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Abstract
In this work, the process of OCM carried out over Mn-Na2WO4/SiO2 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 Mn-Na2WO4/SiO2 catalyst (CH4/O2 = 3.75; Vtot = 77 cm3/min; T = 780°C), the injection of additional 4 cm3/min of oxygen into the bed of Ag/support (working at 250–300°C) leads to a preferential oxidation of CO to CO2.

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

Stresszczenie
W pracy zbadano proces OCM w obecności Mn-Na2WO4/SiO2 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 złoże Ag/nośnik. Wykazano, że w optymalnej temperaturze pracy złoża OCM (CH4/O2 = 3,75; Vcalc = 77 cm3/min; T = 780°C) wprowadzenie dodatkowo 4 cm3/min tlenu nad złoże Ag/nośnik (pracującego w temp. 250–300°C) prowadzi do preferencyjnego utleniania CO do CO2.

Słowa kluczowe: utleniające sprzęganie metanu, integracja z utlenianiem, etylen, katalizatory srebrowe

STUDY OF OXIDATIVE COUPLING OF METHANE INTEGRATED WITH CO OXIDATION

BADANIE PROCESU UTLENIAJĄCEGO SPRZĘGANIA METANU ZINTEGROWANEGO Z DOPALANIEM CO
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-Tropscha [16], oxidative dehydrogenation of ethane [12, 17–19], methanation of CO [20, 21] were also explored.

An interesting issue can also be the integration of OCM with a selective oxidation of CO to CO₂. 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 CO₂ should especially facilitate CH₄ recycling as per-pass conversion of methane that does not exceed 30%. In the case of the most promising catalysts, e.g. Mn-Na₂WO₄/SiO₂ other by-products, such as CO₂ 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 CO₂, 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 CO₂. 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 MnO₂) [28, 34–39] have been investigated. Unfortunately, most of these catalysts are active not only in the oxidation of CO to CO₂, 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 CH₄ [42, 43]. In this work, we have investigated the integration of the OCM process over Mn-Na₂WO₄/SiO₂ multicomponent catalyst with selective CO oxidation over Ag/
SiO₂ or Ag/Al₂O₃ in one reactor. the effects of the feed gas composition (CH₄/O₂ ratio, O₂ 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-Na₂WO₄/SiO₂) was prepared by incipient wetness impregnation. Dry SiO₂ (Aldrich) was impregnated in two steps with an aqueous solution of Mn(NO₃)₂ × 4H₂O (POCh – Polish Reagents) and Na₂WO₄ (Aldrich), respectively. In a typical procedure, 1 g of silica was impregnated with 1 cm³ of aqueous solutions containing the desirable content of each salt needed for obtaining 2 and 5 wt.% of Mn and Na₂WO₄, 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/SiO₂ and Ag/Al₂O₃) were also prepared by impregnation. Dry SiO₂ (Aldrich) and γ-Al₂O₃ (Aldrich) supports were impregnated with aqueous solutions of AgNO₃ (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 CH₄:O₂:He = 3.75:1:2.8, and CH₄:O₂:He = 2.5:1:4.8. The total volumetric flow rate was 77 cm³/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 O₂ and Hayesep Q for separation of H₂, CO₂, H₂O, and hydrocarbons) and thermal conductivity detectors.

The conversion of methane (Xₘ) and selectivity to i-th product (Sᵢ) were calculated according to the following formulas:

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

where:

- \( n_{M(inlet)} \) – 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 (Mn-Na2WO4/SiO2) and the CO oxidation catalyst beds in a tubular flow-type quartz reactor. The bed of CO oxidation is located below the OCM band.

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°C the integration of OCM with CO oxidation in a separate bed exerts a small positive effect on methane conversion and selectivity to C2+. In contrast, at 750°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°C, oxygen reacts in 100% over the OCM bed; therefore, the second CO oxidation bed (Ag/SiO2) has an insignificant effect on product distribution and methane conversion. The situation changes at 750°C and 730°C when unreacted oxygen appears in the mixture on the exit of the OCM bed. This oxygen reacts with CO and C2+ hydrocarbons over Ag/SiO2 catalyst; therefore, the selectivity to CO and C2+ decrease significantly.

A similar explanation can be adopted for results obtained in the presence of mixed Mn-Na2WO4/SiO2 and Ag/SiO2 catalysts (denoted in Table 1 as Mn-Na2WO4/SiO2 + Ag/SiO2). Because Ag/SiO2 catalyst is mixed with Mn-Na2WO4/SiO2, it has permanent contact with oxygen at any investigated temperature; therefore, the selectivity to C2+ hydrocarbons in the presence of mixed catalysts (in one bed) is always lower than in the presence single Mn-Na2WO4/SiO2 catalyst or in the integrated process carried out above 750°C.

The above results indicate that the reaction conditions optimal for the OCM process are not optimal for selective CO oxidation over Ag/SiO2 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

<table>
<thead>
<tr>
<th>OCM catalyst (CO oxidation catalyst)</th>
<th>Set temperature of oven [°C]</th>
<th>Conversion of CH₄ [%]</th>
<th>Conversion of O₂ [%]</th>
<th>Selectivity to C₂⁺ [%]</th>
<th>Selectivity to CO [%]</th>
<th>Selectivity to CO₂ [%]</th>
<th>Selectivity to CO [%]</th>
<th>Ratio of C₂H₄/C₂H₆ [mol/mol]</th>
<th>Temperature in OCM bed [°C]</th>
<th>Temperature in CO oxidation bed [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-Na₂WO₄/SiO₂</td>
<td>800</td>
<td>35,9</td>
<td>99,9</td>
<td>59,2</td>
<td>28,9</td>
<td>11,8</td>
<td>1,9</td>
<td>840–759</td>
<td>–</td>
<td>693–569</td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/SiO₂)</td>
<td>38,4</td>
<td>99,8</td>
<td>60,4</td>
<td>27,8</td>
<td>11,6</td>
<td>2,0</td>
<td>841–758</td>
<td>670–533</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ + Ag/SiO₂</td>
<td>30,5</td>
<td>99,9</td>
<td>47,6</td>
<td>43,5</td>
<td>8,7</td>
<td>1,0</td>
<td>840–757</td>
<td>670–533</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂</td>
<td>780</td>
<td>35,8</td>
<td>99,9</td>
<td>59,8</td>
<td>31,1</td>
<td>8,9</td>
<td>1,8</td>
<td>821–742</td>
<td>–</td>
<td>673–550</td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/SiO₂)</td>
<td>37,4</td>
<td>98,4</td>
<td>60,5</td>
<td>30,2</td>
<td>9,1</td>
<td>1,9</td>
<td>822–740</td>
<td>673–550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ + Ag/SiO₂</td>
<td>30,3</td>
<td>99,9</td>
<td>41,4</td>
<td>48,8</td>
<td>9,6</td>
<td>0,7</td>
<td>825–738</td>
<td>654–520</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂</td>
<td>750</td>
<td>25,2</td>
<td>69,4</td>
<td>59,9</td>
<td>29,0</td>
<td>10,8</td>
<td>1,2</td>
<td>775–716</td>
<td>–</td>
<td>669–540</td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/SiO₂)</td>
<td>27,6</td>
<td>99,5</td>
<td>37,8</td>
<td>55,7</td>
<td>6,0</td>
<td>0,6</td>
<td>775–728</td>
<td>669–540</td>
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<td></td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ + Ag/SiO₂</td>
<td>30,7</td>
<td>99,9</td>
<td>43,96</td>
<td>49,4</td>
<td>6,2</td>
<td>0,6</td>
<td>794–707</td>
<td>623–494</td>
<td></td>
<td></td>
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<tr>
<td>Mn-Na₂WO₄/SiO₂</td>
<td>730</td>
<td>13,4</td>
<td>38,3</td>
<td>55,7</td>
<td>32,3</td>
<td>11,8</td>
<td>0,6</td>
<td>748–694</td>
<td>–</td>
<td>667–526</td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/SiO₂)</td>
<td>22,0</td>
<td>96,5</td>
<td>21,6</td>
<td>74,0</td>
<td>4,1</td>
<td>0,3</td>
<td>747–714</td>
<td>667–526</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ + Ag/SiO₂</td>
<td>28,7</td>
<td>99,9</td>
<td>44,1</td>
<td>50,7</td>
<td>4,7</td>
<td>0,6</td>
<td>774–690</td>
<td>607–480</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a Reaction conditions: Molar ratio of CH₄:O₂:He = 2,5:1:2,8; V_total = 77 cm³·min⁻¹, m_OCM cat. = 400 mg, m_CO ox cat. = 400 mg, Distance between catalyst beds 10 mm; Reaction time 2 h.

*b Temperature measured on top and end of Mn-Na₂WO₄/SiO₂ bed (length of bed was 12 mm).

*c Temperature measured on top and end of Ag/SiO₂ bed (length of bed was 12 mm).
the Ag/SiO₂ 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/SiO₂ bed (change of temperature) or by adding oxygen after the OCM bed (feed gas modification). The modifications are schematically presented in Figure 2.

![Diagram](image)

**Fig. 2.** Scheme illustrates Mn-Na₂WO₄/SiO₂ 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 CH₄/O₂ = 3.8 molar ratio at two different temperatures. In selected cases, a silver catalyst supported with γ-Al₂O₃ was investigated as well. It is clear from Table 2 that the modification of the second bed position gives an insignificant effect when O₂ 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 O₂ 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 C₂⁺ hydrocarbons.

A similar effect of CO oxidation without a significant change in the selectivity to C₂⁺ hydrocarbons is also observed in the case of Ag/Al₂O₃, 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 cm³/min of oxygen leads to almost complete CO oxidation without C₂⁺ 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

<table>
<thead>
<tr>
<th>OCM catalyst (CO oxidation catalyst)</th>
<th>Distance between beds [mm]</th>
<th>Temp. in OCM bed [°C]</th>
<th>Temp. in CO oxidation bed [°C]</th>
<th>Conversion of CH₄ [%]</th>
<th>Conversion of O₂ [%]</th>
<th>Selectivity to C₂⁺ [%]</th>
<th>Selectivity to CO₂ [%]</th>
<th>Selectivity to CO [%]</th>
<th>Ratio of C₂H₄/C₂H₆ [mol/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-Na₂WO₄/SiO₂</td>
<td>10</td>
<td>800–730</td>
<td>–</td>
<td>27.0</td>
<td>98.1</td>
<td>68.1</td>
<td>24.3</td>
<td>7.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/SiO₂) Vadd O₂ = 0</td>
<td>10</td>
<td>800–730</td>
<td>–</td>
<td>27.4</td>
<td>99.1</td>
<td>67.7</td>
<td>24.0</td>
<td>8.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/SiO₂) Vadd O₂ = 00</td>
<td>10</td>
<td>780</td>
<td>–</td>
<td>27.9</td>
<td>100</td>
<td>63.3</td>
<td>31.8</td>
<td>4.6</td>
<td>1.4</td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/Al₂O₃) Vadd O₂ = 0</td>
<td>30</td>
<td>819–755</td>
<td>712–591</td>
<td>27.8</td>
<td>100</td>
<td>69.3</td>
<td>22.5</td>
<td>7.9</td>
<td>1.5</td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/Al₂O₃) Vadd O₂ = 1</td>
<td>30</td>
<td>805–736</td>
<td>426–289</td>
<td>28.2</td>
<td>100</td>
<td>65.4</td>
<td>32.3</td>
<td>1.98</td>
<td>1.5</td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/Al₂O₃) Vadd O₂ = 2</td>
<td>30</td>
<td>813–744</td>
<td>398–307</td>
<td>28.1</td>
<td>100</td>
<td>44.5</td>
<td>54.9</td>
<td>0.2</td>
<td>0.8</td>
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<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/Al₂O₃) Vadd O₂ = 4</td>
<td>50</td>
<td>810–746</td>
<td>429–326</td>
<td>27.8</td>
<td>100</td>
<td>68.9</td>
<td>22.9</td>
<td>8.0</td>
<td>1.5</td>
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<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/Al₂O₃) Vadd O₂ = 1</td>
<td>50</td>
<td>813–753</td>
<td>271–222</td>
<td>27.3</td>
<td>83.5</td>
<td>67.2</td>
<td>29.9</td>
<td>2.7</td>
<td>1.5</td>
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<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/Al₂O₃) Vadd O₂ = 2</td>
<td>50</td>
<td>813–753</td>
<td>275–224</td>
<td>27.4</td>
<td>78.7</td>
<td>61.8</td>
<td>37.6</td>
<td>0.2</td>
<td>–</td>
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<td>Mn-Na₂WO₄/SiO₂ (Ag/SiO₂)</td>
<td>V_{add O₂}</td>
<td>780–734</td>
<td>695–578</td>
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<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/SiO₂)</td>
<td>V_{add O₂} = 0</td>
<td>23.8</td>
<td>99.7</td>
<td>57.7</td>
<td>30.8</td>
<td>11.1</td>
<td>1.0</td>
<td>780–734</td>
<td>695–578</td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/SiO₂)</td>
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<td>18.6</td>
<td>82.2</td>
<td>59.6</td>
<td>39.9</td>
<td>0.0</td>
<td>0.7</td>
<td>768–706</td>
<td>415–283</td>
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<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/SiO₂)</td>
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<td>18.3</td>
<td>68.3</td>
<td>62.1</td>
<td>37.4</td>
<td>0.1</td>
<td>0.7</td>
<td>766–708</td>
<td>418–280</td>
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<td>Mn-Na₂WO₄/SiO₂ (Ag/Al₂O₃)</td>
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<td>21.5</td>
<td>99.9</td>
<td>55.7</td>
<td>43.7</td>
<td>0.0</td>
<td>0.7</td>
<td>774–719</td>
<td>396–305</td>
</tr>
<tr>
<td>Mn-Na₂WO₄/SiO₂ (Ag/Al₂O₃)</td>
<td>V_{add O₂} = 0</td>
<td>24.9</td>
<td>93.6</td>
<td>66.5</td>
<td>27.2</td>
<td>5.9</td>
<td>1.2</td>
<td>779–726</td>
<td>261–217</td>
</tr>
</tbody>
</table>

Table 2

| Mn-Na₂WO₄/SiO₂ (Ag/Al₂O₃) | V_{add O₂} = 2 | 24.8 | 76.3 | 66.4 | 32.0 | 1.2 | 1.2 | 778–726 | 263–219 |

* Reaction conditions: Molar ratio of CH₄:O₂:He = 3.8:1:4.8; V_{total} = 77 cm³·min⁻¹, m_{QCM cat.} = 400 mg, m_{CO ox. cat.} = 400 mg; Reaction time = 2 h.

** X is 0, 1, 2 and 4 cm³/min of additional O₂ injected before oxidation bed. ** 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.

References


