

Oxidative Coupling of Methane to Form Ethylene: Effect of the Preparation Method on the Phase Composition and Catalytic Properties of Li–W–Mn–O–SiO₂ Composite Materials

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Abstract—Production of ethylene by oxidative coupling of methane (OCM) is a promising direct path from methane to ethylene. Li–W–Mn–O–SiO₂ composite materials prepared by various methods—solid-phase synthesis, silica impregnation, sol–gel synthesis—are used as OCM catalysts. The phase states of these composite materials prepared by the different methods has been studied before and after use in the OCM reaction; the study has unexpectedly revealed the effect of the preparation technique on the phase composition of the material and the specific features of its catalytic behavior in OCM. Optimum catalysts provide an ethylene yield of 15% in terms of passed methane.

Keywords: methane, oxidative coupling, ethylene, composite materials

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Oxidative coupling of methane (OCM) is a promising one-step process that provides the conversion of methane to ethylene, which is a basic intermediate of petroleum chemistry, with an admixture of ethane and heavier hydrocarbons (C₂₊). The most efficient OCM catalysts include composite materials containing ions of an alkali metal, tungsten, manganese, and silica [1–10]. Composite materials containing sodium ions have been most extensively studied.

In the pioneering works of the Chinese researchers on the use of Na–W–Mn–O–SiO₂ oxide composites in OCM, owing to a systematic approach of the authors, it has been revealed that the synthesis method used for the composite material has an effect on its catalytic activity [1]. Thus, for composites with a gross composition of 1.9 wt % Mn and 5 wt % Na₂WO₄/SiO₂, depending on the synthesis method—impregnation of amorphous silica with aqueous solutions of manganese, tungsten, and sodium compounds (impregnation method (IM)) or physical mixing (PM) of silica and other components [1, 2]—under the same conditions of OCM ($T = 800^\circ\text{C}$, $V = 36 \text{ L g}^{-1} \text{ h}^{-1}$, $\text{CH}_4 : \text{O}_2 : \text{N}_2 = 3 : 1 : 2.6$), the yield of C₂ products underwent different changes over time: after 0.5 h, it was identical for the two composites (23.9% for each); however, after 30 h, the yield decreased to

9.3% for the IM-composite and remained almost the same (23.7%) for the PM-composite [1]. Despite this fact, which was probably the only one, thereafter, preference was given to the impregnation of silica with aqueous solutions containing Mn, Na, and W compounds with subsequent heat treatment [3].

Some indirect evidences prove that the synthesis primarily affects the structure of the formed complex of crystallites, i.e., the phase composition of the composite; however, it is difficult to reveal a direct correlation between the phase composition of Na–W–Mn–O–SiO₂ and its catalytic activity in OCM on the basis of literature data. On the one hand, in the case of testing a composite containing of 1.9 wt % Mn and 5 wt % Na₂WO₄/SiO₂ in OCM for 1000 h [800–900°C, $V = 8\text{--}15 \text{ L g}^{-1} \text{ h}^{-1}$, $\text{CH}_4 : \text{O}_2 : \text{N}_2 = (2.4\text{--}3.4) : 1 : (0.84\text{--}2.4)$] or 500 h [900–905°C, $V = 5\text{--}5.5 \text{ L g}^{-1} \text{ h}^{-1}$, $\text{CH}_4 : \text{O}_2 : \text{N}_2 = (5.5\text{--}6) : 1 : (2.8\text{--}3)$], the reflections corresponding to Na₂WO₄, Mn₂O₃, and cristobalite that were observed in the initial phase complex (according to XRD) disappeared; in addition, cristobalite was transformed to quartz and tridymite. However, the yield of C₂ products remained at a level of 16–17% [4, 5]. At the same time, composites containing of 2 wt % Mn and 5 wt % Na₂WO₄/SiO₂ prepared by different methods—silica impregnation, mixing of a

silica sol (silica nanoparticles stabilized in water) with salt solutions (mixture slurry method (MSM)), and sol-gel synthesis (SGS, mixing of homogeneous solutions of silicon, manganese, sodium, and tungsten compounds)—had the same initial phase composition: Na_2WO_4 , Mn_2O_3 , and cristobalite (with an admixture of quartz in the case of MSM). However, the synthesis method had an effect on the results of OCM (820°C , $V = 30 \text{ L g}^{-1} \text{ h}^{-1}$, $\text{CH}_4 : \text{O}_2 = 4 : 1$). The yields of C_2 products were as follows: 20.72 (IM), 19.39 (MSM), and 15.53% (SGS) [6].

The authors of [7] have conducted a comparative study of the properties of two $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ composites prepared by a conventional IM and flame spray pyrolysis (FSP) using a solution of the catalyst components, respectively. Under long-term tests in OCM, the catalysts showed stable values of methane conversion, while the selectivity varied in different ways: it increased and decreased in the case of the IM and FSP samples, respectively. The decrease in the selectivity of the sample was accompanied by a decrease in the specific surface area and the crystallization of amorphous silica to cristobalite, as was found by in situ analysis of XRD patterns.

A composite containing 2 wt % Mn and 5 wt % $\text{Na}_2\text{WO}_4\text{-SiO}_2$, prepared by solid-phase synthesis (SPS, annealing of a dry homogenized mixture of solid salts and silica at 800°C) [8] had the same phase composition as its counterpart prepared by MSM discussed in [6]: Na_2WO_4 , Mn_2O_3 , and cristobalite with an admixture of quartz. During OCM [$900\text{--}910^\circ\text{C}$, $V = 53\text{--}56 \text{ L g}^{-1} \text{ h}^{-1}$, $\text{CH}_4 : \text{O}_2 = (2.7\text{--}3) : 1$], the SPS composite showed a C_{2+} yield of 24%, which decreased to 17% after 40 h. The replacement of Na ions by Li ions (a Li-W-Mn-O-SiO_2 composite prepared by SPS) significantly increased the stability of the catalytic performance in OCM. At the same molar ratio of cations of $\text{Li}(\text{Na}) : \text{W} : \text{Mn} : \text{Si} = 2 : 1 : 2.14 : 91$, during the 100-h OCM (900°C , $V = 57\text{--}60 \text{ L g}^{-1} \text{ h}^{-1}$, $\text{CH}_4 : \text{O}_2 = 2.1 : 1$), the C_{2+} yield over Li-W-Mn-O-SiO_2 preserved a constant value of about 20% [8]. At the same time, according to [9–11], for Li-W-Mn-O-SiO_2 samples prepared by the IM, the C_{2+} yield did not exceed 10–15%. It has been shown [8, 10, 11] that the Li-W-Mn-O-SiO_2 composite differs from composites containing Na, K, Rb, and Cs primarily by the fact that, in the presence of Li^+ , silica largely undergoes crystallization of quartz rather than cristobalite, the presence of which is commonly considered to be responsible for the catalytic activity of $\text{Na}(\text{K, Rb, Cs})\text{-W-Mn-O-SiO}_2$ composites in OCM; however, this assumption has been recently disproved [7]. In addition, note that the polymorphism of Li_2WO_4 [12] and the presence of tungstates Li_6WO_6 [10] and $\text{Li}_6\text{W}_2\text{O}_9$ [12, 13] have been found for Li-W-Mn-O-SiO_2 .

To reveal the causes of changes in the rate of heterogeneously catalyzed reactions, including OCM, during an experiment or from one experiment to another,

it is necessary to take into account many factors, which include the total contact surface accessible to reactants, the fraction of the surface occupied by active sites, the structure and state of these sites, etc.

In this study, the OCM process catalyzed by Li-W-Mn-O-SiO_2 composite materials prepared by the different synthesis methods—SPS, SGS, and IM—using reactants with different chemical nature has been examined. The OCM results are compared to the data on the phase composition of Li-W-Mn-O-SiO_2 composites synthesized by the different methods. The phase composition of the composites after involvement thereof in the OCM reaction has been determined. The features of the phase composition of the Li-W-Mn-O-SiO_2 composites that affect the efficiency of these materials in OCM have been estimated.

EXPERIMENTAL

The studied Li-W-Mn-O-SiO_2 composite materials had a gross ratio of cations of $n_{\text{Li}} : n_{\text{W}} : n_{\text{Mn}} : n_{\text{Si}} = 2 : 1 : 2.14 : 91$.

Sample 1 was prepared by SPS via grinding a mixture of special purity grade amorphous silicon(IV) oxide (Specifications TU 6-09-4901-80), reagent grade lithium carbonate Li_2CO_3 (TU 6-09-3728-83), analytical grade ammonium tungstate $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot n\text{H}_2\text{O}$ (TU 6-09-3924-75), and analytical grade manganese(III) oxide Mn_2O_3 (CAS 1317-34-6) and subsequently calcining the resulting powder in a muffle furnace at 800°C .

Sample 2 was prepared by SPS using reagent grade aerosil A-300 SiO_2 (State Standard GOST 14922-77) as a source of silicon. Sample 3 was prepared also by SPS using analytical grade manganese(II) acetate $(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$ (GOST 16538-79) as a source of manganese. Samples 1 and 2 were homogenized in a ball mill with tungsten carbide balls; sample 3, in a ball mill with porcelain balls.

Samples 4 and 5 were prepared by a method that can be attributed to SGS because the aerosil used as a source of silica was dissolved in ammonia water. Reagent grade aerosil A-300 (GOST 14922-77) was introduced into an aqueous solution of ethanol under vigorous stirring; after that, preliminarily prepared solutions of ammonium tungstate in 8% ammonia water, $\text{Li}(\text{CO}_3)_2$ in special purity grade acetic acid (GOST 19814-74), and manganese acetate in distilled water were sequentially added to the resulting mixture under stirring. The mixture was alkalinized with special purity grade 25.0% ammonia (CAS no. 1336-21-6) to a pH of 8 to dissolve the aerosil. The resulting solution was thoroughly mixed, dried at 80°C , and then heated at 200°C for 4 h and calcined at 800°C for 6 h. The weight of synthesized samples 4 and 5 was 10 g and 4.5 kg, respectively.

Samples 6 and 7 were based on sample 5 prepared by SGS. Sample 6 was prepared from a powder of sam-

ple 5 wetted with an aerosil A-300 solution in ammonia water and pelletized under a pressure of 300 kg/cm². The pellets were calcined in a muffle furnace at 800°C for 6 h. Sample 7 was prepared by a similar technique except that pelletizing was conducted under a pressure of 50 kg/cm².

To prepare sample 8 (combined SGS method), a weighed portion of Li(CO₃)₂ and manganese acetate was dissolved in acetic acid and distilled water, respectively; the solutions were mixed and normalized to a pH of 8–9 by a dropwise addition of ammonia water. Ammonium tungstate was dissolved in an 8% aqueous solution of ammonia under heating. The resulting solutions were poured into a mixture of distilled water and ethanol (a volume ratio of 2 : 1) with suspended aerosil A-300 under vigorous stirring. Ammonia water was added under stirring to adjust the pH value to 8. The resulting solution was evaporated, dried at 80°C, and heated at 200°C for 4 h. The dried product was calcined at 800°C for 6 h. A solution of ammonium tungstate in colloidal silica sol KZ-TM-40 (TU 2145-004-12979928-2001, a 40% SiO₂ slurry in an ammonia medium, a particle size of 21.4 nm, a pH of ~9) was prepared separately; the resulting solution was admixed with a mixture of solutions of Li(CO₃)₂ in acetic acid and manganese acetate in distilled water normalized with ammonia water to a pH of 8–9. After that, the preliminarily synthesized powder was mixed with the resulting solution in amounts providing the desired molar ratio of the elements. The resulting clay-like mass was extruded; the cuttings were dried at 80°C for 1 h, heated at 200°C for 4 h, and calcined at 800°C for 6 h.

Samples 9 and 10 were prepared by the IM. Sample 9 was prepared by the sequential impregnation of special purity grade amorphous silicon(IV) oxide (TU 6-09-4901-80) with aqueous solutions of ammonium tungstate, lithium carbonate, and manganese acetate with intermediate drying at 140°C. The resulting product was calcined at 800°C three times for 6 h each time with intermediate cooling to room temperature and trituration in an agate mortar.

Sample 10 was prepared of silica gel KSKG (GOST 3956-76) treated with steam to prevent cracking and impregnated with an aqueous solution of lithium tungstate prepared from Li₂CO₃ and (NH₄)₁₀W₁₂O₄₁ · nH₂O with subsequent stepwise drying in a desiccator in a temperature range of 90–300°C. The resulting material was impregnated with a manganese acetate solution and stepwise dried in a desiccator in a range of 90–300°C. After that, the material was calcined in a muffle furnace at 800°C for 6 h.

The synthesized samples differed in both the chemical nature of precursors, i.e., sources of Li, W, Mn, and Si cations, and the synthesis method; it will be shown below that this difference had a significant effect on the phase composition and catalytic properties of the composite.

The phase composition of the composites was determined by XRD on a Rigaku MiniFlex 600 diffractometer (CuK_α radiation, λ = 1.54187 Å). The phase composition of the catalysts was determined using the database of the International Centre for Diffraction Data (ICDD).

The specific surface area of the catalysts, which was determined by thermal desorption of argon on a Sorbometr instrument (Katakona, Novosibirsk, Russia), did not exceed 1 m²/g for all the samples; this value could not have a considerable effect on the differences in catalytic activity.

The catalytic properties of the composites in the OCM reaction were examined as described in [8] using a mixture of methane (TU 51-841-87) and special purity grade oxygen (TU 6-21-10-83) that was not diluted with an inert gas.

To conduct catalytic tests, each of the samples prepared in the form of a powder was pelletized using an X-Press 3636 press (Spex Sample Prep., United States) under a pressure of up to 8 ton; the resulting pellets were ground to select a fraction of 0.5–1 mm. The samples prepared in the form of pellets or extrudates were crushed to select a fraction of 0.5–1 mm. The weight of the catalysts was 0.2 g; the bulk density was 0.6 g/cm³.

RESULTS AND DISCUSSION

The table shows the results of OCM using catalysts 1–10 ($T = 860\text{--}930^\circ\text{C}$, $W = 53\text{--}57\text{ L g}^{-1}\text{ h}^{-1}$, CH₄ : O₂ ~ 2 : 1). It is evident from the table that, for the composites prepared by SPS, the yield of the target C₂₊ products (ethylene, ethane, propylene, propane, butenes) decreases in the sequence: sample 1 (17–20%), sample 2 (14–15%), sample 3 (7–10%). The methane conversion and the selectivity for ethylene, which is the most valuable product, decrease in the same sequence. In the case of samples 4–8 prepared by SGS, the C₂₊ yield is approximately the same and varies in a range of 14–21% depending on the conditions of OCM. The methane conversion and the yield of the most valuable product—ethylene—reaching 14–15% differ only slightly from the values for catalyst 1, which is the best in the set of the SPS samples.

The composites prepared by the IM exhibited a low yield of C₂₊ (14–15 and 11% for samples 9 and 10, respectively), while the yield of undesirable CO_x products was significant.

Although the results of OCM for sample 1 (SPS) and the SGS composites were close, the SGS method seems to be more appropriate in terms of technology because it can be more easily implemented at a catalyst factory. Mixing of the solutions and their subsequent drying makes it possible to prepare a properly homogenized material that can be easily shaped by extrusion. The SPS method requires milling of dry reactants, which complicates the homogenization procedure in

Results of OCM in the presence of Li–W–Mn–O–SiO₂ composites

| Sample no., synthesis method | $\frac{\text{CH}_4}{\text{O}_2}$ | $W,$ L/g/h | $T, ^\circ\text{C}$ | Conversion, % | | Selectivity, % | | | | | | Yield, % | | |
|------------------------------------|----------------------------------|---------------|---------------------|-----------------|----------------|-------------------------------|-------------------------------|-----------------|-----------------|----|-----------------|-----------------|-----------------|-------------------------------|
| | | | | CH ₄ | O ₂ | C ₂ H ₄ | C ₂ H ₆ | C ₂₊ | CO ₂ | CO | CO _x | C ₂₊ | CO _x | C ₂ H ₄ |
| 1 SPS | 2.2 | 54 | 864 | 43 | 94 | 33 | 6 | 45 | 19 | 35 | 55 | 19 | 23 | 14 |
| | 1.9 | 57 | 883 | 43 | 93 | 35 | 5 | 46 | 16 | 38 | 54 | 20 | 23 | 15 |
| | 2.0 | 54 | 905 | 43 | 94 | 33 | 3 | 43 | 15 | 42 | 57 | 19 | 25 | 14 |
| | 1.6 | 57 | 921 | 43 | 96 | 31 | 2 | 40 | 14 | 46 | 60 | 17 | 26 | 13 |
| 2 SPS | 2.1 | 54 | 879 | 38 | 86 | 30 | 5 | 40 | 17 | 43 | 60 | 15 | 23 | 12 |
| | 1.9 | 55 | 899 | 40 | 90 | 29 | 4 | 39 | 15 | 46 | 61 | 15 | 24 | 11 |
| | 2.4 | 53 | 913 | 41 | 89 | 27 | 3 | 37 | 14 | 49 | 63 | 15 | 25 | 11 |
| | 1.9 | 54 | 921 | 39 | 93 | 27 | 3 | 37 | 12 | 51 | 63 | 14 | 25 | 11 |
| 3 SPS | 2.0 | 54 | 879 | 18 | 43 | 24 | 13 | 40 | 6 | 53 | 60 | 7 | 11 | 4 |
| | 1.9 | 53 | 894 | 23 | 53 | 25 | 9 | 38 | 6 | 57 | 62 | 9 | 14 | 6 |
| | 2.0 | 53 | 910 | 29 | 64 | 23 | 6 | 33 | 7 | 60 | 67 | 10 | 19 | 7 |
| | 2.1 | 53 | 926 | 34 | 75 | 22 | 5 | 29 | 8 | 64 | 72 | 10 | 24 | 7 |
| 4 SGS | 2.0 | 54 | 886 | 39 | 99 | 34 | 4 | 43 | 14 | 44 | 58 | 17 | 23 | 13 |
| | 2.0 | 54 | 901 | 41 | 99 | 32 | 3 | 42 | 14 | 46 | 60 | 17 | 25 | 13 |
| | 2.0 | 54 | 912 | 42 | 100 | 31 | 2 | 42 | 13 | 48 | 61 | 17 | 26 | 13 |
| | 1.9 | 54 | 920 | 43 | 100 | 30 | 2 | 42 | 13 | 49 | 62 | 18 | 26 | 13 |
| 5 SGS | 2.0 | 56 | 870 | 25 | 74 | 37 | 11 | 55 | 19 | 27 | 45 | 14 | 11 | 9 |
| | 2.0 | 56 | 889 | 44 | 84 | 34 | 7 | 48 | 19 | 33 | 52 | 21 | 23 | 15 |
| | 2.0 | 56 | 911 | 40 | 90 | 26 | 3 | 36 | 16 | 48 | 64 | 14 | 26 | 11 |
| | 1.9 | 55 | 924 | 43 | 95 | 24 | 4 | 37 | 15 | 48 | 63 | 16 | 27 | 10 |
| 6 SGS | 1.8 | 55 | 860 | 32 | 77 | 32 | 7 | 43 | 21 | 36 | 57 | 14 | 18 | 11 |
| | 2.1 | 53 | 884 | 37 | 85 | 31 | 5 | 41 | 20 | 39 | 59 | 15 | 22 | 11 |
| | 2.0 | 54 | 901 | 39 | 91 | 30 | 3 | 39 | 18 | 42 | 61 | 15 | 24 | 12 |
| | 2.1 | 52 | 912 | 42 | 93 | 29 | 3 | 39 | 16 | 45 | 61 | 16 | 26 | 12 |
| 7 SGS | 1.8 | 55 | 860 | 42 | 98 | 30 | 7 | 41 | 21 | 38 | 59 | 17 | 24 | 12 |
| | 1.7 | 55 | 884 | 43 | 98 | 32 | 4 | 42 | 17 | 40 | 58 | 18 | 25 | 14 |
| | 1.8 | 54 | 899 | 47 | 98 | 29 | 8 | 44 | 19 | 37 | 56 | 21 | 27 | 14 |
| | 1.7 | 55 | 919 | 44 | 98 | 31 | 3 | 42 | 14 | 44 | 58 | 19 | 26 | 14 |
| 8 SGS | 1.9 | 55 | 862 | 34 | 82 | 32 | 6 | 42 | 24 | 34 | 58 | 14 | 19 | 11 |
| | 2.0 | 55 | 881 | 39 | 89 | 31 | 4 | 42 | 20 | 39 | 58 | 16 | 23 | 12 |
| | 2.1 | 53 | 902 | 43 | 95 | 30 | 5 | 41 | 18 | 41 | 59 | 18 | 25 | 13 |
| | 1.9 | 53 | 921 | 43 | 98 | 27 | 3 | 39 | 16 | 45 | 61 | 17 | 26 | 12 |
| 9 IM | 2.0 | 54 | 880 | 36 | 83 | 31 | 5 | 40 | 18 | 42 | 60 | 15 | 22 | 11 |
| | 2.0 | 53 | 896 | 38 | 84 | 29 | 5 | 40 | 15 | 45 | 60 | 15 | 23 | 11 |
| | 2.2 | 53 | 908 | 39 | 85 | 28 | 3 | 38 | 13 | 49 | 62 | 15 | 24 | 11 |
| | 2.0 | 53 | 918 | 40 | 89 | 26 | 4 | 36 | 12 | 52 | 64 | 14 | 26 | 10 |
| 10 IM | 2.0 | 54 | 878 | 33 | 79 | 27 | 5 | 35 | 18 | 47 | 65 | 11 | 22 | 9 |
| | 1.8 | 55 | 901 | 39 | 91 | 22 | 2 | 28 | 18 | 53 | 71 | 11 | 27 | 9 |
| | 1.9 | 55 | 920 | 41 | 96 | 18 | 1 | 26 | 9 | 65 | 74 | 11 | 30 | 8 |

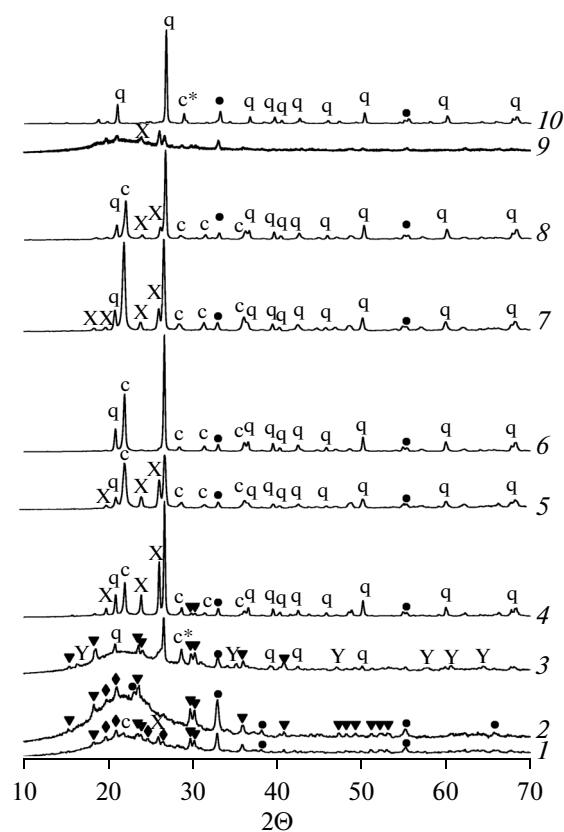


Fig. 1. XRD patterns of Li–W–Mn–O–SiO₂ composite samples (1–10) before OCM. Notations: q, quartz; c, cristobalite; rhomb, rhombohedral Li₂WO₄; inverted triangle, MnWO₄; circle, Mn₂O₃; X—phase based on Li_xWO₃; Y—phase (Al₆Si₂O₁₃).

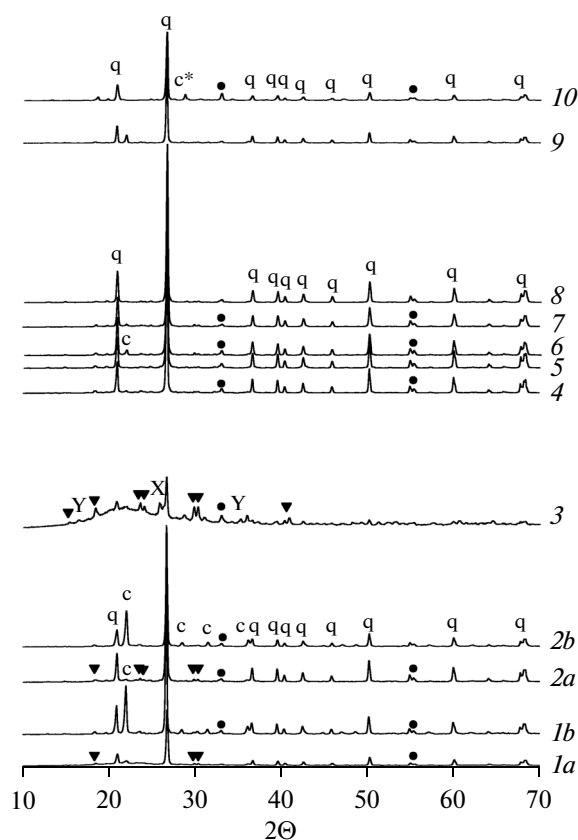


Fig. 2. XRD patterns of Li–W–Mn–O–SiO₂ composite samples (1–10) (1a, 2a, 3) after 5-h OCM and (1b, 2b) after 10-h OCM. Notations are the same as in Fig. 1.

the case of large volumes of loading. Calcination of a dry powder results in the formation of a difficult-to-mold ceramic material. The IM does not seem advantageous either because of a poor catalytic performance of the resulting materials in OCM.

Thus, the data in the table show that, although the composite materials prepared by the different methods have an identical composition, they exhibit different catalytic behavior in OCM. To reveal the causes of this behavior, the phase composition of the composites prepared by the different methods was studied.

The XRD patterns of original (prior to OCM) samples 1–10 are shown in Fig. 1. Comparison of the XRD patterns shows the following.

—SPS samples 1 and 2 comprise uncrystallized silica and phases of hubnerite MnWO₄, bixbyite Mn₂O₃, and rhombohedral Li₂WO₄.

—Sample 3 prepared by SPS differs from samples 1 and 2 by the presence of quartz, hubnerite MnWO₄, bixbyite Mn₂O₃, and an impurity Y-phase, which is displayed as mullite Al₆Si₂O₁₃; the presence of this phase is apparently associated with the grinding of the reactants in a ball mill with porcelain balls.

—SGS samples 4–8 comprise silica crystallized in the form of quartz and cristobalite and contain bixbyite Mn₂O₃ and an X-phase (except sample 6); the last-mentioned phase is not identified either as one of the polymorphous modifications of Li₂WO₄ or as one of tungsten oxides WO₃; apparently, this phase is tungsten bronze Li_xWO₃ [14].

—Sample 9 prepared by the IM is poorly crystallized and contains quartz, cristobalite, bixbyite Mn₂O₃, rhombohedral Li₂WO₄, an X-phase, and traces of hubnerite MnWO₄.

—Sample 10 mostly comprises crystallized quartz and bixbyite Mn₂O₃.

According to the peak bifurcation at 55°C, all the studied samples, except samples 1 and 2, comprise two—cubic and orthorhombic—modifications of bixbyite Mn₂O₃.

Comparison of the XRD patterns of the studied samples after OCM (Fig. 2) to the data in Fig. 1 shows the following.

—Samples 1 and 2 (SPS), during a 5-h OCM, undergo crystallization of silica to quartz (Fig. 2, 1a, 2a); after a 10-h OCM, an appreciable amount of cristobalite is formed (Fig. 2, 1b, 2b).

—Poorly crystallized sample 3 (SPS) remained almost unchanged during OCM. It comprises quartz, hubnerite MnWO_4 , bixbyite Mn_2O_3 , and X- and Y-phases.

—The involvement of samples 4–8 (SGS) and 10 (IM) in OCM has led to the formation of composites containing quartz and bixbyite Mn_2O_3 .

—In initially poorly crystallized sample 9 (IM; Fig. 1, 9), in addition to quartz and bixbyite Mn_2O_3 , cristobalite is formed after OCM.

—In samples 4, 5, 7, and 8, the involvement in OCM leads to the disappearance of the X-phase and the formation of hubnerite MnWO_4 .

Comparing the data of XRD and OCM, we should primarily point out a low efficiency of catalysts 3 (SPS) and 10 (IM) and a relatively low efficiency of catalysts 2 (SPS), 6 (SGS), and 9 (IM). Sample 3, which is the least efficient in the catalysis of OCM and the formation of ethylene, did not form crystalline SiO_2 either before or after catalysis and was characterized by the presence of a stable impurity Y-phase, which probably limits the yield of C_{2+} products.

It should be noted that a specific feature of samples 2 and 9, which exhibit relatively low efficiency in OCM, is that they underwent crystallization only during the catalysis of OCM. However, the same phenomenon is observed in the case of sample 1, which is an efficient OCM catalyst. In general, the initially well-crystallized samples were more efficient in catalysis of OCM; however, sample 10 and, to some extent, sample 6 fall out of this series. These samples, unlike their counterparts that are more efficient in catalysis of OCM, did not contain an X-phase in the initial state prior to the involvement in OCM (Fig. 1). Apparently, the achievement of a maximum yield of C_{2+} products and ethylene is provided by the use of Li–W–Mn–O– SiO_2 composites that comprise well-crystallized phases of SiO_2 and an X-phase apparently attributed to tungsten bronze Li_xWO_3 after synthesis. It should also be noted that, in efficient OCM catalysts prepared by SGS (samples 4, 5, 7, and 8), the cristobalite phase disappears during catalysis because it is transformed to quartz. In the case of less efficient sample 6, this transformation occurs to a lesser extent.

Comparison of the catalytic activity of Li–W–Mn–O– SiO_2 composites with an identical composition prepared by the different methods (SPS, SGS, and IM) in the OCM reaction has shown that the synthesis technique has an effect on the results of OCM. The catalysts prepared by SGS provide a higher ethylene yield of 14–15% in terms of passed methane at $\text{CH}_4/\text{O}_2 = 2$, $W = 50\text{--}60 \text{ L g}_{\text{cat}}^{-1} \text{ h}^{-1}$, and $T = 900\text{--}930^\circ\text{C}$.

It has been shown that the achievement of a maximum yield of C_{2+} products and ethylene is provided by the use of Li–W–Mn–O– SiO_2 composites that comprise well-crystallized phases of SiO_2 (quartz) and a phase attributed to tungsten bronze Li_xWO_3 after synthesis. That is, the degree of homogenization achieved in the synthesis of the samples is responsible for the crystallizability of the catalysts: the use of a SGS technique makes it possible to prepare samples with the highest degree of crystallinity.

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