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Design of Highly Efficient Catalyst for Rational Way of Direct Conversion of Methane

I.Z. Ismagilov1*, E.V. Matus1, M.A. Kerzhentsev1, I.P. Prosvirin1, R.M. Navarro2, J.L.G. Fierro2, G. Gerritsen3, E. Abbenhuis3, Z.R. Ismagilov1,4

1Boreskov Institute of Catalysis SB RAS, pr. Akademika Lavrentieva 5, 630090 Novosibirsk, Russia
2Instituto de Catálisis y Petrolequímica, CSIC, Marie Curie 2, 28049 Madrid, Spain
3Hybrid Catalysis B.V., Den Dolech 2, Eindhoven 5612, AZ, the Netherlands
4Institute of Coal Chemistry and Material Science SB RAS, pr. Sovetskiy 18, 650000 Kemerovo, Russia

1. Introduction

Design of highly efficient catalyst for rational way of conversion of methane will solve such problems as effective utilization of natural gas and environmental protection [1-7]. The production of C2 hydrocarbons (i.e. ethylene + ethane) through the oxidative coupling of methane (OCM) is an attractive direct way of the natural gas utilization into the value added products (Eqs. (1), (2)):

\[
2\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O} \quad (1)
\]

\[
\text{C}_2\text{H}_6 + 0.5\text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad (2)
\]

Although considerable efforts have been placed on the search of commercially suitable OCM catalyst, the C2 yield is still less than the 30% threshold for practical application [2, 8, 9]. The limit of C2 yield is connected with the thermodynamically favoured nonselective oxidation of hydrocarbons to CO and CO2. According to the OCM reaction mechanism [8, 10, 11], the active surface species play a key role in the methyl radical formation. The radicals should recombine selectively to ethane, which is then dehydrogenated to ethylene oxidatively. Methoxy species formed on the surface or in the gas phase finally react to carbon dioxide. The reduction of gaseous oxygen concentration can provide the increase of selectivity of C2 formation [10].

Many different reactor concepts were proposed to improve the C2 yield such as fixed bed reactor, fluidized bed reactor, porous and dense membrane reactors, solid oxide fuel cell reactor [12, 13]. It was demonstrated that membrane reactor exhibits appreciable advantages over traditional packed bed reactor [14-16]. The most significant potential of membrane reactor in OCM process is its ability to increase the C2 selectivity by controlling of the oxygen addition. In recent years, a great deal of effort has been directed towards OCM with the use of mixed ionic-electronic conducting membranes (MIECM membranes), but only a few examples demonstrated a C2 yield higher than 30% [14-16].

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Abstract

Effects of composition and preparation method of MnNaW/SiO2 and LaSr/CaO catalysts on their physical-chemical properties and performance in oxidative coupling of methane (OCM) have been studied. For MnNaW/SiO2 catalysts the synthesis method and type of SiO2 have a significant effect on the texture, while the Na/W ratio determines the phase composition. The variation of preparation method and temperature of catalyst calcination allows regulation of the metal surface concentration and mode of metal distribution across the SiO2 support. For LaSr/CaO catalysts the synthesis method determines the specific surface area, surface and phase composition. Correlations between catalyst performance, preparation method and state of the catalyst were established. The rational preparation procedure and perspective composition of OCM catalyst have been developed. The 20La/CaO catalysts prepared by citrate sol-gel method were shown to provide ~20% C2 yield and ~40% methane conversion at 800 ºC.
It was postulated that for the further enhancement of $C_2$ yield in membrane reactor, efficient catalyst systems should be provided and the development of a high permeation flux MIEC membrane alone is not a sufficient strategy for the successful industrial implementation of an OCM membrane reactor [16]. In addition, the kinetic compatibility requires a good match between oxygen permeation rate and reaction rate as crucial for OCM reaction [14]. Thus the goal of this study is creation of an efficient catalyst for OCM to be used in catalytic membrane reactor (CMR). MnNaW/SiO$_2$ and LaSr/CaO type catalysts were shown to be among the most suitable for this purpose, and therefore we have undertaken a systematic synthesis, physicochemical and catalytic characterization study of a series of such compositions and their modifications, with a perspective of their integration into the CMR. These studies will be applied to understand the structure-property-performance relationships and elucidate crucial factors, variation of which at the stage of catalyst preparation allows regulation of the OCM reaction parameters.

2. Experimental

2.1 Catalyst preparation

The series of OCM catalysts were synthesized by different preparation routes. The abbreviation in the bracket indicates the preparation method: (I) is the incipient wetness impregnation method, (M) is the mixture slurry method, (S) is the sol-gel method and (PM) is physical mixing. The number in the sample formula indicates the nominal metal content (wt.%). The MnNaW/SiO$_2$ (I) catalysts were prepared by sequential incipient wetness impregnation method. At first a SiO$_2$ support was impregnated by an aqueous solution of sodium tungstate dihydrate Na$_2$WO$_4·2$H$_2$O and sodium oxalate Na$_2$C$_2$O$_4$ taken in an appropriate amounts. Then NaW/SiO$_2$ was dried at 120 °C for 6 h and impregnated by an aqueous solution of manganese acetate tetrahydrate Mn(CH$_3$COO)$_2·4$H$_2$O taken in an appropriate concentration. The catalysts were then dried at 120 °C for 6 h and calcined in air at 850 °C for 6 h. The nature of the SiO$_2$ substrate was varied and the main characteristics of SiO$_2$ sources are presented in Table 1.

The modification of MnNaW/SiO$_2$ (I) catalyst by Ce, La, Zr, Cl, P or S was performed [17]. In this case the corresponding metal precursor of promoter (cerium nitrate Ce(NO$_3$)$_3·6$H$_2$O, lanthanum nitrate La(NO$_3$)$_3·6$H$_2$O, oxchloride of zirconium ZrOCl$_2·8$H$_2$O, sodium sulphate Na$_2$SO$_4$, sodium thiosulphate Na$_2$S$_2$O$_3$, disodium hydrogen phosphate Na$_2$HPO$_4·12$H$_2$O, monosodium phosphate NaH$_2$PO$_4·2$H$_2$O, sodium chloride NaCl) was added into the impregnating solution. The SiO$_2$-3 silica was used for this series of catalysts.

The MnNaW/SiO$_2$ (M) catalysts were prepared by the mixture slurry method. Aqueous solutions of salts (manganese acetate tetrahydrate Mn(CH$_3$COO)$_2·4$H$_2$O, sodium tungstate dihydrate Na$_2$WO$_4·2$H$_2$O, sodium oxalate Na$_2$C$_2$O$_4$) taken in appropriate concentrations were added dropwise to silica sol (SiO$_2$-5, Table 1) with stirring, and the mixture was agitated vigorously for several hours. The mixture slurry was dried at 120 °C for 6 h and calcined in air at 850 for 6 h.

The LaSr/CaO (S) catalysts were prepared by citrate sol-gel method. Aqueous solutions of salts (lanthanum nitrate La(NO$_3$)$_3·6$H$_2$O, strontium nitrate Sr(NO$_3$)$_2$, calcium nitrate Ca(NO$_3$)$_2·4$H$_2$O) taken in a required ratio were added to a solution of citric acid (CA) at 60 °C. The reagents were used in molar ratio (La + Ca + Sr) : CA = 1 : 1. Then this mixture was kept at 60 °C for the time required to form a highly viscous gel, which was dried at 100 °C and then self-ignited producing a dry powder. The obtained product was dried at 120 °C and then calcined in air at 850 °C for 6 h.

LaSr/CaO (PM) catalysts were prepared by physical mixing of nitrate metal salts (lanthanum nitrate La(NO$_3$)$_3·6$H$_2$O, calcium nitrate Ca(NO$_3$)$_2·4$H$_2$O, strontium nitrate Sr(NO$_3$)$_2$) taken in a required ratio. The obtained product was dried at 120 °C and then calcined in air at 850 °C for 6 h.

Table 1

| Sample | Description | Textural data | XRD data |
|--------|-------------|---------------|----------|
|        |             | S$_{BET}$ m$^2$/g | V$_{pore}$ cm$^3$/g | D$_{pore}$ nm | amorphous SiO$_2$ |
| SiO$_2$-1 | custom-made (hydrolysis of TEOS at 50 °C) | 56 | 0.31 | 22.0 |
| SiO$_2$-2 | commercial Silica gel 60, Merck | 274 | 0.71 | 10.3 |
| SiO$_2$-3 | commercial Silica gel Davisil 646 | 323 | 1.13 | 14.1 |
| SiO$_2$-4 | commercial Silica Si 4-5P, Akzo | 393 | 1.03 | 10.5 |
| SiO$_2$-5 | sol LUDOX LS, 30 wt.% SiO$_2$, Sigma-Aldrich | particle size of sol 8-20 nm | - |

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2.2. Characterization of catalysts

The chemical composition of the prepared catalysts was determined by X-ray fluorescence spectroscopy (XFS) using an ARL analyzer with a Rh anode of an X-ray tube and inductively coupled plasma-atomic emission spectrometry (ICP-AES) method.

BET surface area ($S_{\text{BET}}$), pore volume ($V_{\text{pore}}$) and average pore diameter ($D_{\text{pore}}$) of the supports and catalysts were determined in a Micromeritics ASAP 2400 instrument using $N_2$ adsorption at -196°C. Prior to surface area determination, the powders were degassed under vacuum ($10^{-5}$ mbar) at 423°C for 4 h.

The phase composition was determined by X-ray diffraction (XRD) in a 2-theta range of 10-80° in an HZG-4C (Freiberger Prazisionmechanik) diffractometer with a CoKα (λ = 1.59021 Å) radiation source and a graphite monochromator. Phases were identified using the JCPDF database.

Transmission electron microscopy (TEM) measurements were realized in a high-resolution JEOL JEM-2010 microscope operating at 200 kV with a structural resolution of 0.14 nm. The samples were deposited on perforated carbon supports attached to copper grids. The local elemental analysis of the samples was performed by an energy dispersive X-ray analysis (EDX) method using an EDAX spectrometer equipped with a Si (Li) detector with a resolution of 130 eV.

X-ray photoelectron spectra (XPS) were recorded in a SPECS spectrometer (Germany) using a hemispherical PHOIBOS-150-MCD-9 analyzer (AlKα radiation, hυ = 1486.6 eV). The binding energy (BE) scale was pre-calibrated using the positions of the peaks of Au4f7/2 (BE = 84.0 eV) and Cu2p3/2 (BE = 932.67 eV) core levels. The samples in the form of small granules were loaded onto a conducting double-sided copper scotch. The Si2p peak of SiO2 catalyst support at 103.3 eV was used to correct charge effects on the sample. Survey spectra were recorded at an analyzer pass energy of 50 eV, and high resolution narrow energy windows at 20 eV. The atomic concentration ratios of elements on the catalyst surface were calculated from the integral photoelectron peak intensities (Mn2p, W4f, Na1s, O1s, Cl1s, Si2s), which were corrected with theoretical sensitivity factors based on the Scofield’s photo-ionization cross sections [18].

2.3. Catalytic activity tests

OCM experiments were performed in a 14 mm i.d. quartz fixed-bed reactor with a feed composition of $\text{CH}_4 : \text{O}_2 : \text{He}$ equal to 4 : 1 : 2 under atmospheric pressure, at temperatures 650-950 °C and gas flow rate 175 ml/min. The gas purity was 99.95% CH4, 99.995% O2 and 99.995% He. Prior to each activity test, the catalysts were calcined in an O2 flow (100 ml/min) at 700 °C for 2 h. In order to minimize the catalyst overheating, the 500 mg sample (fraction of 0.25–0.50 mm) was diluted with an equal amount of SiC. Analysis of both inlet and outlet reaction mixtures were accomplished using a Stanford Research Systems QMS 300 mass spectrometric gas analyzer.

Calculation of the reaction parameters was performed from mass flows considering the change of the reaction volume, which can be determined from the change of He concentration. Selectivity to the reaction products (C2H4, C2H6, CO and CO2) was determined using flow rates of products after the reactor. Yield of products was calculated as selectivity multiplied by methane conversion.

3. Results and Discussion

3.1. OCM tests

The results of OCM tests of a wide set of catalysts shows that precise regulation of product yields can be achieved by appropriate variation of catalyst preparation conditions (Figs. 1-5). As follows from Fig. 1, catalyst composition has some effect on C2 yield. The C2 hydrocarbons yield tends to increase when i) silica with initial specific surface area 300 m2/g is used; ii) Mn content is decreased from 3 to 2 wt.%; iii) Na2WO4 content is increased from 3 to 5-7 wt.%; iv) the Na/W molar ratio is increased from 1 to 2 (Fig. 1a). The variation of Na content and preparation mode has a more obvious influence on C2 yield value (Fig. 1b). It can be varied in the range of 6-15%. The mixture slurry method provides formation of more active OCM materials at Na content less than 1.5 wt.%, while the impregnation method have an advantage at Na content above 1.5%. This is probably connected with particularity of crystallization and polymorphic transformations of different sources of SiO2 (amorphous SiO2 powder (I) and SiO2 sol (M)) that leads to different phase composition and texture characteristics of catalysts, as well as behaviour of metal distribution across support, red-ox properties of supported species and metal-support interaction.

The C2 product yield in the OCM reaction over MnNaW-X/SiO2 catalysts was strongly affected by the type and content of the promoter X [17]. Among all promoters (X = La, Ce, Zr, S, P, Cl) only Cl introduction leads to notable improvement of catalyst performance and shifts the maximum of C2 yield to low-temperature region (Fig. 2). However this catalyst shows unstable performance under a durability test in the OCM reaction (Fig. 3). The modification of MnNaW/SiO2 samples by La (2-5 wt.%) or Ce
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(2 wt.%) only slightly influences the activity but improves the stability of the catalyst during the durability test in the OCM reaction (Fig. 3). On the contrary, at modification by Zr (0.3-3.3 wt.%) catalyst performance goes down (Fig. 2a): the methane conversion and \( \text{C}_2 \) yield decrease from 35 to 6-30% and from 15 to 2-10%, respectively. The S or P introduction also leads to a considerable decrease of both \( \text{C}_2 \) yield and \( \text{C}_2 \) selectivity – generally at the expense of a decrease of \( \text{C}_2\text{H}_4 \) formation (Fig. 2b).

Literature data on the stability of the MnNaW/SiO\(_2\) catalyst under OCM reaction conditions are very contradictory [19-26]. In particular, it was found that the catalyst retained its initial activity for a long time (20–97 [19–21], 450 [23], or 500 h [22]). On the contrary, according to data [24–26], the yield of \( \text{C}_2 \) hydrocarbons began to decrease even after 14 h OCM reaction. The main reasons for decreasing OCM process characteristics with time are the following: a change in the phase composition of the catalyst under the action of a reaction mixture the loss of an active component or a redistribution of the active component between the surface and the bulk of a support, and agglomeration [24, 26, 27]. It was postulated that the deactivation of the MnNaW/SiO\(_2\) catalyst upon its treatment with methane was caused by the reduction of Mn ions [11, 28, 29].

For the modified 2Mn1.6Na3W/SiO\(_2\) catalysts it is obvious that the formation of additional phases containing modifier elements (both individual and combined with the basic components) can change the concentration of surface oxygen-containing centres, which are active in the methane activation [17]. In particular, the improvement of OCM process characteristics in the presence of Cl-modified samples (Fig. 2b) can be explained by increase in the concentration of active sites because of the formation of metal oxyhalides or chlorides and a decrease in the concentration of deep oxidation sites [30]. However in course of OCM reaction the removal of chlorine due to a reaction with water occurs which seems to cause the instability of 2Mn1.6Na3W-1Cl/SiO\(_2\) performance in the long-term test (Fig. 3). It is proposed that stable OCM process performance in the presence of 2Mn1.6Na3W-2La/SiO\(_2\) catalyst is connected with the formation of difficult-to-reduce compounds (La–Mn–Si–O and La–W–O) and the retention of the surface chemical composition of the catalyst upon a long-term exposure to a reaction atmosphere [17].
Figure 3. Effect of catalysts composition on their performance in OCM of CH\textsubscript{4} at 850 ºC. (a) methane conversion vs. time on stream; (b) C\textsubscript{2} yield vs. time on stream. Catalyst composition: (1) – 2Mn1.6Na3W/SiO\textsubscript{2}, (2) – 2Mn1.6Na3W-1Cl/SiO\textsubscript{2}, (3) – 2Mn1.6Na3W-2La/SiO\textsubscript{2}.

Figure 4 shows the effect of the calcination temperature of 2Mn1.6Na3W-2La/SiO\textsubscript{2} catalyst on its activity in the OCM reaction. The methane conversion and C\textsubscript{2} yield increase with an increase of the calcination temperature from 800 to 850 ºC. The further increase of calcination temperature up to 1000 ºC leads to worsening of catalyst performance that can be connected with changes of phase and surface compositions of catalyst. The values of C\textsubscript{2} production selectivity are similar (45-50%) for all samples of this series.

Figure 5 shows the results of a study of the catalytic activity of LaSr/CaO catalysts. It is evident that the conversion of methane increased as the reaction temperature was increased from 600 to 800 ºC, and it insignificantly decreased upon a further increase in the temperature. The C\textsubscript{2} yield increased with the reaction temperature (a maximum at 800 ºC) and then began to lower. The yield of reaction by-products (CO + CO\textsubscript{2}) increased with the reaction temperature in the entire test range. The observed temperature dependences of OCM reaction characteristics are consistent with previously obtained data, and they reflect the special features of the homogeneous–heterogeneous mechanism of this reaction [30, 31].

The catalytic performance of LaSr/CaO samples is also strongly affected by the chemical composition. The methane conversion increases from 25 to 41%, C\textsubscript{2} yield increases from 11 to 19%, molar ratio C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} increases from 0.3 to 0.5 in following order: 20Sr/CaO (S) < 15La-15Sr/CaO (S) < 20La/CaO (S) (Fig. 5). The values of selectivity of C\textsubscript{2} formation for these samples change in the same mode at T < 800 ºC, their values are the same (~45%) at T = 800 ºC. At temperature T > 800 ºC the values of selectivity of C\textsubscript{2} formation increase in the opposite order. The methane conversion increases from 29 to 41%, C\textsubscript{2} yield – from 14 to 19% when the sol-gel method of preparation instead of physical mixing is used (Fig. 5).

The comparison of LaSr/CaO and MnNaW/SiO\textsubscript{2} catalytic systems represented by their best samples (20La/CaO (S) and 2Mn1.6Na3W/SiO\textsubscript{2} (I)) shows that a more wide temperature range of high catalyst performance is provided by the 20La/CaO (S) catalyst (Fig. 6).

Fig. 4. Effect of temperature of catalyst calcination on the activity of 2Mn1.6Na3W-2La/SiO\textsubscript{2} catalyst in OCM reaction.
Thus it is shown that the catalyst performance in the OCM reaction can be regulated by catalyst composition, calcination temperature and preparation method of catalyst. Further improvement of OCM reaction parameters can be achieved by variation of reaction conditions. As an example, effects of space velocity and O₂/CH₄ ratio on the C₂ product yields by OCM are presented in Table 2. It is shown that optimal reaction conditions to achieve the maximum efficiency in the C₂ products formation in the OCM reaction are the following: the temperature is 850 °C; the O₂/CH₄ ratio is 0.25 – 0.375; the gas space velocity is 175 ml/min·g. The 2Mn1.6Na₃W/SiO₂-3 (I) catalyst under optimal reaction conditions provides C₂ hydrocarbons yield of 23.5% and 41% methane conversion at 850 °C. These values are comparable with or better than those recently reported [2, 8].

### Table 2

Effect of space velocity and O₂/CH₄ ratio on OCM reaction parameters on 2Mn1.6Na₃W/SiO₂-3 (I) at 850 °C.

| Catalyst loading, g | Gas space velocity, mL/min·g | O₂/CH₄ ratio | Reaction parameters |
|---------------------|-------------------------------|--------------|---------------------|
|                     |                               |              | C₂H₆ yield, % | C₂H₄ yield, % | C₂ yield, % |
| 0.5                 | 350                           | 0.25         | 6.9              | 11.0          | 17.9         |
| 1.0                 | 175                           | 0.25         | 9.0              | 14.5          | 23.5         |
| 1.5                 | 117                           | 0.25         | 7.0              | 9.2           | 16.2         |
| 0.5                 | 175                           | 0.125        | 5.4              | 3.4           | 8.8          |
| 0.5                 | 175                           | 0.375        | 6.1              | 12.1          | 18.2         |
| 0.5                 | 175                           | 0.50         | 4.1              | 10.3          | 14.4         |
3.2. Characterization of OCM catalysts

3.2.1. MnNaW/SiO₂

The detailed characterization of the studied catalysts was performed by ICP-AES, XRF, N₂ adsorption, XRD, HRTEM-EDX and XPS techniques. It can be noted that in all cases the chemical composition of samples is in good agreement with calculated values. The differences between the nominal and experimental metal content are less than 10% (Table 3).

The addition of metal components to silica followed by calcination at 850 ºC leads to a considerable decrease of specific surface area (from 320 to 1-3 m²/g), pore volume (from 1.1 to 0.002-0.006 cm³/g) and average pore diameter (from 14.1 to 6.2-12.7 nm) of support SiO₂ (Tables 2 and 3). It can be explained by the transition of amorphous silica into α-cristobalite and tridymite phases during the calcination.

Table 3: Effect of SiO₂ source and metal content on textural properties of MnNaW/SiO₂ catalysts

| Sample            | Chemical composition, wt.% | S_BET, m²/g | V_pore, cm³/g | Average pore diameter, Å |
|-------------------|-----------------------------|-------------|---------------|--------------------------|
|                   | Na  | W  | Mn  |                             |                          |                          |                           |
| Effect of support |     |    |     |                             |                          |                          |                           |
| 2Mn0.8Na3W/SiO₂-1 | 0.8 | 3.3 | 1.9 | 1.0                       | 0.002                    | 90                       |
| 2Mn0.8Na3W/SiO₂-2 | 0.9 | 3.2 | 2.0 | 2.6                       | 0.007                    | 110                      |
| 2Mn0.8Na3W/SiO₂-3 | 0.9 | 3.5 | 2.1 | 1.7                       | 0.004                    | 85                       |
| 2Mn0.8Na3W/SiO₂-4 | 0.8 | 3.3 | 2.0 | 2.5                       | 0.005                    | 75                       |
| Effect of Mn content |    |    |     |                             |                          |                          |                           |
| 1Mn0.8Na3W/SiO₂-2 | 0.9 | 3.5 | 1.2 | 2.5                       | 0.006                    | 95                       |
| 3Mn0.8Na3W/SiO₂-2 | 0.9 | 3.4 | 3.2 | 1.4                       | 0.006                    | 165                      |
| Effect of Na₂WO₄ content |  |    |    |                             |                          |                          |                           |
| 2Mn0.5Na2W/SiO₂-2 | 0.5 | 2.0 | 2.1 | 2.9                       | 0.008                    | 110                      |
| 2Mn1.1Na4W/SiO₂-2 | 1.0 | 4.4 | 2.1 | 2.0                       | 0.005                    | 95                       |
| Effect of Na content |    |    |     |                             |                          |                          |                           |
| 2Mn1.1Na3W/SiO₂-3 | 1.2 | 2.8 | 1.8 | 1.5                       | 0.003                    | 85                       |
| 2Mn1.6Na3W/SiO₂-3 | 1.6 | 3.5 | 2.2 | 0.8                       | 0.002                    | 85                       |

As follows from Table 3, some increase of specific surface area (from 1.0-1.4 to 2.5-2.9 m²/g) and pore volume (from 0.002 to 0.007 cm³/g) occurs with i) application of silica support with high specific surface area (300-400 m²/g) or ii) decrease of metal content.

It can be seen from Fig. 7, modification of MnNaW/SiO₂ by different modifying additives leads to some variation of S_BET, behaviour of which depends on the type and content of promoter X [17]. It was established that some increase of specific surface area (from 0.8 to 1.2-2.9 m²/g) and pore volume (from 0.002 to 0.006 cm³/g) occurred upon the addition of La, Ce or Zr cationic promoters. This effect is more pronounced for the Zr additive in comparison with the La and Ce additives and, probably, connected with the presence of different anions in the salt-precursors. The surface area of the catalysts also increased (up to 2-4 times) with the addition of S or Cl anionic promoter, but P additive has practically no effect on S_BET value.

Fig. 7. Effect of X/Mn molar ratio (X = La, Ce, Zr) (a) and X/Na molar ratio (X = S, P, Cl) (b) on S_BET of MnNaW-X/SiO₂ catalysts. Calcination temperature is 850 ºC.
Figure 8 illustrates the effect of the preparation mode and temperature of catalyst calcination on the catalyst texture. As a rule, the use of the mixture slurry method instead of impregnation leads to lower value of \( S_{\text{BET}} \). The specific surface area decreases from 1.5 to 0.2 m²/g at an increase of calcination temperature from 800 to 1000°C. Because of the low pore volume (~ 0.002-0.005 cm³/g) and specific surface area (~ 1-3 m²/g) of MnNaW-SiO₂, \( S_{\text{BET}} \) is mainly related to their external surfaces. It can be suggested that dopant can act as a crystallite growth inhibitor for the silica-based materials, while an increase of calcination temperature leads to crystal sintering. Another reason of \( S_{\text{BET}} \) variation is different phase compositions of samples (Figs. 9-11).

The \( \alpha \)-cristobalite (2θ = 25.6°, 33.2°, 36.7°, 42.2° and other, JCPDS 39-1425), tridymite (2θ = 24.1°, 27.1°, 35.2°, JCPDS 42-1401), Na₂WO₄ (2θ = 19.5°, 32.2°, 37.9°, 50.6 and 61.3°, JCPDS 12-0772) and Mn₂O₃ (2θ = 38.5°, 65.1°, JCPDS 41-1442) phases are observed in the non-modified MnNaW/SiO₂ catalyst after calcination at 850°C. The content of phases depends on the chemical composition of the samples. The Na₂WO₄ phase content increases with an increase of Na₂WO₄ content from 3 to 7 wt.% or an increase of Na/W from 1.0 to 2.0. An increase of Mn content from 1 to 3 wt.% or a decrease of Na content from 2 to 0.8 wt.% lead to an increase of Mn₂O₃ phase content.

An increase of Na content as well as an increase of temperature of catalyst calcination lead to an increase of tridymite phase content (Fig. 9). The effect of variation of silica type or preparation techniques on the phase composition of MnNaW/SiO₂ catalysts is insignificant. However, the contents of different SiO₂ polymorphic forms (tridymite/\( \alpha \)-cristobalite ratio) depend on the preparation mode. At equal content of Na the content of tridymite phase is higher in case of materials prepared by the mixture slurry method in comparison with samples prepared by the impregnation method (Fig. 9a).

Figure 10 shows XRD pattern of 2Mn₁.₆Na₃W/SiO₂ catalyst modified by cationic (Fig.10a) and anionic (Fig. 10b) promoters. At introduction of promoters (La, Ce, Zr, P, Cl), phases which are observed in non-modified samples (\( \alpha \)-cristobalite, tridymite, Na₂WO₄ and Mn₂O₃) generally remain and formation of additional phases also takes place [17]. In case of La, the formation of La₂O₃ and La(OH)₃ phases is observed. In case of Ce additive, the CeO₂ phase was detected (Fig. 10). For Ce-modified samples, the Mn₂O₃ phase presence is masked by line superposition from CeO₂. The content of CeO₂ phase increases when the content of Ce is increased from 0.5 to 5 wt.% in MnNaW-Ce/SiO₂. In case of Zr additive, the unidentified phase with lines at 2θ = 27.5°, 33.7°, 39.4°, 44.1°, 48.6° and 60.5° was detected in all studied Zr-containing samples. This phase is also observed in Cl-modified samples (Fig. 10b). It can be supposed that formation of this phase is induced by the presence of Cl anions in the material. The source of Cl in the Zr-modified catalysts is ZrOCl₂·8H₂O reagent which is used for the preparation of MnNaW-Zr/SiO₂ catalysts. In addition, in the MnNaW-Zr/SiO₂ catalyst with the highest Zr content (3.3 wt.%) an unidentified phase with lines at 2θ = 31.4° and 35.2° was found (Fig. 10a). Probably it is associated with formation of some Zr-containing phase. In case of P additive the Na₃PO₄ phase is found in all prepared MnNaW-P/SiO₂ samples. It is noted that intensity of lines of the Na₃PO₄ phase in diffraction pattern grows with a growth of P content, which may be due to an increase of Na₃PO₄ phase content. A different behaviour is observed in case of S additive. In particular, the presence of the highest content of S additive (~ 1 wt.%) leads to disappearance of Na₂WO₄ phase in the MnNaW-S/SiO₂ sample which, probably, can be the reason for worsening in the its catalytic properties (Fig. 2b). There are no sign of any additional phases in XRD pattern of these samples.
Fig. 9. Tridymite phase content vs. preparation condition: effect of Na content (a) and temperature of catalyst calcination (b).

Fig. 10. Effect of promoter type on phase composition of MnNaW-X/SiO₂ catalysts. Calcination temperature is 850 °C. (1) – α-cristobalite, (2) – 2Mn₁.₆Na₃W/SiO₂, (3) – 2Mn₁.₆Na₃W-5La/SiO₂, (4) – 2Mn₁.₆Na₃W-5Ce/SiO₂, (5) – 2Mn₁.₆Na₃W-3Zr/SiO₂, (6) – MnNaW-1S/SiO₂, (7) – 2Mn₁.₆Na₃W-1P/SiO₂, (8) – 2Mn₁.₆Na₃W-1Cl/SiO₂.

Figure 11 shows TEM typical images of SiO₂-based catalysts. As examples, fresh non-modified MnNaW/SiO₂ catalyst (Fig. 11a-c [17]) and La modified MnNaW-2La/SiO₂ catalysts (Fig. 11d-i) which are different by calcination temperature are examined. The 2Mn₁.₆Na₃W/SiO₂ (I) catalyst prepared by impregnation consists of big globular SiO₂ particles of 5-10 μm. On the surface of SiO₂ support two kinds of particles are found: with high (1-2 nm, Fig. 11a,b) and rough (up to 50-100 nm, Fig. 11c) dispersion. According to the EDX data, the composition of particles of high dispersion is very variable and all supported metals (Mn, W and Na) are present in their composition. The particles of rough dispersion have mainly good crystallinity and different composition ((MnO₃)₃MnSiO₃, MnOₓ, WOₓ/Na₂WO₄). It is noted that Na₂WO₄ phase is present as a rule in the form of an amorphous compound, on the surface of which small WO₃ crystals are observed. It is noted that Na₂WO₄ phase is not stable under irradiation during TEM study, as it was previously shown for Gdₓ(WO₄)₃ [32]. Concerning the 2Mn₁.₆Na₃W/SiO₂ (M) catalyst prepared by mixture slurry method, it consists of globular SiO₂ particles 0.5-0.6 μm in size. In other respects this sample resembles the MnNaW/SiO₂ (I) sample.

La introduction leads to the formation of crystallized bimetallic oxide particles (La-Mn-O, La-W-O) of 50-500 nm size (Fig. 11e,f [17]). There are also particles of high dispersion (Fig. 11d) as well as individual oxides (MnOₓ, WO₃) which are observed in non-modified sample. At low La content (0.5 wt.% (MnO₃)₃MnSiO₃ (up to 50 nm) and WO₃ (0.5-2 nm) particles are main supported species. At an increase of La content up to 5 wt.% or an increase of temperature of catalyst calcination, in addition to (MnO₃)₃MnSiO₃ and WO₃, particles of mixed oxide La-Mn-Si-O (as an example, La₄Mn(Si₂O₇)₂(MnO₄)₂) and La-Si-O (as an example, La₅Si₂O₇) species are observed (Fig. 11g), which confirms strong interaction between metals and silica support. The crystalline phases of particles detected on the SiO₂ support by HRTEM do not exactly correspond to the phase compositions detected by XRD. In particular, (MnO₃)₃MnSiO₃ and La₄Mn(Si₂O₇)₂(MnO₄)₂ phases are not observed by XRD (Fig. 9). Nevertheless, according to TEM data these phases are present in all La-containing samples. Plausible reasons are: i) the particles have dimensions below the detection limit of XRD (ca. 3 nm); ii) low phase content; iii) complex XRD pattern of multicomponent materials in which some individual compounds have identical reflections.
The metal dispersion and distribution across the support in catalysts was estimated from XPS data. In case of MnNaW-2La/SiO₂ sample prepared by impregnation the surface Mn : Si, Na : Si, W : Si and La : Si ratios are higher than the bulk ratios, denoting that the metals reside preferentially on the silica surface than in the bulk (Table 4). This effect is more pronounced for Na. In case of MnNaW-2La/SiO₂ sample prepared by the mixture slurry method the surface Mn : Si, W : Si and La : Si ratio is close to the bulk ratio. So, as follows from XPS data, the mixture slurry method instead of the impregnation method provides more uniform distribution of Mn and W supported species across the SiO₂ matrix.

Figure 12b indicates that the chemical states of Mn are similar in all studied samples. The Mn 2p binding energy of 641.6 ± 0.1 eV is characteristic of the Mn³⁺ oxidation state on the surface [33, 34]. Na 1s peak at 1071.8 ± 0.1 eV observed by XPS indicates the Na⁺² state [35]. The analysis of W 4f spectra shows BE = 35.6 ± 0.1 eV expected for W⁶⁺ [36, 37], and the spectra of different catalysts are similar to each other. It is not possible to distinguishWO₃ and Na₂WO₄ phases by XPS because of identical W⁶⁺ state in both phases [37]. Thus, the data of XPS demonstrates that preparation mode and temperature of calcinations doesn’t affect the electronic states of MnNaW/SiO₂ catalyst components on the surface, while it significantly influences the distribution of active species across the support.

### Table 4

| Preparation mode                  | Mn/Si | Na/Si | W/Si | La/Si |
|-----------------------------------|-------|-------|------|-------|
| Surface                          |       |       |      |       |
| Bulk                             |       |       |      |       |
| impregnation                      | 0.05  | 0.20  | 0.03 | 0.03  |
| mixture slurry method             | 0.03  | 0.17  | 0.05 | 0.014 |
As rule, for the OCM reaction, as an example of homogeneous-heterogeneous reaction, large surface areas and small particle sizes of catalyst are not beneficial [30, 38, 39]. Figure 13 a shows that variation of $S_{BET}$ in the range 0.2-1.2 has practically no effect on the C$_2$ yield in the OCM reaction over 2Mn1.6Na3W-La/SiO$_2$ catalysts. Consequently, in this case, a correlation between the activity of a catalyst and its specific surface area was absent, and the catalytic properties of the samples were primarily caused by their phase composition, the state and surface concentration of metals, and the redox properties of the catalysts.

It is demonstrated that the Mn$^{3+}$ is found as a proper oxidation state in the OCM reaction responsible for the methane activation [27, 40], and oxidized state of catalyst is necessary to maintain high C$_2$ selectivity [11]. Our XPS data confirm this observation (Fig. 13b): at an increase of Mn$^{3+}$/Si and W$^{6+}$/Si surface molar ratio the C$_2$ yield tends to increase. It is expected that the stability of OCM catalyst against deactivation should be related with stability of surface composition of catalyst during the OCM reaction. So the introduction of La seemingly leads to the stabilization of metal/Si atomic surface ratio and provides stable catalyst performance in the OCM reaction (Fig. 3). While the low activity of the catalyst which was calcined at 1000 ºC is mainly connected with the decrease of Mn/Si surface concentration (Fig. 4, 12a, 13b).

All these results clearly confirm that the MnNaW/SiO$_2$ catalyst performance in the OCM process can be regulated by the catalyst nanostructure design through variation of the catalyst preparation mode, temperature of calcination and introduction of cationic or anionic additives. At present it is difficult to unambiguously establish exactly which of the studied properties (phase composition, dispersion and distribution of supported metal-containing species) has a crucial influence on the catalyst performance. Further investigation of the effects of SiO$_2$ morphology and red-ox properties on the performance of silica-based catalyst in the OCM reaction is required and these topics are the subject of our current study.

### 3.2.2. LaSr/CaO

Table 5 shows main characteristics of LaSr/CaO catalysts which were prepared at variation of chemical composition and preparation method (physical
mixing (PM), citrate sol-gel method (S)). The catalysts prepared by the sol-gel method have a higher value of SBET than those for catalysts prepared by the physical mixing method. The specific surface area increases in the order: CaO (PM) ≈ 20Sr/CaO (PM) < 20La/CaO (PM) < 15La15Sr/CaO (PM) and CaO (S) ≈ 20Sr/CaO (S) < 15La15Sr/CaO (S) ≈ 20La/CaO (S). Thus La adding to CaO led to a growth of the specific surface area of the LaSr/CaO samples. The modification of La/CaO catalysts by Na (0.5–1.5 wt.%) has no influence on the phase composition of samples, but leads to a considerable decrease of specific surface area (from 11.5 to 2.5 m²/g). According to XRD data, the CaO phase is the main phase of the prepared samples. For two-component systems with La (~20 wt.%), in addition of CaO phase the formation of La₂O₃ phase (JCPDS 5-602) occurs. It is noted that for 20La/CaO (S) sample, in contrast to 20La/CaO (PM) sample, trace amount of La(OH)₃ phase (JCPDS 36–1481) is detected. Probably, it is related to higher S_{BET} of 20La/CaO (S) sample in comparison with 20La/CaO (PM) sample. In the former case larger surface area provides higher interaction rate between La and water and, consequently, formation of La(OH)₃. For catalysts with Sr (~20 wt.%), the type of Sr-containing phase depends on the preparation method: SrO (JCPDS 6–520) is detected in case of 20Sr/CaO (PM) sample, while SrCO₃ (JCPDS 5–418) in case of 20Sr/CaO (S) sample. One can see from Table 6 that surface atomic ratios of 20La/CaO (PM) and 20La/CaO (S) fresh catalysts are different. The Ca surface concentration for 20La/CaO (S) catalyst is considerably higher than that for 20La/CaO (PM) catalyst, which is probably controlled by the preparation method. However the values of La surface concentration are the same for the both samples (Table 6).

According to TEM study, the fresh 20La/CaO (S) catalyst consists of big aggregates (~ 1 μm) of CaO and La₂O₃ particles of 50–200 nm size (Fig. 14). There are also small CaO particles 50 nm in size and region of oxide interfaces.

Thus, it is shown that for the LaSr/CaO catalysts the preparation method determines both value of specific surface area, surface and phase compositions. According to the mechanism of the reaction [30], the active oxygen species ZO₂⁺ (O₂⁻, O₂²⁻) on the catalyst surface are necessary for methane activation. The formation of active oxygen centers by means of substitution of regular cations M⁺ of oxide lattice by other cations M’[n-1]⁺ is one of the approaches for developing active and stable OCM catalysts. So the growth of catalytic performance in the order: 20Sr/CaO (S) < 15La15Sr/CaO (S) < 20La/CaO can be explained by the increase of La⁺ (against Sr²⁺) content and, consequently, concentration of active oxygen species. This question has not been thoroughly investigated and will be studied in our next work. It is also expected that in case of La/CaO (S) catalyst prepared by the sol-gel method demonstrating higher catalytic activity in comparison to La/CaO (PM) catalyst prepared by the physical mixture method, the higher substitution degree of regular cations of oxide is realized because of intimate contact between oxides precursors at the stage of sol preparation.

### Table 5

Characteristics of La-Sr/CaO catalysts: effect of chemical composition and preparation method

| Sample          | XRD data       | Chemical composition, wt. % | S_{BET}, m²/g | Vₚore, cm³/g | Average pore diameter, Å |
|-----------------|----------------|-----------------------------|---------------|--------------|--------------------------|
| 20La/CaO (PM)   | CaO, La₂O₃    | 19.6 - 47.8                 | 1.4           | 0.005        | 140                      |
| 20La/CaO (S)    | CaO, La₂O₃, La(OH)₃ | 21.0 - 56.1              | 11.5          | 0.0039       | 137                      |
| 15La15Sr/CaO (PM) | CaO, La₂O₃, SrO | 14.0 - 12.1                | 2.7           | 0.010        | 139                      |
| 15La15Sr/CaO (S) | CaO, La₂O₃, SrCO₃ | 16.1 - 13.7                | 12.0          | 0.056        | 186                      |
| 20Sr/CaO (PM)   | CaO, SrO      | - 17.2 - 59.0              | 1.0           | 0.004        | 153                      |
| 20Sr/CaO (S)    | CaO, SrCO₃    | - 17.6 - 58.4              | 5.9           | 0.018        | 125                      |

### Table 6

XPS Si 2p, Ca 2p and La 3d binding energies (eV) and surface atomic ratios of 20La/CaO (S) and 20La/CaO (PM) fresh catalysts

| Sample            | Binding energy (eV) | Surface atomic ratio |
|-------------------|---------------------|----------------------|
|                   | Si 2p 3/2           | Ca 2p 3/2            | La 3d 5/2 | Ca/Si | La/Si |
| 20La/CaO (S)      | 103.3               | 347.1 (Ca²⁺)         | 835.5, 838.7 (La³⁺) | 0.843 | 0.092 |
| 20La/CaO (PM)     | 103.3               | 346.8 (Ca²⁺)         | 835.2, 838.5 (La³⁺) | 0.164 | 0.103 |
4. Conclusions

Representative series of OCM catalysts have been prepared and studied by a complex of physical-chemical methods. It was found that precise regulation of C\textsubscript{2} product yields in the OCM reaction could be achieved by appropriate variation of composition and preparation conditions of catalysts. The most perspective formulae of OCM catalysts were selected and the rational procedure of their synthesis was developed. High activity of 20La/CaO (prepared by the sol-gel method) and 2Mn1.6Na3.1W-2La/SiO\textsubscript{2} (prepared by the impregnation) determines prospective application of these catalysts in a catalytic membrane reactor, which seems really promising in further OCM studies. Presently, a prototype OCM membrane reactor is being built by our DEMCAMER project partners (HyGear B.V., the Netherlands, VITO, Belgium). The reactor will be tested with the developed OCM catalyst, and the results of the membrane reactor tests will be a topic of the next publication.

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