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STRUCTURE AND STABILITY OF $MnO_x-Na_2WO_4/SiO_2$ CATALYST FOR OXIDATIVE CONDENSATION OF METHANE

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Samples of $MnO_x-Na_2WO_4/SiO_2$ based on a mesoporous silica matrix were synthesized using manganese acetate, sodium tungstate, tetraethoxysilane (TEOS) as precursors and cetyltrimethylammonium bromide (CTAB), citric acid and triethanolamine as pore generating agent and characterized by scanning electron microscopy with energy dispersive elemental analysis (SEM/EDS), X-ray diffractometry (XRD), electron magnetic resonance (EMR), N_2 adsorption-desorption measurements and tested as a catalyst for the reaction of oxidative condensation of methane (OCM). It is shown that the $MnNaW/SiO_2$ catalyst consists of Mn_2O_3 , MnO_2 , Na_2WO_4 and SiO_2 phases. The EMR and SEM/EDS data indicate a noticeable effect of the reaction conditions on the surface structure and the distribution of catalytically active components in the catalyst structure. Significant changes in the values of the specific surface area and pore volume of the samples with increasing temperature and duration of the reaction were found (the values of the specific surface area and pore volume, respectively, 116.8 m^2/g and 0.590 cm^3/g - up to and 46.1 m^2/g and 0.232 cm^3/g after 15 hours of catalyst operation in the OCM reaction at 800 °C). It has been shown that under the conditions of the OCM reaction, the elemental composition of the surface of the $MnO_x-Na_2WO_4/SiO_2$ catalyst changes, and the degree of change depends on the duration of the OCM reaction. Under the influence of the reaction mixture CH_4/O_2 , the content of Mn and W decreases in the first two hours, and the trend towards a decrease in their amount on the catalyst surface with an increase in the duration of the OCM reaction is generally preserved. A detailed X-ray phase analysis also indicates a change in the phase composition of this catalyst under the influence of the CH_4/O_2 reaction mixture. It is assumed that under the reaction conditions (700–800 °C) the $MnO_x-Na_2WO_4/SiO_2$ catalyst is silicon dioxide particles basely with the cristabolite structure, the surface of which is coated with molten sodium tungstate containing nanosized particles of MnO_x structures activated by sodium ions and WO_x .

Keywords: $MnO_x-Na_2WO_4/SiO_2$, surface structure, phase composition, SEM/EDS, XRD, EPR

INTRODUCTION

Over the past 10–15 years, a fairly large number of works have been published on the preparation of $MnNaW/SiO_2$ catalysts, the study of their structural and catalytic peculiarities in the oxidative coupling of methane (OCM). Catalysts of such composition are considered promising catalysts for this reaction [1–4]. At the same time, there are very few studies on the stability of these catalysts and their regeneration. Moreover, the processes that occur with a catalyst during its life cycle are not sufficiently considered, while the history of catalyst preparation, its heat treatment, and reaction conditions can significantly affect the state of the active components of the catalyst and its operation at elevated temperatures [5, 6].

This paper presents the results of studying the effect of the preliminary treatment

temperature of the sample and reaction duration on the morphology, distribution of active elements in the catalyst composition, phase composition, textural, magnetic, and catalytic properties of the $MnO_x-Na_2WO_4/SiO_2$ oxide system in the OCM reaction using scanning electron microscopy combined with elemental analysis (SEM/EDS), X-ray diffractometry (XRD), electron magnetic resonance (EMR), measurement of textural parameters and catalytic activity.

EXPERIMENTAL

Preparation of catalysts and characterization of its structure. The mesoporous silica matrix preliminarily were synthesized, using tetraethoxysilane (TEOS) as precursor and cetyltrimethylammonium bromide (CTAB), citric acid and triethanolamine as pore generating agent. For this purpose the reaction

mixture containing an aqueous solution of surfactant, TEOS and ammonia was kept in a thermostat for several hours at room temperature until mesoporous silica was formed. Then the solution was filtered, the resulting precipitate was washed with distilled water and dried in air at room temperature. Salts of the manganese Mn(CH₃COO)₂·4H₂O and tungsten Na₂WO₄·2H₂O were introduced into the prepared mesoporous silica by impregnating with aqueous solutions of salts. The resulting gel after drying at room temperature was placed in a drying oven and kept at 80–90 °C for 3–4 hours until completely dry. The obtained sample was divided into two part and both parts were calcined in a muffle furnace at 850 and 1000 °C for 2, 4 and 10 hours.

The surface morphology and distribution of active elements on the surface of prepared catalysts were characterized by a Jeol, JSM-6610 LV microscope combined with elemental analyzer, a Rigaku MiniFlex 300/600 X-ray diffractometer and paramagnetic species - by an EMXmicro, Bruker EPR spectrometer. The textural characteristics (specific surface area and total pore volume) of the samples were determined by low-temperature nitrogen

adsorption/desorption on a Belsorp Mini II, BEL, Japan Inc. device.

Catalytic measurements. An integrated microreactor-mass-spectrometer system from Hiden Analytical, UK is used for testing the MnNaW/SiO₂ catalysts in the OCM reaction. This system allowed to carry out the on line measurements up to 1000 °C, identify the gas-phase reaction products, collect the data on the dependences of their concentration in gas-phase products on the reaction conditions (temperature, CH₄/O₂ ratio, contact time, duration) in the range 600–900 °C.

RESULTS AND DISCUSSION

Below the SEM/EDS pictures (Figs. 1, 2) and data on distribution of elements in these catalysts (Tables 1, 2) before and after the OCM reaction are given.

SEM images (Fig. 1) show significant changes in the surface structure of the samples after the reaction. EDS data (Tables 1, 2) indicate the presence of manganese and tungsten and the effect of the reaction mixture on their distribution in the samples, for each cases before and after the reaction Mn/W ratio (atomic %) is >1.

Table 1. EDS data for the sample 0.8Na3.2W2Mn/SiO₂ calcined at 850 °C: *a* – before and *b*, *c*, *d* – after 2, 4, 10 hours of the reaction at 800 °C

	Weight %				Atomic%				Comp.%				Formula
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	
Na K	0.67	0.68	0.78	0.89	0.62	0.62	0.71	0.80	0.91	0.91	1.05	1.20	Na ₂ O
Si K	42.44	42.53	43.08	43.30	31.66	31.83	31.97	32.00	90.80	90.98	92.16	92.64	SiO ₂
Mn K	3.66	2.13	1.98	2.02	1.40	0.81	0.75	0.76	4.73	2.75	2.56	2.60	MnO
W M	2.83	4.25	3.35	2.82	0.32	0.49	0.38	0.32	3.57	5.36	4.23	3.56	WO ₃
O	50.39	50.42	50.80	50.97	66.00	66.25	66.19	66.12					
total	100.00	100.00	100.00	100.00									

Table 2. EDS data for the sample 0.8Na3.2W2Mn/SiO₂ calcined at 1000 °C: *e* – before the reaction and *f*, *g*, *h* – after 2, 4, 10 hours of the reaction at 800 °C

	Weight %				Atomic%				Comp.%				Formula
	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	
Na K	0.59	0.80	0.84	0.70	0.54	0.72	0.77	0.63	0.79	1.07	1.13	0.94	Na ₂ O
Si K	42.43	43.25	42.38	43.52	31.79	32.06	31.73	32.10	90.77	92.53	90.67	93.11	SiO ₂
Mn K	2.56	1.48	2.35	2.18	0.98	0.56	0.90	0.82	3.31	1.91	3.03	2.81	MnO
W M	4.07	3.55	4.10	2.49	0.47	0.40	0.47	0.28	5.13	4.48	5.17	3.14	WO ₃
O	50.35	50.91	50.33	51.11	66.22	66.25	66.14	66.17					
total	100.00	100.00	100.00	100.00									

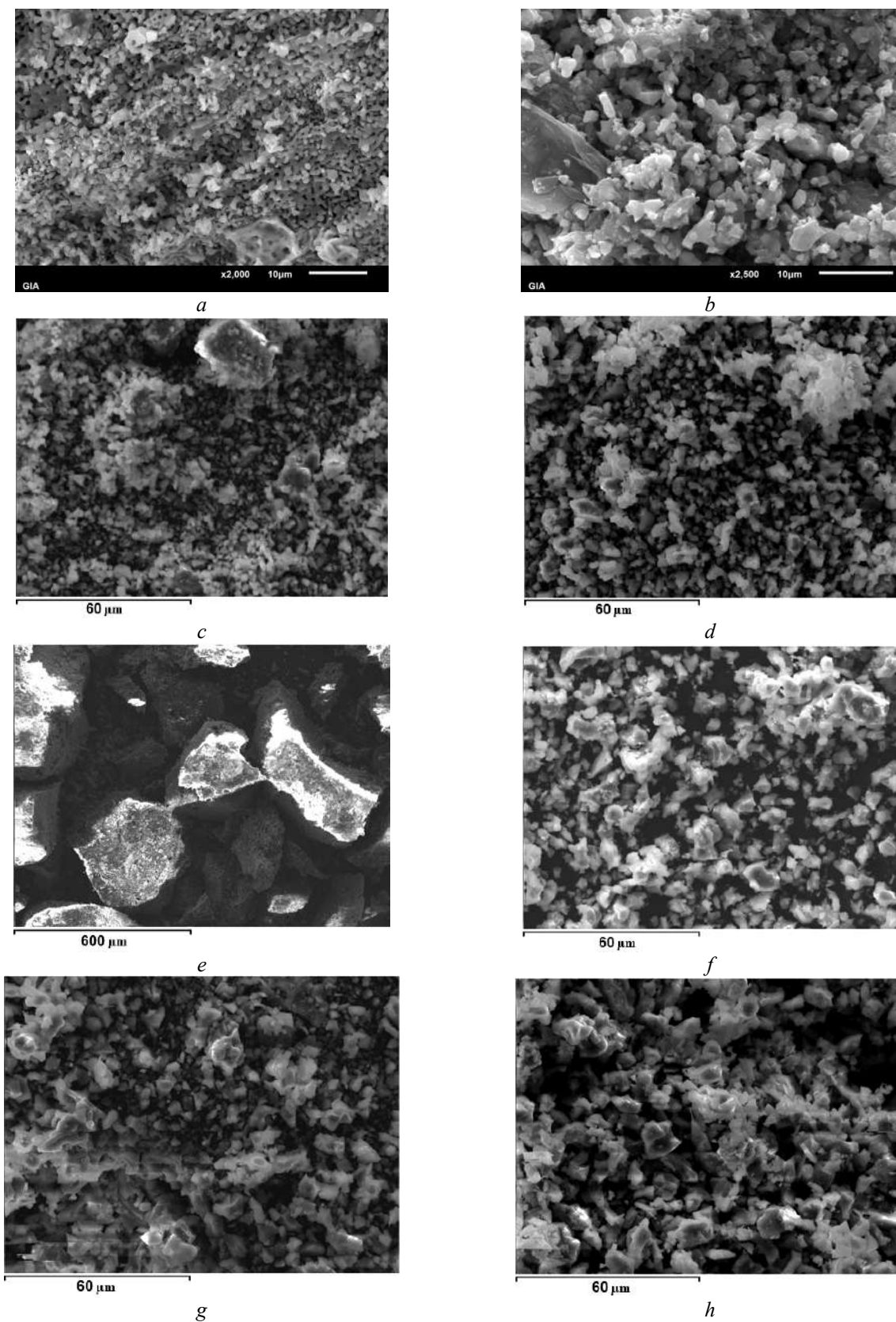


Fig. 1. SEM microphotographs of the samples $0.8\text{Na}_3.2\text{W}_2\text{Mn}/\text{SiO}_2$ calcined at $850\text{ }^\circ\text{C}$: *a* – before and *b*, *c*, *d* – after 2, 4 and 10 hours of the reaction at $800\text{ }^\circ\text{C}$; *e* – calcined at $1000\text{ }^\circ\text{C}$ before the reaction; *f*, *g*, *h* – calcined at $1000\text{ }^\circ\text{C}$ and after 2, 4, 10 hours of the reaction at $800\text{ }^\circ\text{C}$

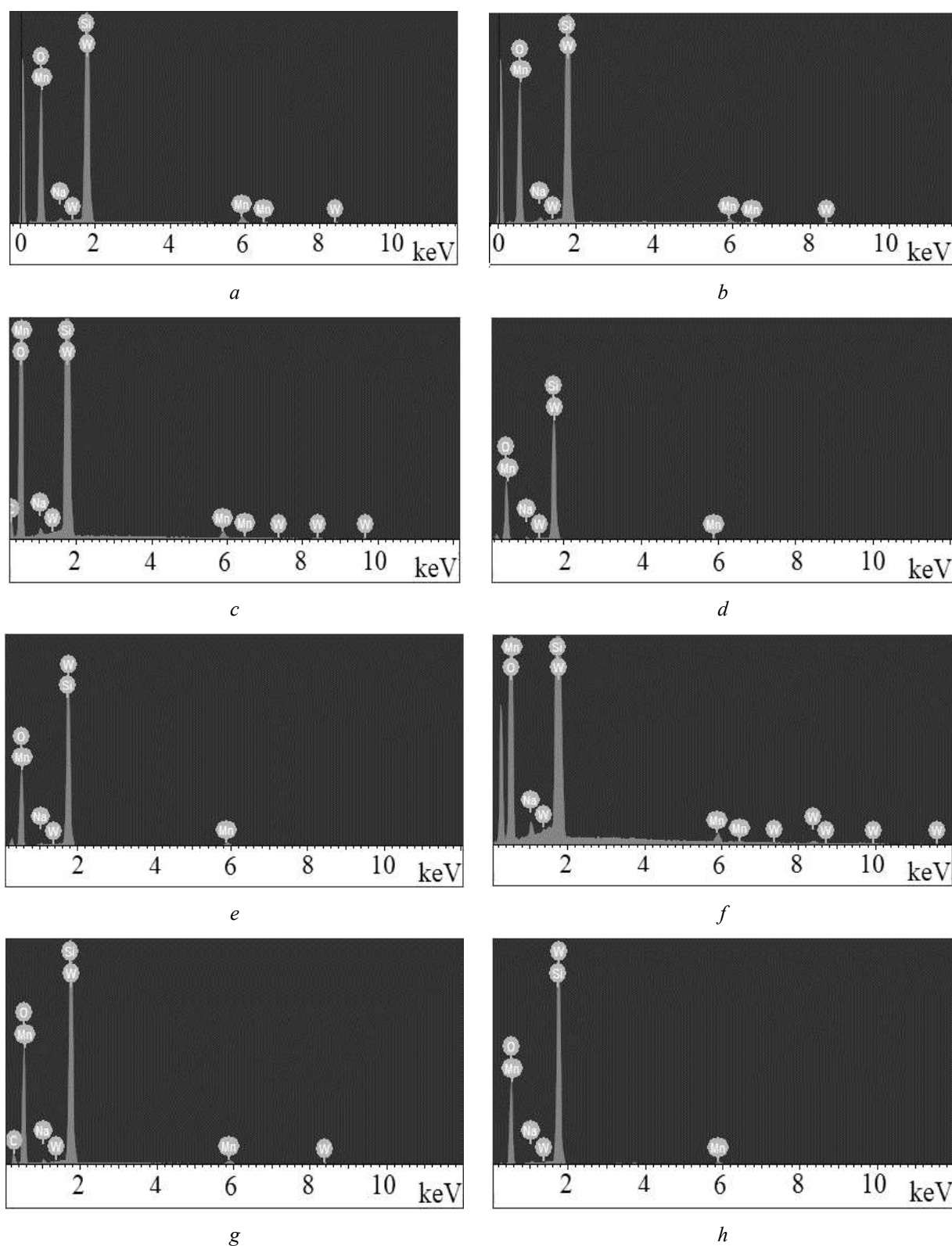


Fig. 2. EDS pictures of the sample $0.8\text{Na}_3.2\text{W}_2\text{Mn}/\text{SiO}_2$ calcined at $850\text{ }^\circ\text{C}$: *a* – before and *b*, *c*, *d* – after 2, 4 and 10 hours of the reaction at $800\text{ }^\circ\text{C}$; calcined at $1000\text{ }^\circ\text{C}$: *e* – before and *f*, *g*, *h* – after 2, 4, 10 hours of the reaction at $800\text{ }^\circ\text{C}$

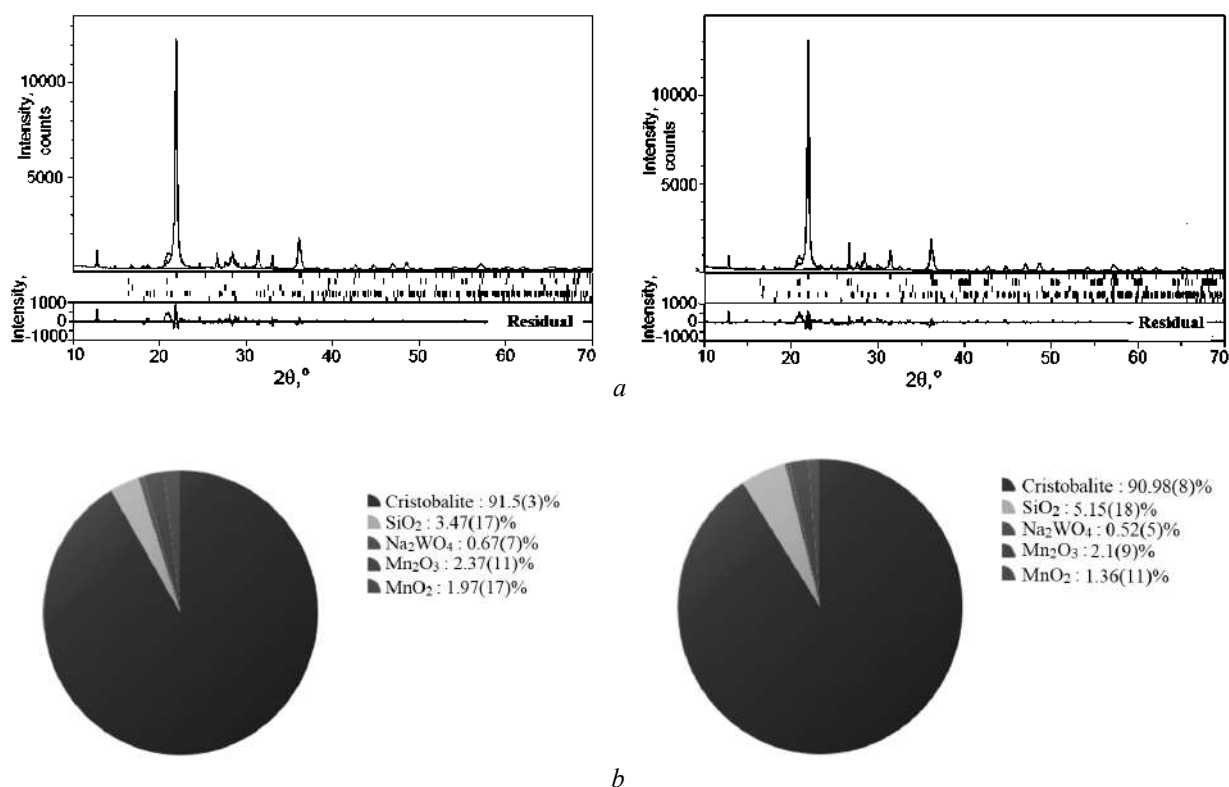


Fig. 3. *a* – X-ray experimental and calculated diffractograms and *b* – WPPF weight fraction of MnO_x-Na₂WO₄/SiO₂ catalyst 1-before, 2-after the reaction at 800 °C

Table 3. Lattice parameters for the sample 0.8Na₃.2W2Mn/SiO₂ calcined at 850 °C: *a* – before and *b* – after 2 hours of the reaction at 800 °C

Phase name	<i>a</i> , Å		<i>b</i> , Å		<i>c</i> , Å		volume, Å ³	
	before	after	before	after	before	after	before	after
Cristobalite	4.98547	4.97781	4.98547	4.97781	6.94837	6.93825	171.982	171.673
SiO ₂	4.91764	4.91292	4.91864	4.91392	5.40881	5.40362	112.824	112.608
Na ₂ WO ₄	9.14307	9.13983	9.14307	9.13983	9.14307	9.13983	763.409	758.869
Mn ₂ O ₃	9.19879	9.57740	9.44003	9.19922	9.58400	9.52055	824.246	777.779
MnO ₂	9.80086	9.78202	9.80086	9.78202	2.81391	2.84241	272.977	272.603

The significant changes of the values of specific surface area and pore volume of samples after 15 hours working in OCM reaction at 800 °C were observed (116.8 m²/g and 0.590 cm³/g before and 46.1 m²/g and 0.232 cm³/g after). Two types of EPR spectra belonging to MnO_x nanoparticles with $g = 2.121$, $\Delta H \sim 1020$ G and $g = 2.040$, $\Delta H \sim 615$ G, before and after the reaction, respectively, were detected [7, 8]. XRD data (Fig. 3, Table 3) show, that the used MnO_x-Na₂WO₄/SiO₂ catalyst consists of Mn₂O₃, MnO₂, Na₂WO₄ and SiO₂

phases. The used Rietveld method allows to evaluate the amount of each registered phases, their lattice parameters.

Catalytic measurements show [3] a decrease in the catalytic activity of the samples by ~ 15 % for 10 hours of catalyst operation at CH₄/O₂ = 4. The used micro-reactor-mass-spectrometer allowed to identify CH₄, O₂, C₂H₆, C₂H₄, C₃H₆, C₃H₈, C₂H₂, H₂O, CO, CO₂ in the gas-phase products. For this samples methane conversion of up to 47.7 % and a selectivity of C₂ and C₃ hydrocarbons in the amount of up to 86.7 % and

a yield of up to 27.4 % were observed. The selectivity ratio $(C_2+C_3)/(CO+CO_2)$ is approximately 1 with a fairly high yield (25.2 %) (C_2+C_3) for sample 1 and slightly more than 1 for sample 2 (for yield) 24.3 %. The ratio of $C_2H_4 / (CO+CO_2)$ is approximately 1 for both samples with the same yield of C_2+C_3 hydrocarbons. An increase in temperature from 778 to 874 °C leads to an increase in ethylene selectivity and the yield of C_2+C_3 hydrocarbons.

It is generally accepted that the activity of the catalyst in the OCM reaction is due to lattice oxygen ions associated with sodium, manganese and/or tungsten ions. The responsibility of which of these lattice oxygen ions of the $MnO_x-Na_2WO_4/SiO_2$ catalyst for its activity and selectivity in the OCM reaction is still a matter of debate. It is natural to assume that under the reaction conditions at a ratio of CH_4/O_2 equal to 4, i.e. in a reducing medium, manganese ions Mn^{3+} and Mn^{4+} in the phases Mn_2O_3 and MnO_2 , respectively, should be reduced to Mn^{2+} ions. However, in the diffraction patterns of the $MnO_x-Na_2WO_4/SiO_2$ catalyst exposed to the reaction mixture at a temperature of 800 °C, only a decrease in the content of these phases present in the samples before the reaction is observed. In this case, the observed EPR spectra for samples $MnO_x-Na_2WO_4/SiO_2$ subjected to this reaction mixture should be attributed to Mn^{2+} ions in highly dispersed, amorphous oxide structures formed during the reduction of Mn_2O_3 and MnO_2 oxide phases present in samples oxidized at 850 °C in air flow before the reaction. A similar assumption - the reduction of tungsten W^{6+} ions present in the catalyst before the reaction to the states W^{4+} and W^{5+} according to the scheme: $W^{6+} \rightarrow W^{4+}$; $W^{6+}+W^{4+} \leftrightarrow 2W^{5+}$). But tungsten ions W^{5+} ($5d^1$ – electronic configuration) are not detected in the EPR spectra in our case, although these ions are easily detected in the EPR spectra, especially those that have a strong $W=O$ bond. Regarding the behavior of sodium ions during the formation of the catalyst, it can be noted that sodium ions most likely activate the MnO_x , WO_x structures, forming alkali-tungsten bronzes $Na_{1-y}WO_3$ and alkali-manganese structures $Na_{1-y}MnO_2$, where $y \ll 1$. However, we did not detect phases of this type in X-ray patterns. We

also assume that the decrease in catalyst activity with an increase in the duration of the OCM reaction may be associated with the formation of volatile tungsten compounds and their removal from the catalyst during its operation. Studies show that at a CH_4/O_2 ratio ≥ 4 , the resulting ethane and ethylene are dehydrogenated to acetylene C_2H_2 , followed by condensation to benzene, toluene and, ultimately, carbon deposits, which may also be one of the reasons for the deactivation of the catalyst in the OCM reaction. Note, as indicated above, the activity of the $MnO_x-Na_2WO_4/SiO_2$ catalyst in the OCM reaction after 10 hours of operation decreases by approximately 15 %.

CONCLUSION

The above results show that under the conditions of the OCM reaction, the elemental composition of the surface of the $MnO_x-Na_2WO_4/SiO_2$ catalyst changes, and the degree of change depends on the duration of the OCM reaction. Under the influence of the reaction mixture CH_4/O_2 , the content of Mn and W decreases in the first two hours, and the trend towards a decrease in their amount on the catalyst surface with an increase in the duration of the OCM reaction is generally preserved. A detailed X-ray phase analysis also indicates a change in the phase composition of this catalyst under the influence of the CH_4/O_2 reaction mixture. There is no clear understanding of the role of the catalytically active structures of the $MnO_x-Na_2WO_4/SiO_2$ oxide system in the OCM reaction. It can be assumed that under the reaction conditions (700–800 °C) the $MnO_x-Na_2WO_4/SiO_2$ catalyst is silicon dioxide particles, the surface of which is coated with molten sodium tungstate containing nanosized particles of MnO_x and WO_x structures activated by sodium ions.

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Структура та стабільність $MnO_x-Na_2WO_4/SiO_2$ каталізатора окиснювальної конденсації метану

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Зразки $MnO_x-Na_2WO_4/SiO_2$ на основі мезопористої кремнеземної матриці були синтезовані з використанням ацетату мангану, вольфрамату натрію, тетраетоксисилану (TEOS) як попередників і броміду цетилтриметиламонію (СТАВ), лимонної кислоти та триетаноламіну як порутворювача, охарактеризовані за допомогою скануючої електронної мікроскопії з енергодисперсійним елементним аналізом (SEM/EDS), рентгенівської дифрактометрії (XRD), електронного магнітного резонансу (EMR), вимірюванням адсорбції-десорбції N_2 і випробувані як каталізатор реакції окиснювальної конденсації метану (ОСМ). Показано, що каталізатор $MnNaW/SiO_2$ складається з фаз Mn_2O_3 , MnO_2 , Na_2WO_4 та SiO_2 . Дані EMR та SEM/EDS свідчать про помітний вплив умов реакції на структуру поверхні та розподіл каталітично активних компонентів у структурі каталізатора. Встановлено значні зміни значень питомої поверхні та об'єму пор зразків зі збільшенням температури та тривалості реакції (значення питомої поверхні та об'єму пор відповідно $116.8 \text{ м}^2/\text{г}$ та $0.590 \text{ см}^3/\text{г}$ – до $46.1 \text{ м}^2/\text{г}$ і $0.232 \text{ см}^3/\text{г}$ після 15 годин роботи каталізатора в реакції ОКМ при $800 \text{ }^\circ\text{C}$). Показано, що в умовах реакції ОКМ елементний склад поверхні MnO_x -каталізатор Na_2WO_4/SiO_2 змінюється, і ступінь зміни залежить від тривалості реакції ОКМ. Під впливом реакційної суміші CH_4/O_2 вміст Mn і W зменшується в перші дві години, причому тенденція до зменшення їхньої кількості на поверхні каталізатора зі збільшенням тривалості реакції ОКМ в цілому зберігається. Детальний рентгенофазовий аналіз також свідчить про зміну фазового складу цього каталізатора під впливом реакційної суміші CH_4/O_2 . Передбачається, що за умов реакції ($700\text{--}800 \text{ }^\circ\text{C}$) каталізатор $MnO_x-Na_2WO_4/SiO_2$ є частинками діоксиду кремнію в основі зі структурою кристаболіту, поверхня яких покрита розплавленим вольфраматом натрію, що містить нанорозмірні частинки структур MnO_x , активованих іонами натрію та WO_x .

Ключові слова: $MnO_x-Na_2WO_4/SiO_2$, структура поверхні, фазовий склад, SEM/EDS, XRD, EPR

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