this research is to investigate

the effect of different supports material on the structure and morphology of OCM catalysts prepared by the impregnation method.

The prepared catalysts characterized by XRD, SEM, AAS and BET methods, also Activity and selectivity of the catalysts in oxidative coupling of methane reaction at different temperatures was investigated.

## 2. Experimental

### 2.1. Catalyst preparation

In general the W/Mn/SiO<sub>2</sub> or W/Mn /SiO<sub>2</sub>/MgO catalysts were prepared by the impregnation and precipitation methods. Five different supports were prepared and abbreviated as Impo1 to Impo5, which their properties and characterization are listed in table 1. The Impo1 (W/Mn/SiO<sub>2</sub>) to Impo3 (W/Mn/SiO<sub>2</sub>) catalysts support (pure SiO<sub>2</sub>) were prepared using the precipitation method using sodium silicate and sulfuric acid solutions, in a pH range of 8-9, temperature range of 80-85°C and aging time of 30 minutes. The Impo1 and Impo3 supports (pure SiO<sub>2</sub>) were then dried for overnight in 120°C and then calcinated at 400°C for 4h. The support for Impo1 was used as a powder through the impregnation. The support for catalyst Impo3 was first meshed (30-40), calcinated, and then used for Impregnation. The Impo2 support was suspended in water, spray dried and then calcinated at 400°C for 4h. The BET specific surface area of the supports was 42 m<sup>2</sup>/g. Impo4 and Impo5 were prepared by mixing different amounts of MgO/SiO<sub>2</sub> (Impo4 (50/50wt%): 2.5g MgO powder + 2.5g SiO<sub>2</sub> (100g Silica sol)) (Ludox) and Impo5 (75/25wt%): 3.75g MgO+1.25g SiO<sub>2</sub> (50g Silica sol) (Ludox) with a magnet stirrer and then dried at 90°C for 4h and then at 120°C overnight. The prepared supports were added to Na<sub>2</sub>WO<sub>4</sub> solution, and dried at 120°C for 4h and calcinations at 400°C for 8h, then this was added to (i. e. Mn(NO<sub>3</sub>)<sub>2</sub> (MERCK)) solution, to obtain a 5% for Na<sub>2</sub>WO<sub>4</sub> and 2% for Mn respectively. The required amount of solvent was measured by absorbed water, and then each of the mentioned metals was added. After preparation of the salt solution, the support was slowly added to the salt solution and mixed with a magnet stirrer and then dried in a rotary evaporator at 80°C and 70 mbar and further dried in oven at 120°C overnight and then calcinated at 850°C for 12 h.

### 2.2. Catalyst characterization

The X-ray diffraction patterns of the catalysts were obtained by Philips PW 1840 diffractometer using Cu K<sub>α</sub> radiation. Diffractograms were recorded from 2θ = 2-90° with the detector moving in Δ2θ = 0.01° steps to achieve good angular resolution. The BET-surface areas of catalysts were measured using ASAP 2000 micrometrics. The morphology of the catalysts was determined by SEM Scanning Electron Microscopy model S360 Cambridge instrument UK. Elemental-Analyses of the catalyst component were obtained with a Perkin-Elmer model 200 atomic-absorption-spectroscopy (AAS).

### 2.3. Activity tests

The OCM reactor contains a fixed bed and is coupled with a gas chromatograph (GC) ChromoPack CP5000. The water content of the product was eliminated and then analyzed by GC. The feed gas and products along with the O<sub>2</sub>, CH<sub>4</sub> and CO were separated using a 13X molecular sieve column and CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> were separated using a Haysep (Q+T) column. The analyses were carried out using thermal conductivity detector (TCD) and flame ionization detector (FID).

The molar ratio of the feed gas was adjusted using 99.996% methane, 99.99% oxygen and 99.99% helium. The feed gas flow was controlled using Brooks mass flow controllers. The reaction zone includes a fixed bed quartz tubular reactor of 22 cm length and an outer diameter of 1.2 cm. The reactor was heated utilizing a thermally adjustable furnace with a high accuracy up to 1200°C. The reactor placed in the furnace and the reaction temperature was measured and controlled by a K-type thermocouple (Ni-Cr-Ni) of 1.5 mm thickness located in the thermo well.

## 3. Results and discussion

The effects of different supports were investigated on structure and morphology of the OCM catalysts, reactant conversion, product selectivity and yield on the OCM reaction. A series of catalysts, namely Impo1-Impo6 (Table 1) was prepared with the different supports. Impo1, Impo2 and Impo3 were prepared using a pure SiO<sub>2</sub> in

crystoballite phase. Figure 1 illustrates the XRD patterns of all catalysts supports. As it can be seen, the characteristic phase for  $\text{SiO}_2$  is  $\alpha$ -crystoballite, for Mn oxide is  $\text{Mn}_2\text{O}_3$ , and for  $\text{Na}_2\text{WO}_4$  is  $\text{Na}_2\text{WO}_4$  [9-11]. Impo4, Impo5 and Impo6 in which different mixtures of  $\text{SiO}_2/\text{MgO}$  are used as the support material (Table 1), depending on the amount of MgO form different phases (figure 1). Impo4 with a 50/50 composition, forms a  $\text{Mg}_2\text{SiO}_4$  (Magnesium silicate) phase and the crystoballite phase is not observed. However, other phases such as  $\text{Na}_2\text{WO}_4$  and small peaks which indicate the presence of  $\text{Mn}_2\text{O}_3$  are also observed. By increasing the amount of MgO, the MgO phase increases and the corresponding peaks became more obvious (Figure 1).

Table1 The composition of different supported OCM catalyst and the result of AAS and BET surface area.

Catalyst	Composition	wt %	Active Component % Mn / $\text{Na}_2\text{WO}_4$ <sup>a)</sup>	BET Surface Area [ $\text{m}^2/\text{g}$ ] <sup>b)</sup>
Impo1	$\text{SiO}_2/\text{MgO}$	100/0	2/5	1.25
Impo2	$\text{SiO}_2/\text{MgO}$	100/0	2/5	1.75
Impo3	$\text{SiO}_2/\text{MgO}$	100/0	2/5	1.65
Impo4	$\text{SiO}_2/\text{MgO}$	50/50	2/5	29
Impo5	$\text{SiO}_2/\text{MgO}$	25/75	2/5	19.2

a) The result of the AAS atomic absorption analysis elementary analysis

b) The result of BET- surface area

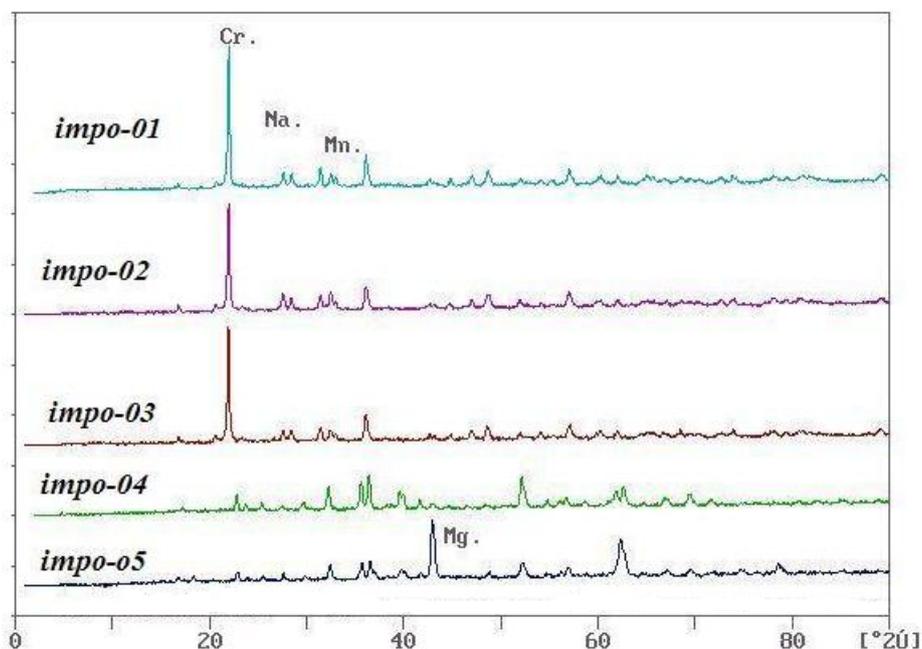


Fig. 1. XRD patterns of different supported OCM catalysts  $\text{Mn}_2\text{O}_3/\text{Na}_2\text{WO}_4/\text{SiO}_2$  (Impo01-03) and  $\text{Mn}_2\text{O}_3/\text{Na}_2\text{WO}_4/\text{SiO}_2/\text{MgO}$  (Impo04-06). Cr: Crystoballite, Na:  $\text{Na}_2\text{WO}_4$ , Mn:  $\text{Mn}_2\text{O}_3$  Mg: MgO

The SEM of Impo 2 and Impo 4 are shown in Figures 2 and 3. Before calcinations, both catalysts do not show any specific crystallites and are amorphous structures. However, after impregnating the active metals on the support and calcinations at  $850^\circ\text{C}$  for 12 hours, the catalysts form ordered structures, the XRD of which indicates the presence of crystoballite phases. By increasing MgO with respect to silica-sol, the morphology of the support changes to MgO-structure (Impo5), which is observed in the corresponding XRD (Figure 1) and SEM (Figure 4).

These differences on various phases can influence the morphology of catalysts and also Product selectivity and OCM reaction activities.

The results obtained from the reactor tests of different catalysts (impo1-impo5) with identical operational conditions ( $\text{CH}_4/\text{O}_2 = 4/1$  40% He and GHSV  $6000 \text{ h}^{-1}$ ) are shown in Table 2. Also, the changes in the selectivity and activities of the catalysts, by changing the temperature, are presented in Table 2. The results show increasing methane conversion with temperature at constant GHSV of  $6 \times 10^3 \text{ h}^{-1}$  and  $\text{CH}_4$  to  $\text{O}_2$  ratio of 4:1. The spray-dried support has the lowest selectivity toward CO and  $\text{CO}_2$  and the highest

activity and selectivity toward  $C_2$  Hydrocarbons (Table 2). On the other hand, as shown in the XRD spectra, Impo1, Impo2 and Impo3 catalysts, have crystoballites,  $Mn_2O_3$  and  $Na_2WO_4$  phases respectively, and their activities are hence not the same. Impo2, which is prepared through the impregnation of the active elements on comparing the results for Impo1 to Impo3 and Impo5 catalysts indicate that pure  $SiO_2$  is a good support for OCM reaction.

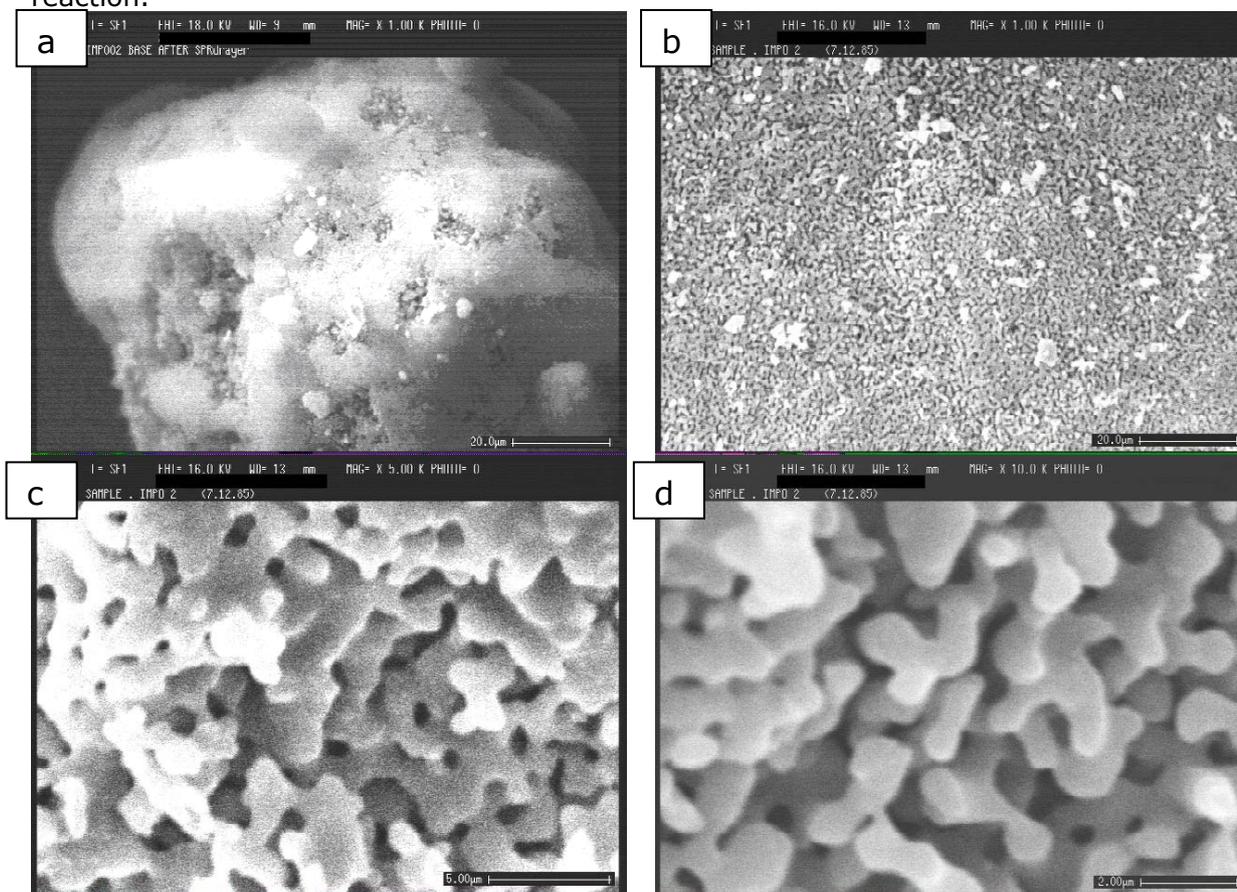


Fig.2.The SEM images of Impo-2 catalyst. (a) Before calcinations, magnification (1000K) (b) After calcinations, magnification (1000 K) (c) After calcinations, magnification (5000K) (d) After calcinations, magnification (10000K).

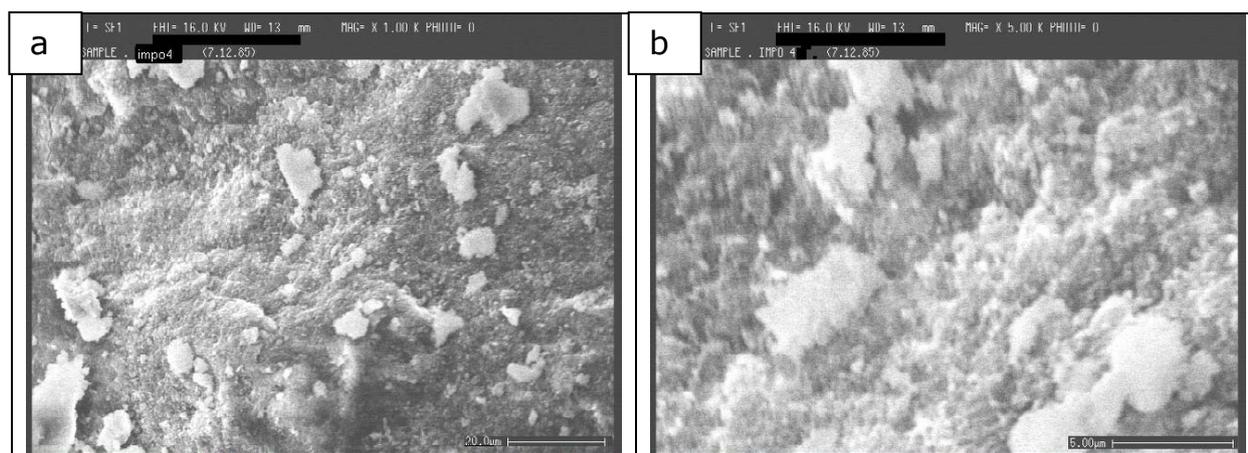


Fig.3.The SEM images of Impo-4 after calcinations (a) SEM of Impo-04 after calcinations, magnification (1000K) (b) SEM of Impo4 after calcinations, magnification (5000)

The effect of the temperature on catalysts is different, but as it can be seen Impo5 with a  $MgO/SiO_2$  ratio of 75/25wt% undergoes ignorable reactivity changes by increasing the temperature with its maximum conversion reaching 15.4% at  $850^\circ C$ . On the other hand, the conversion of Impo4 with a  $MgO/SiO_2$  ratio of 50/50wt%, reaches 24.5% in  $850^\circ C$ . Impo3, prepared by the impregnation of the support (mesh 30-40), which is prepared through the precipitation, possesses a better conversion (29.45%), which does not change very much by changing the temperature from

800 °C to 850 °C. The best activity is observed in the case of Impo2 with a conversion of 37.25%. The conversion of this catalyst is relatively very high (35.7%) even at 800 °C compared to many of the previously reported OCM catalysts, prepared using the impregnation method [8-11].

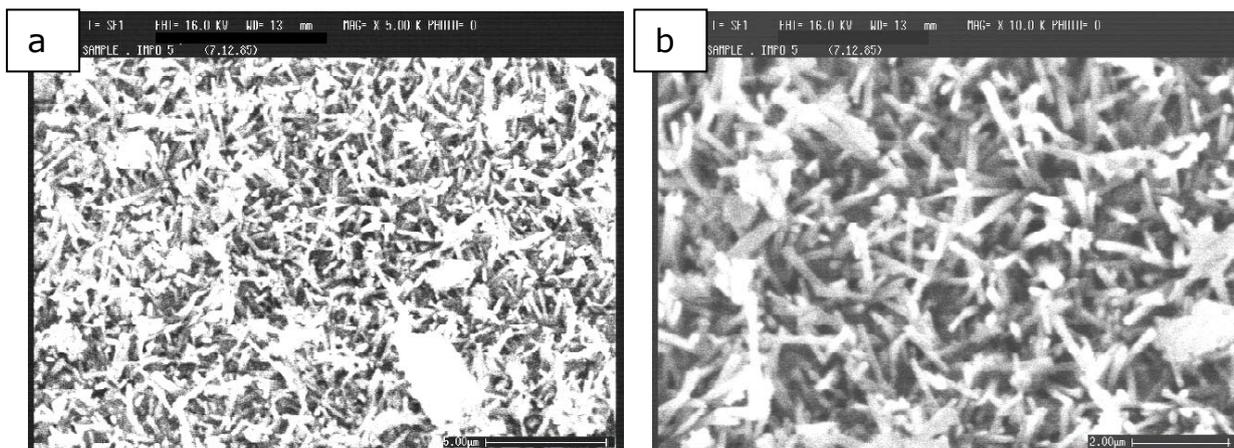


Fig.4. The SEM of Impo5 after calcinations (a) SEM of Impo 05 after calcinations, magnification (5000K) (b) SEM of Impo 05 after calcinations, magnification (10000K).

The selectivity of Impo1 to Impo5 was also studied. Figure 5 shows the selectivity of different catalysts with respect to the C<sub>2</sub> hydrocarbons by temperature. The C<sub>2</sub> selectivity of Impo2 and Impo3 are nearly the same and the selectivity's of both catalysts increase as the temperature increases from 750 °C to 800 °C. These selectivity's, however, show a very small decrease from 825 °C to 850 °C. The highest methane conversion, C<sub>2</sub> selectivity and yield are observed in the case of Impo2 at 800 °C, respectively reaching 35, 5%, 80%, and 27% for C<sub>2+</sub> species, which shows an improvement with respect to the previous works [8-11].

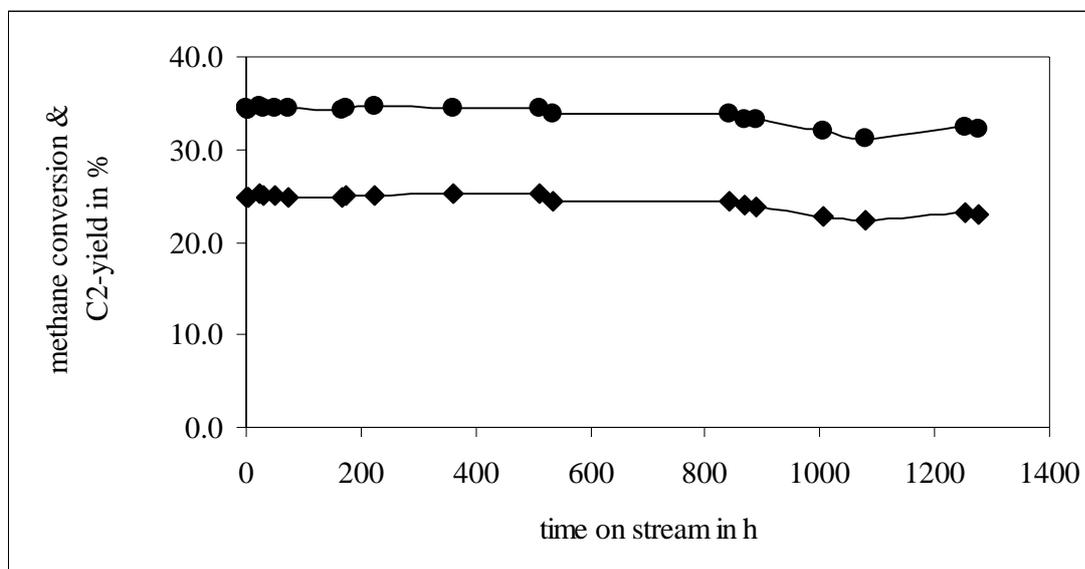


Fig.5. The methane conversion and yield of C<sub>2</sub> as a function of time in the constant Temperature 825 °C, (GHSV of 6000 h<sup>-1</sup> (CH<sub>4</sub>/O<sub>2</sub> + He) and a CH<sub>4</sub> to O<sub>2</sub> ratio of 4/1 Catalyst Impo2), • methane conversion; • C<sub>2</sub> yield

The selectivity of Impo3 is also almost equal to that of Impo2, indicating that the impregnation method can lead to good and (providing that suitable supports are chosen) reproducible results. Between Impo4 and Impo5 with mixed SiO<sub>2</sub>/MgO supports, the selectivity of Impo4 is not considerable as compared to Impo2 and Impo3. Increasing the amount of MgO over 50wt% in Impo5 decreases the selectivity in comparison to pure-SiO<sub>2</sub> based catalysts. The above results, and the comparison of the different supports, indicate that pure SiO<sub>2</sub>, prepared through precipitation, is an ideal support for OCM catalysts.

Table 2 shows the changes in the yields of different catalysts by changing the temperature in a GHSV of 6000 h<sup>-1</sup> and CH<sub>4</sub>/O<sub>2</sub> ratio of 4. As shown, the yields of

different catalysts have different thermal behaviors, but in general increasing the temperature from 750 °C to 800 °C, leads to dramatic increases in the yields.

Table 2 The conversion, selectivity and yield of different catalysts as a function of changing the temperature are in a (GHSV of 6000 h<sup>-1</sup> and a CH<sub>4</sub> to O<sub>2</sub> ratio of 4/1).

*Catalyst	T (°C)	Conversions[%]			Selectivity [%]			Yield [%]	
		O <sub>2</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub>
Impo01	750	8.9	5.5	0.9	64.7	0.00	34.5	0.0	1.9
Impo02	750	27.6	16.3	2.8	24.5	25.8	46.8	4.2	11.9
Impo03	750	37.5	11.9	1.7	25.6	35.2	37.6	4.2	8.6
Impo04	750	43.7	11.2	2.9	43.3	18.1	35.7	1.7	4.9
Impo05	750	64.7	10.6	15.1	84.9	0.0	0.0	0.0	0.0
Impo01	800	26.4	13.8	2.7	26.8	22.1	48.3	3.1	9.8
Impo02	800	87.1	35.7	5.1	15.3	47.6	32.0	16.2	27.0
Impo03	800	92.6	28.7	4.5	21.3	47.3	26.9	13.6	21.3
Impo04	800	81.3	19.6	2.6	35.1	34.1	28.3	6.6	12.0
Impo05	800	67.2	12.9	22.4	62.7	1.6	13.3	0.2	1.9
Impo01	825	59.1	21.6	4.2	20.8	38.6	36.3	8.3	16.2
Impo02	825	98.2	37.3	6.1	18.6	51.4	24.3	19.2	28.2
Impo03	825	99.0	29.5	4.7	23.3	50.8	21.3	14.9	21.2
Impo04	825	98.2	24.2	2.0	28.6	36.2	33.3	8.8	16.8
Impo05	825	68.7	14.1	20.4	49.7	7.6	22.4	1.1	4.2
Impo01	850	94.5	25.4	4.5	24.7	50.9	19.8	12.9	17.9
Impo02	850	98.7	36.0	6.5	18.5	51.2	23.7	18.9	27.8
Impo03	850	99.3	29.3	5.0	24.1	51.3	19.6	15.0	20.6
Impo04	850	89.5	24.5	2.4	30.4	38.7	28.5	9.2	16.0
Impo05	850	80.9	15.4	20.0	54.4	14.2	11.3	2.2	3.9

\*Catalyst: Impo1: pure SiO<sub>2</sub> as Support (powder), Impo2: pure SiO<sub>2</sub> as Support spray dried.  
 Impo3: pure SiO<sub>2</sub> mesh 30-35 micron Impo4: SiO<sub>2</sub>/MgO 50: 50, Impo5: SiO<sub>2</sub>/MgO 75/25,  
 The ratio of active component is for all catalyst 2%Mn/ 5%Na<sub>2</sub>WO<sub>4</sub>

As discussed, Impo2 has a better catalytic yield than the other catalysts, and has the highest yield (19% for C<sub>2</sub>H<sub>4</sub> and 28.2 for C<sub>2</sub> species) at 825 °C, which is far better than those of the other catalysts under the same operational conditions.

Studying the deactivation of Impo 2 for about 200 h revealed that the conversion and yield of the catalyst do not change under the same operational conditions (GHSV of 6000 h<sup>-1</sup> and CH<sub>4</sub>/O<sub>2</sub> ratio of 4) figure 5.

It is also noteworthy that the highest yield reported in previous works [8-11] was 15% for silica gel and aluminum silicate based catalysts.

#### 4. Conclusion

Studying the effects of different support on the structure and morphology of the catalysts shows that the Mn-WO<sub>4</sub>/SiO<sub>2</sub> catalyst with a small amount of Na after calcinations at 850 °C for 12 h is a promising OCM catalyst to produce useful C<sub>2</sub> hydrocarbons. It also is shown that the impregnation method is more appropriate method for the preparation of OCM catalysts. Comparing to the co-precipitation, it is found that the impregnation method is easier to handle and control the amount of active component, has fewer steps and gives more reproducible results.

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