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## STUDY OF OXIDATIVE COUPLING OF METHANE INTEGRATED WITH CO OXIDATION

### BADANIE PROCESU UTLENIAJĄCEGO SPRZĘGANIA METANU ZINTEGROWANEGO Z DOPALANIEM CO

#### Abstract

In this work, the process of OCM carried out over  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$  integrated with selective oxidation over Ag/support was investigated. The effect of feed gas composition and OCM bed temperature as well as the position of Ag/support bed and additional oxygen injection before this bed were investigated. At optimal OCM conditions for the  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$  catalyst ( $\text{CH}_4/\text{O}_2 = 3.75$ ;  $V_{\text{tot}} = 77 \text{ cm}^3/\text{min}$ ;  $T = 780^\circ\text{C}$ ), the injection of additional  $4 \text{ cm}^3/\text{min}$  of oxygen into the bed of Ag/support (working at  $250\text{--}300^\circ\text{C}$ ) leads to a preferential oxidation of CO to  $\text{CO}_2$ .

**Keywords:** oxidative coupling of methane, integration with oxidation, ethylene, silver catalyst

#### Streszczenie

W pracy zbadano proces OCM w obecności  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$  zintegrowany w jednym reaktorze z procesem selektywnego utleniania CO prowadzonym na katalizatorze Ag/nośnik. Zbadano wpływ zmiany parametrów prowadzenia procesu OCM, takich jak skład surowca i temperatury oraz efekt dodatku tlenu nad złożo Ag/nośnik. Wykazano, że w optymalnej temperaturze pracy złoża OCM ( $\text{CH}_4/\text{O}_2 = 3.75$ ;  $V_{\text{cal.}} = 77 \text{ cm}^3/\text{min}$ ;  $T = 780^\circ\text{C}$ ) wprowadzenie dodatkowo  $4 \text{ cm}^3/\text{min}$  tlenu nad złożo Ag/nośnik (pracującego w temp.  $250\text{--}300^\circ\text{C}$ ) prowadzi do preferencyjnego utleniania CO do  $\text{CO}_2$ .

**Słowa kluczowe:** utleniające sprzężenie metanu, integracja z utlenianiem, etylen, katalizatory srebrne

## 1. Introduction

The direct conversion of methane to useful chemical intermediates, such as hydrocarbons (saturated, unsaturated and aromatic), methanol and formaldehyde, is one of the topics. Among all these direct processes, the closest one to commercialization is the oxidative coupling of methane (OCM) to ethylene and ethane [1, 2]. However, a still low per-pass conversion of methane (below 20–30%) in order to achieve high selectivity (70–80%) as well as stability of catalysts at high reaction temperatures (780–850°C) limits its industrial implementation [3].

An integration of OCM with other processes may improve the attractiveness of this process. Up to now, most attention was devoted to the integration of the OCM process with dry and steam reforming of methane [2, 4–9]. Several other possibilities for the integration of OCM with aromatization [10–12], benzene alkylation [13], pyrolysis [14], conversion to acetic acid and/or ethanol [15], synthesis Fischer-Tropsch [16], oxidative dehydrogenation of ethane [12, 17–19], methanation of  $\text{CO}_x$  [20, 21] were also explored.

An interesting issue can also be the integration of OCM with a selective oxidation of CO to  $\text{CO}_2$ . Such coupling of two exothermic reactions in one reactor (two catalytic beds in one reactor) can be attractive from the technological point of view. The combustion of CO, which is produced on an OCM bed as a by-product, may simplify the separation of the reaction mixture. The total conversion of CO to  $\text{CO}_2$  should especially facilitate  $\text{CH}_4$  recycling as per-pass conversion of methane that does not exceed 30%. In the case of the most promising catalysts, e.g.  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ , other by-products, such as  $\text{CO}_2$  and water, it has no negative impact on the OCM process, so, in many cases, it is not required to clean the recycled methane from these gases, which can be used as a diluent [22–24]. However, in the case of integration in a single reactor, there are several problems due to the presence of many chemical compounds in the stream leaving the OCM catalyst bed, which e.g. may cause a deactivation of the CO oxidation catalyst. Moreover, hydrocarbon products and unreacted methane on a CO oxidation bed can be oxidized. Thus, the selection of a suitable catalyst is difficult because, usually, the catalysts active in the oxidation of CO also catalyze the total oxidation of hydrocarbons. An alternative solution can be the separation of ethylene and ethane from the reaction mixture before oxidation of CO to  $\text{CO}_2$ , but this solution requires an additional reactor for CO oxidation, which increases the amount of operations.

There are many catalysts active in the selective oxidation of CO to  $\text{CO}_2$ . A lot of noble metal-based catalysts, especially of the platinum group [25–29] and ones that are gold-based [29–33] as well as non-noble metal oxide-based catalysts (e.g. containing CoO, CuO and  $\text{MnO}_x$ ) [28, 34–39] have been investigated. Unfortunately, most of these catalysts are active not only in the oxidation of CO to  $\text{CO}_2$ , but also in the oxidation of hydrocarbons [40]. For example, methane in the presence of a catalyst based on Pd can be oxidized even at around 300°C [41].

Our attention turned to silver-based catalysts. These catalysts have been recognized to show a relatively high activity in the oxidation of CO and a low activity in the oxidation of  $\text{CH}_4$  [42, 43]. In this work, we have investigated the integration of the OCM process over  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$  multicomponent catalyst with selective CO oxidation over Ag/

SiO<sub>2</sub> or Ag/Al<sub>2</sub>O<sub>3</sub> in one reactor. the effects of the feed gas composition (CH<sub>4</sub>/O<sub>2</sub> ratio, O<sub>2</sub> addition below second bed) and temperature on the product distribution and the conversion of substrates were carefully investigated.

## 2. Experimental

### 2.1. Catalyst preparation

The OCM catalyst (Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>) was prepared by incipient wetness impregnation. Dry SiO<sub>2</sub> (Aldrich) was impregnated in two steps with an aqueous solution of Mn(NO<sub>3</sub>)<sub>2</sub> × 4H<sub>2</sub>O (POCh – Polish Reagents) and Na<sub>2</sub>WO<sub>4</sub> (Aldrich), respectively. In a typical procedure, 1 g of silica was impregnated with 1 cm<sup>3</sup> of aqueous solutions containing the desirable content of each salt needed for obtaining 2 and 5 wt.% of Mn and Na<sub>2</sub>WO<sub>4</sub>, sequentially. After each impregnation, the materials were dried for 8 h at 120°C and calcined at 900°C for 8 h.

The catalysts of total oxidation (Ag/SiO<sub>2</sub> and Ag/Al<sub>2</sub>O<sub>3</sub>) were also prepared by impregnation. Dry SiO<sub>2</sub> (Aldrich) and γ-Al<sub>2</sub>O<sub>3</sub> (Aldrich) supports were impregnated with aqueous solutions of AgNO<sub>3</sub> (Polish Chemical Reagents). The content of precursor in the solution was desirable for obtaining 15-wt.% of Ag. the thermal pretreatment procedures and conditions were the same as in the case of the OCM catalyst.

### 2.2. Catalytic performance

Catalytic tests were carried out in a flow-type tubular quartz reactor with the dimensions of (internal diameter) × (length) × (wall thickness) = 8 × 270 × 1 mm. Before the process, the catalyst placed in the reactor was heated in dry helium for 30 min at 800°C. The weight of the catalyst was 400 mg (grain size 0.2–0.3 mm) and the temperature of the process was in the range between 730 –800°C. The reactor was fed with the mixture of CH<sub>4</sub>:O<sub>2</sub>:He = 3.75 :1:2,8, and CH<sub>4</sub>:O<sub>2</sub>:He = 2.5:1:4,8. The total volumetric flow rate was 77 cm<sup>3</sup>/min in all runs. The reagents mixture was analyzed using the Agilent 6890 N gas chromatograph equipped with two columns (molecular sieve 5A for separation of CO and O<sub>2</sub> and Haysep Q for separation of H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and hydrocarbons) and thermal conductivity detectors.

The conversion of methane ( $X_m$ ) and selectivity to *i*-th product ( $S_i$ ) were calculated according to the following formulas:

$$X_M = \frac{n_{M(inlet)} - n_{M(outlet)}}{n_{M(inlet)}} \cdot 100\% \quad S_i = \frac{\sum a_i \cdot n_i}{n_{M(inlet)} - n_{M(outlet)}} \cdot 100\%$$

where:

$n_{M(inlet)}$ ,  $n_{M(outlet)}$  – the numbers of methane moles in the inlet and the outlet of the reactor, respectively;

$n_i$  – the number of moles of the *i*-th product in the outlet

$a_i$  – the number of carbon atoms in the “*i*” product (ethane, ethene, propane and propene).

### 3. Results and discussion

#### 3.1. Effect of additional bed position

Figure 1 illustrates the position of the oxidative coupling of methane ( $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ ) and the CO oxidation catalyst beds in a tubular flow-type quartz reactor. the bed of CO oxidation is located below the OCM band.

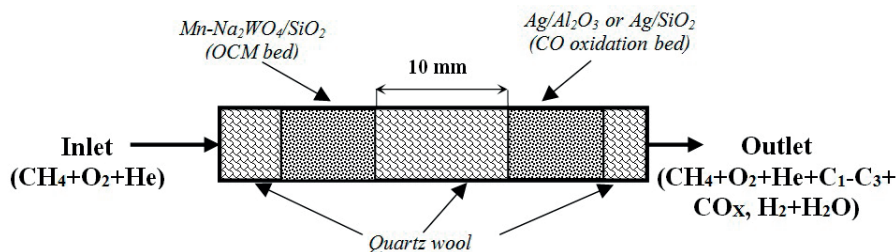


Fig. 1. Scheme illustrating  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$  and  $\text{Ag}/\text{support}$  bed positions in the flow-type tubular reactor

Table 1 summarizes the catalytic results obtained in the presence and absence of an additional CO oxidation catalyst as a function of temperature. To clarify the effect of integration (in two separated beds), additional catalytic tests concerning the mixture of OCM and CO oxidation catalysts (in one bed) were investigated as well. A comparison of results obtained in the absence and presence of additional CO oxidation bed reveals that above  $750^\circ\text{C}$  the integration of OCM with CO oxidation in a separate bed exerts a small positive effect on methane conversion and selectivity to  $\text{C}_{2+}$ . In contrast, at  $750^\circ\text{C}$  and below this temperature, the integration exerts a significant negative influence on the product distribution. the dramatic difference in the catalytic behavior vs. temperature can be explained based on oxygen conversion over the OCM bed (in single OCM process). It is clear from table 1 that, above  $750^\circ\text{C}$ , oxygen reacts in 100% over the OCM bed; therefore, the second CO oxidation bed ( $\text{Ag}/\text{SiO}_2$ ) has an insignificant effect on product distribution and methane conversion. the situation changes at  $750^\circ\text{C}$  and  $730^\circ\text{C}$  when unreacted oxygen appears in the mixture on the exit of the OCM bed. This oxygen reacts with CO and  $\text{C}_{2+}$  hydrocarbons over  $\text{Ag}/\text{SiO}_2$  catalyst; therefore, the selectivity to CO and  $\text{C}_{2+}$  decrease significantly.

A similar explanation can be adopted for results obtained in the presence of mixed  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$  and  $\text{Ag}/\text{SiO}_2$  catalysts (denoted in Table 1 as  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2 + \text{Ag}/\text{SiO}_2$ ). Because  $\text{Ag}/\text{SiO}_2$  catalyst is mixed with  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ , it has permanent contact with oxygen at any investigated temperature; therefore, the selectivity to  $\text{C}_{2+}$  hydrocarbons in the presence of mixed catalysts (in one bed) is always lower than in the presence single  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$  catalyst or in the integrated process carried out above  $750^\circ\text{C}$ .

The above results indicate that the reaction conditions optimal for the OCM process are not optimal for selective CO oxidation over  $\text{Ag}/\text{SiO}_2$  catalyst. In the integrated process,

**Table 1.** Catalytic performance in oxidative coupling of methane process carried out in the presence and absence of additional oxidation catalyst bed

OCM catalyst (CO oxidation catalyst)	Set temperature of oven [°C]	Conversion of CH <sub>4</sub> [%]	Conversion of O <sub>2</sub> [%]	Selectivity to C <sub>2+</sub> [%]	Selectivity to CO <sub>2</sub> [%]	Selectivity to CO [%]	Ratio of C <sub>2</sub> H <sub>4</sub> / C <sub>2</sub> H <sub>6</sub> [mol/mol]	Temperature in OCM bed [°C] <sup>b</sup>	Temperature in CO oxidation bed [°C] <sup>c</sup>
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	800	35,9	99,9	59,2	28,9	11,8	1,9	840-759	-
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/SiO <sub>2</sub> )		38,4	99,8	60,4	27,8	11,6	2,0	841-758	693-569
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> + Ag/SiO <sub>2</sub>		30,5	99,9	47,6	43,5	8,7	1,0	840-757	670-533
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	780	35,8	99,9	59,8	31,1	8,9	1,8	821-742	-
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/SiO <sub>2</sub> )		37,4	98,4	60,5	30,2	9,1	1,9	822-740	673-550
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> + Ag/SiO <sub>2</sub>		30,3	99,9	41,4	48,8	9,6	0,7	825-738	654-520
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	750	25,2	69,4	59,9	29,0	10,8	1,2	775-716	-
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/SiO <sub>2</sub> )		27,6	99,5	37,8	55,7	6,0	0,6	775-728	669-540
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> + Ag/SiO <sub>2</sub>		30,7	99,9	43,96	49,4	6,2	0,6	794-707	623-494
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	730	13,4	38,3	55,7	32,3	11,8	0,6	748-694	-
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/SiO <sub>2</sub> )		22,0	96,5	21,6	74,0	4,1	0,3	747-714	667-526
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> + Ag/SiO <sub>2</sub>		28,7	99,9	44,1	50,7	4,7	0,6	774-690	607-480

<sup>a</sup> Reaction conditions: Molar ratio of CH<sub>4</sub>:O<sub>2</sub>:He = 2,5:1:2,8; V<sub>total</sub> = 77 cm<sup>3</sup>·min<sup>-1</sup>, m<sub>OCM.cat.</sub> = 400 mg, m<sub>CO.oxi.cat.</sub> = 400 mg, Distance between catalyst beds 10 mm; Reaction time 2 h.

<sup>b</sup> Temperature measured on top and end of Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> bed (length of bed was 12 mm).

<sup>c</sup> Temperature measured on top and end of Ag/SiO<sub>2</sub> bed (length of bed was 12 mm).

the Ag/SiO<sub>2</sub> catalyst participates not only in CO oxidation, but also in the total oxidation of hydrocarbons. the range of temperature between 730–800°C is too high for selective CO oxidation.

Assuming initial catalytic results in the next parts of the experiments, we modified the conditions of the second CO oxidation bed by changing the positions of the Ag/SiO<sub>2</sub> bed (change of temperature) or by adding oxygen after the OCM bed (feed gas modification). the modifications are schematically presented in Figure 2.

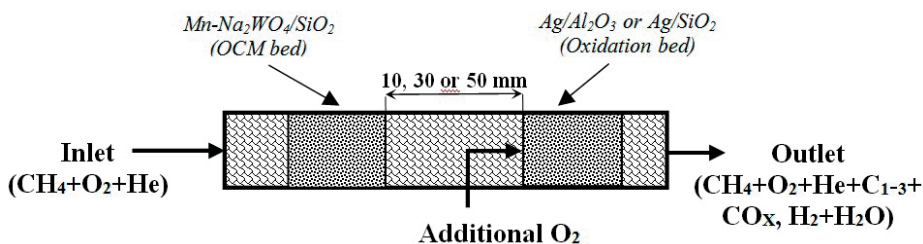


Fig. 2. Scheme illustrates Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> and Ag/support bed positions in the flow-type tubular reactor as well as modifications in the bed position and feed gas composition injected into the second bed zone

The results obtained after the modifications are reported in Table 2. the process of OCM in the presence and absence of CO oxidation bed was carried out using a feed mixture with CH<sub>4</sub>/O<sub>2</sub> = 3.8 molar ratio at two different temperatures. In selected cases, a silver catalyst supported with γ-Al<sub>2</sub>O<sub>3</sub> was investigated as well. It is clear from Table 2 that the modification of the second bed position gives an insignificant effect when O<sub>2</sub> is converted in 100% over the OCM bed (e.g. at 780°C). The integration effect can be improved either by decreasing CO oxidation bed temperature or by O<sub>2</sub> co-feeding. In most cases, a change of the oxidation bed position (decrease of the temperature) leads to the preferential CO oxidation. Such a modification enhances the selectivity to C<sub>2+</sub> hydrocarbons.

A similar effect of CO oxidation without a significant change in the selectivity to C<sub>2+</sub> hydrocarbons is also observed in the case of Ag/Al<sub>2</sub>O<sub>3</sub>, which is an industrial catalyst for selective oxidation of ethene to ethylene oxide. It should be pointed out that, under the reaction conditions investigated in this work, any additional products of partial oxidation of ethene, ethane or methane are formed.

The best effect of integration is achieved when the OCM process is carried out at 780°C and the bed of CO oxidation is located at the end of the oven where the temperature drops to 230–250°C. In such conditions, the injection of additional 4 cm<sup>3</sup>/min of oxygen leads to almost complete CO oxidation without C<sub>2+</sub> selectivity changes. Nevertheless, even at such a low temperature, we did not observe any additional oxygenates in the product mixture, such as ethylene oxide or acetaldehyde. Further experiments concerning the modification of the oxidation catalyst composition and the optimization its work conditions as well as the influence of gaseous promoters are now in progress.

**Table 2.** Catalytic performance in oxidative coupling of methane process carried out in the presence and absence of additional CO oxidation bed

OCM catalyst (CO oxidation catalyst) $V_{\text{add O}_2} = X [\text{cm}^3/\text{min}]^b$	Distance between beds [mm]	Temp. [°C]	Conversion of $\text{CH}_4$ [%]	Conversion of $\text{O}_2$ [%]	Selectivity to $\text{C}_{2+}$ [%]	Selectivity to $\text{CO}_2$ [%]	Selectivity to CO [%]	Ratio of $\text{C}_2\text{H}_4$ / $\text{C}_2\text{H}_6$ [mol/mol]	Temp. in OCM bed [°C] <sup>c</sup>	Temp. in CO oxidation bed [°C] <sup>c</sup>
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	–	780	27.0	98.1	68.1	24.3	7.4	1.4	800–730	–
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/SiO <sub>2</sub> ) $V_{\text{add O}_2} = 0$	10		27.4	99.1	67.7	24.0	8.1	1.5	819–755	712–591
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/SiO <sub>2</sub> ) $V_{\text{add O}_2} = 0$	30		27.6	100	68.8	23.7	7.2	1.4	805–736	426–289
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/SiO <sub>2</sub> ) $V_{\text{add O}_2} = 1$	30		27.9	100	63.3	31.8	4.6	1.4	805–735	435–291
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/Al <sub>2</sub> O <sub>3</sub> ) $V_{\text{add O}_2} = 0$	30		27.8	100	69.3	22.5	7.9	1.5	813–745	398–308
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/Al <sub>2</sub> O <sub>3</sub> ) $V_{\text{add O}_2} = 1$	30		28.2	100	65.4	32.3	1.98	1.5	813–744	398–307
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/Al <sub>2</sub> O <sub>3</sub> ) $V_{\text{add O}_2} = 4$	30		28.1	100	44.5	54.9	0.2	0.8	810–746	429–326
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/Al <sub>2</sub> O <sub>3</sub> ) $V_{\text{add O}_2} = 1$	50		27.8	100	68.9	22.9	8.0	1.5	813–753	271–222
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/Al <sub>2</sub> O <sub>3</sub> ) $V_{\text{add O}_2} = 2$	50		27.3	83.5	67.2	29.9	2.7	1.5	813–753	275–224
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/Al <sub>2</sub> O <sub>3</sub> ) $V_{\text{add O}_2} = 4$	50		27.4	78.7	61.8	37.6	0.2	1.4	–	–

Table 2

Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	-		16.9	62.3	63.7	27.26	8.72	0.8	761-703	-
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/SiO <sub>2</sub> )V <sub>add O2</sub> = 0	10		23.8	99.7	57.7	30.8	11.1	1.0	780-734	695-578
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/SiO <sub>2</sub> )V <sub>add O2</sub> = 0	30		18.6	82.2	59.6	39.9	0.0	0.7	768-706	415-283
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/SiO <sub>2</sub> )V <sub>add O2</sub> = 1	30	750	18.3	68.3	62.1	37.4	0.1	0.7	766-708	418-280
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/Al <sub>2</sub> O <sub>3</sub> )V <sub>add O2</sub> = 0	30		21.5	99.9	55.7	43.7	0.0	0.7	774-719	396-305
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/Al <sub>2</sub> O <sub>3</sub> )V <sub>add O2</sub> = 0	50		24.9	93.6	66.5	27.2	5.9	1.2	779-726	261-217
Mn-Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub> (Ag/Al <sub>2</sub> O <sub>3</sub> )V <sub>add O2</sub> = 2	50		24.8	76.3	66.4	32.0	1.2	1.2	778-726	263-219

<sup>a</sup> Reaction conditions: Molar ratio of CH<sub>4</sub>:O<sub>2</sub>:He = 3,8:1:4,8; V<sub>total</sub> = 77 cm<sup>3</sup>·min<sup>-1</sup>, m<sub>OCM.cat.</sub> = 400 mg, m<sub>CO<sub>2</sub>.cat.</sub> = 400 mg; Reaction time = 2 h.

<sup>b</sup> X is 0, 1, 2 and 4 cm<sup>3</sup>/min of additional O<sub>2</sub> injected before oxidation bed. <sup>c</sup> Description as in Table 1.

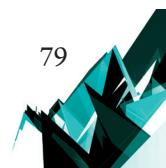


#### 4. Conclusions

The integration of the OCM process with selective CO oxidation in a single reactor was investigated. It has been found that, under conditions suitable for the OCM process, controlling the selectivity in CO oxidation is very difficult. In most cases, CO and hydrocarbons are oxidized simultaneously over the oxidation bed. Preferential CO oxidation is possible only when the second oxidation bed is located at the end of the oven where the temperature is below 300°C and additional oxygen is injected before this bed.

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