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Synthesis of Co–Mn catalysts for deep oxidation of CO and propane based on natural opoka by low-temperature combustion

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Abstract. Natural opoka from the Taskalin deposit in the Republic of Kazakhstan was used as a support for Co–Mn catalysts in the deep oxidation of CO and hydrocarbons. After preliminary preparation of the opoka samples by water washing (opoka *I*), calcination at 500 °C (opoka *II*), HCl treatment (opoka *III*), or combined HCl treatment and calcination at 500 °C (opoka *IV*), an active phase (AP) consisting of 5 wt. % Co + 5 wt. % Mn (based on metals) was applied via low-temperature combustion of a metal nitrates and urea mixture. The support and catalyst samples were analyzed using XRD and SEM/EDS, and their specific surface area was measured by the BET method. The primary phases identified in the support and catalyst compositions were various modifications of SiO_2, as well as Na-, Ca-, and Mg-aluminosilicates. Due to their low content, AP components in the form of cobalt oxyhydroxide and potassium manganite were detected only on two of the catalyst samples. According to SEM/EDS data, the original nanoscale honeycomb structures on the opoka surface were almost completely destroyed during opoka processing and after AP application. Elemental composition showed notable variability across different granules of both the support and the catalyst, likely due to the natural structural heterogeneity of opoka. It was established that as the complexity of opoka treatment increased, its specific surface area tripled, from 21.0 to 64.1 m²/g. In contrast, the specific surface area of catalysts based on these opoka samples varied irregularly. Testing of the resulting catalysts in the deep oxidation of CO and propane over a temperature range of 150–540 °C revealed substantial activity, with the best performance observed in the catalyst based on water-washed opoka without further treatment. This sample achieved 100 % CO conversion at *T* = 500 °C and 97 % propane conversion at 540 °C. Thus, natural opoka with minimal processing can serve as an effective support for deep oxidation catalysts for CO and hydrocarbons.

Keywords: opoka, support, low-temperature combustion, Co–Mn catalysts, carbon monoxide, propane, deep oxidation

Синтез в процессе низкотемпературного горения на основе природной опоки Co–Mn-катализаторов глубокого окисления CO и пропана

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Аннотация. Природная опока Таскалинского месторождения Республики Казахстан использована как носитель Co–Mn-катализаторов глубокого окисления CO и углеводородов. После предварительной подготовки ее образцов путем промывки водой (опока *I*), прокалки при температуре 500 °C (опока *II*), обработки HCl (опока *III*) или обработки HCl и прокалки при 500 °C (опока *IV*) на них в процессе низкотемпературного горения смеси нитратов металлов и мочевины была нанесена активная фаза (АФ) состава 5 мас. % Co + 5 мас. % Mn в пересчете на металлы. Образцы носителя и катализатора исследовались методами РФА и SEM/EDS, измерена удельная поверхность по БЭТ. Показано, что основными фазами в составе носителей и катализаторов являются различные модификации SiO_2, а также Na-, Ca- и Mg-алюмосиликаты. Компоненты АФ вследствие их низкого содержания в виде оксогидроксида кобальта и манганита калия были обнаружены только на двух образцах катализаторов. Согласно данным SEM/EDS в ходе обработки опоки и после нанесения АФ исходные наноразмерные сотовые структуры на поверхности практически полностью разрушаются. Имеет место неравномерность элементного состава на поверхности разных гранул как носителя, так и катализатора, связанная, по-видимому, с неоднородностью природной структуры опоки. Установлено, что по мере усложнения обработки опоки ее удельная поверхность монотонно возрастает в 3 раза – с 21,0 до 64,1 м²/г. С другой стороны, удельная поверхность катализаторов на основе этих образцов опоки изменяется нерегулярно. Испытания полученных катализаторов в процессе глубокого окисления CO и пропана в интервале температур от 150 до 540 °C выявили их достаточно высокую активность, причем наилучшие характеристики показал катализатор на основе промытой водой опоки без последующей обработки. На этом образце 100 %-ная конверсия CO была получена уже при *T* = 500 °C, а конверсия пропана при 540 °C достигла 97 %. Таким образом, природная опока с минимальной обработкой может служить эффективным носителем катализаторов глубокого окисления CO и углеводородов.

Ключевые слова: опока, носитель, низкотемпературное горение, Co–Mn-катализаторы, оксид углерода, пропан, глубокое окисление

Introduction

Supported catalysts represent the most widely used class of heterogeneous catalysts. Active phases (AP) are very often deposited on supports made of simple and complex oxides of elements from the main subgroups of the middle of the Periodic Table, such as γ-Al_2O_3, SiO_2 (typically in hydrated form as silica gel), amorphous and crystalline aluminosilicates, and their complexes with oxides of transition and rare-earth metals. Generally, synthetic materials with a fixed set of physicochemical properties are used. However, there remains significant interest in using natural high-porosity materials as supports due to their low cost and environmental friendliness. The primary challenge usually involves standardizing these natural materials since even within a single deposit, their composition and properties can vary considerably.

The literature documents the use of natural minerals such as bentonite clays (specifically montmorillonite), which are hydroxylated nanoscale-layered aluminosilicates, as acid-base catalysts [1], catalyst supports [2; 3], and photocatalysts [4; 5]. Of particular interest is their dehydrated modification – multilayered aluminosilicate nanotubes known as the natural mineral halloysite [6; 7]. Another popular catalyst support in various processes discussed in the literature is

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the highly porous silica rock, diatomite [8; 9]. Closely related to diatomite in composition and properties is opoka – a microporous, high-silica sedimentary rock containing up to 92–98 wt. %[1] SiO_2. It is widely used in construction as a thermal and sound insulation material, and due to its high adsorption, filtration, and ion-exchange properties, opoka is also employed as an adsorbent and filter filler [10–14]. However, there is no information in the literature regarding its use as a support for AP in catalysis.

Deep catalytic oxidation processes are essential for purifying anthropogenic gas emissions and have long been crucial from an environmental standpoint. Additionally, these processes are applied in flameless heat generators, catalytic burners, fuel cells, and gas composition monitoring systems within fire- and explosion-hazardous industries, among others. According to the literature, catalyst development for these applications is advancing rapidly. It is well established that the most effective catalysts for such reactions are those with AP containing noble metals, effective in both CO oxidation [15; 16] and the deep oxidation of hydrocarbons [17–19].

However, aside from their high cost, a major drawback of noble metal catalysts is their low resistance to catalytic poisons (see, for example, [20]). Consequently, a significant focus in the global literature is on developing and researching new catalytic systems based on non-noble transition and rare-earth elements, particularly in nanoscale forms. Among the most active elements in these systems, Co and Mn are often highlighted, both as supported catalysts on various substrates – such as sialon [21], the previously mentioned diatomite [8], γ-Al_2O_3 [22], silica gel modified with aluminum oxide [23], foamed silicalite-1 [24], and nanostructured CeO_2 [25] – and in monolithic complex oxide forms [26–29].

One of the promising methods for producing supported catalysts is the low-temperature combustion method, also known as self-propagating surface thermosynthesis [22; 23; 30; 31]. This method involves impregnating the support with a solution mixture of oxidizers (usually nitrates of active metals) and a reducer or fuel (a water-soluble organic compound), followed by drying and heating the sample to initiate the combustion reaction. This technique offers several advantages over traditional impregnation methods, including low energy consumption, short reaction time, the formation of highly dispersed (including nanoscale) oxide and/or metallic active phases on the pore surfaces of the support, and the absence of harmful gas emissions (typically only CO_2, nitrogen, and water vapor

are released). The low combustion temperature (in our practice, ≤ 360 °C) minimizes the interaction between the AP and the support, preventing particle sintering of the resulting AP.

Previously, using this method, we produced Co-, Mn-, and Ni-containing catalysts on various supports [7; 22; 23], which demonstrated high activity in the deep oxidation of propane and CO.

The aim of this study is to synthesize and examine the physicochemical and catalytic properties of new 5 % Co – 5 % Mn catalyst samples, with the active phase deposited on pre-treated opoka from the Taskalin deposit in Kazakhstan [32] (referred to hereafter as 5Co5Mn/opoka *I–IV*). These catalysts were evaluated in the deep oxidation of propane and CO.

Before applying the AP, the natural opoka samples underwent several preliminary treatment procedures. A common step for all samples was washing to remove impurities of water-soluble salts and easily washable clay contaminants. The purpose of calcination at 500 °C was to burn off organic impurities in the air and to dehydrate the remaining clay impurities. Treatment with HCl solution was performed to remove oxide impurities, complex oxides, and carbonates containing transition metals, primarily iron, as well as alkaline earth metal carbonates. These procedures were applied to different samples to assess the impact of each treatment step.

Research methodology

Before use, all opoka samples were ground to a particle size of 0.1–0.3 mm, washed several times with distilled water, and dried in an oven at 90 °C. The first part (opoka *I*) was set aside without further treatment, the second (opoka *II*) was additionally calcined at 500 °C, the third (opoka *III*) was washed with a 10 % HCl solution and then rinsed with distilled water, while the fourth (opoka *IV*) was also washed with a 10 % HCl solution, rinsed with distilled water, and then calcined at 500 °C.

The prepared supports, each weighing 5 g, were impregnated with a solution mixture of metal nitrates $(Co(NO_3) \cdot 6H_2O + Mn(NO_3)_2 \cdot 6H_2O)$ and urea, with concentration ratios calculated to yield the pure metals. The sample was dried at 90 °C and placed in a flat-bottomed quartz tube reactor, sealed with a dust collection system and purged with argon. The heater at the bottom of the reactor was turned on, and its power remained constant throughout the process. Temperature was monitored by a thermocouple placed in the sample layer at the center of the reactor. After the reaction and cooling, the sample in the argon-filled reactor was

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[1] All percentages are by weight (wt. %) unless otherwise indicated.

stabilized with a 5 % H_2O_2 solution to prevent spontaneous ignition of any highly dispersed metallic phases in the active phase. The sample was then washed with distilled water and dried at 90 °C. Particles smaller than 0.1 mm were removed from the resulting catalyst. The setup and synthesis procedure were previously described in detail [22; 23].

X-ray diffraction analysis (XRD) of the samples was conducted using a DRON-3M diffractometer (Russia) with FeK_α radiation.

The morphology and elemental composition of the catalyst surfaces were examined with a high-resolution field-emission scanning electron microscope, the Zeiss Ultra Plus, based on the Ultra 55 platform (Carl Zeiss, Germany), equipped with an INCA Energy 350 XT microanalysis system from Oxford Instruments. The specific surface area was measured through nitrogen physical adsorption by the BET method on an apparatus designed according to GOST 23401-90.

The obtained samples were tested on a catalytic setup with a flow-through quartz reactor containing a fixed bed of catalyst (1 cm³ of 0.1–0.3 mm fraction). Analysis of the initial gas mixture and reaction products from deep oxidation was conducted using a 5-component gas analyzer, Avtotest 02.03P, with zero-class accuracy (Meta, Russia). The initial gas mixture had the following composition by vol. %: propane – 0.15, CO – 0.6, O_2 – 1.6, nitrogen – up to 100 %. The gas flow rate was 120,000 h⁻¹. Experiments were carried out within a temperature range from 150 to 540 °C in 50 °C intervals. CO and propane conversions during deep oxidation were calculated using the formula

$$X_{R.T} = \frac{C_{R,0} - C_{R,T}}{C_{R,0}} 100 \text{ %},$$

where $C_{R,0}$ and $C_{R,T}$ are the concentrations of the reactant (CO or propane) in the initial gas mixture and at the reactor outlet at temperature T, respectively, vol. %.

Results and discussion

Fig. 1 shows thermograms of the catalyst synthesis process on opoka samples prepared as described above. The self-ignition temperatures (T_S) at the start of the combustion wave and the maximum temperatures (T_{max}) within the combustion wave were recorded. As shown, the T_S values for samples on opokas *I* and *II* are nearly identical, though the T_{max} on opoka *II* is noticeably higher. The highest self-ignition (192 °C) and combustion (322 °C) temperatures were recorded during synthesis on sample *III*. Secondary peaks at lower temperatures, likely corresponding to the afterburning wave, were observed on opokas *I–III*. This phenomenon was also noted in our previous synthesis of a similar AP-based catalyst on γ-Al_2O_3 [22]. Synthesis on opoka *IV* proceeded in a low-intensity mode, with minimal T_S and T_{max}.
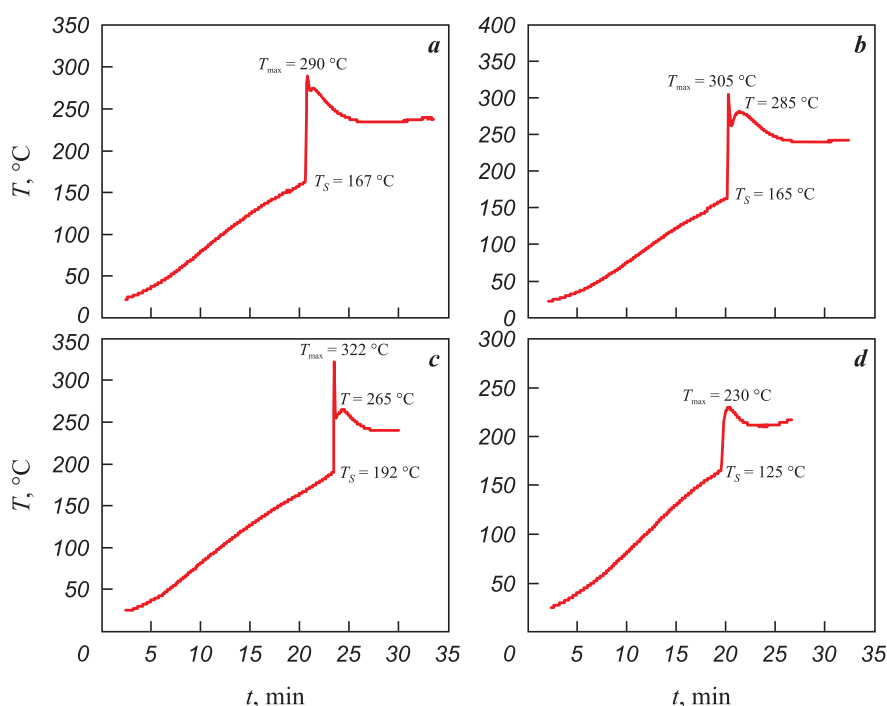
Fig. 1. Thermograms of the synthesis process for catalysts 5Co5Mn/opoka *I* (***a***), *II* (***b***), *III* (***c***), and *IV* (***d***)

Рис. 1. Термограммы процесса синтеза катализаторов 5Co5Mn/опока *I* (***a***), *II* (***b***), *III* (***c***), *IV* (***d***)

XRD patterns of the prepared supports and their corresponding catalysts are shown in Figs. 2 and 3. Notably, opoka samples *I* and *II* contain complex oxide impurity phases of iron and magnesium, which disappear after HCl treatment (see Fig. 2). The primary phases present are various modifications of SiO_2, along with Na-, Ca-, and Mg-aluminosilicates, with a significant portion of amorphous phases also observed.

As shown in Fig. 3, Co- and Mn-containing APs appeared only on two catalyst samples – those based on opokas *I* and *III*, and separately: in sample *I*, likely as trivalent Co oxyhydroxide, and in opoka *III* as potassium manganite. This likely results from the low AP component content, which is near the detection limit of the XRD analysis. Aluminosilicate phases were preserved only in samples based on opokas *I* and *II*, while in samples with supports *III* and *IV*, the amount of silica phase modifications increased.

The morphology and surface elemental composition of supports *II* and *IV*, as well as the catalyst based on opoka *II*, were studied using SEM/EDS. The results are shown in Figs. 4–6.

It can be noted that a characteristic feature of the support granule surfaces, both before (Fig. 4) and after (Fig. 5) acid washing, is the presence of nanoscale honeycomb structures with wall thicknesses of ≤ 50 nm, which are clearly visible in Fig. 4. After HCl treatment and calcination, the honeycomb walls appear to melt and thicken noticeably (Fig. 5), though only the application of AP almost completely destroys these formations (Fig. 6). Only isolated elements of the honeycomb structures remain. Notably, as the sample treatment procedures become more complex (opoka *I* → opoka *II* → opoka *III* → opoka *IV*, followed by AP application), the morphology of the support and catalyst granule surfaces takes on an increasingly fragmented, amorphous appearance.

Elemental microanalysis data show significant variability in the element content across individual granules of both the supports and the catalyst. This applies not only to impurity elements but also to the primary structural elements (Si, Al). This variability may be related to the structural heterogeneity of natural minerals, as noted above. Some samples show detectable
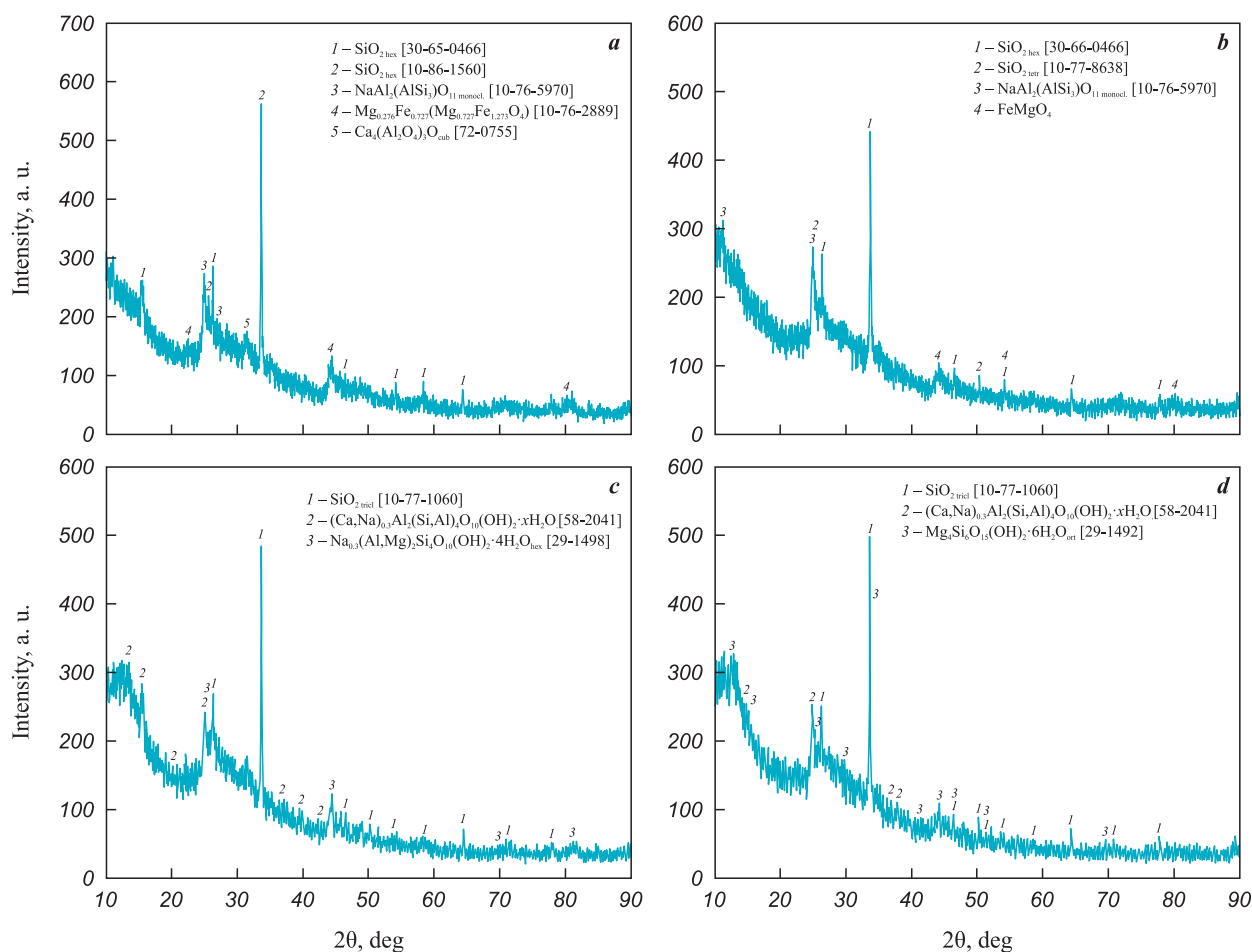

Fig. 2. XRD patterns of support samples opoka *I* (**a**), *II* (**b**), *III* (**c**), and *IV* (**d**)

Рис. 2. Рентгенограммы образцов носителя опок *I* (**a**), *II* (**b**), *III* (**c**), *IV* (**d**)

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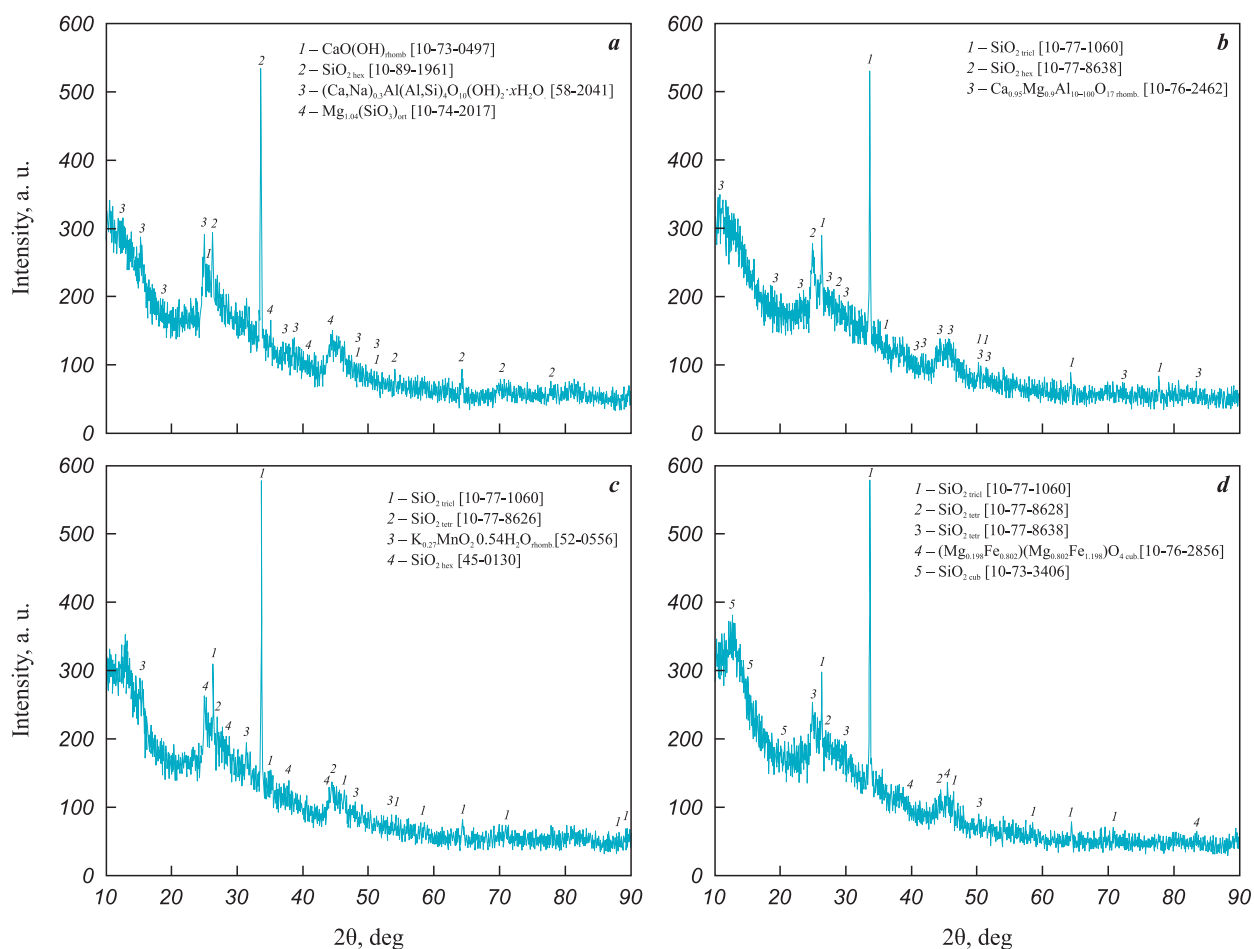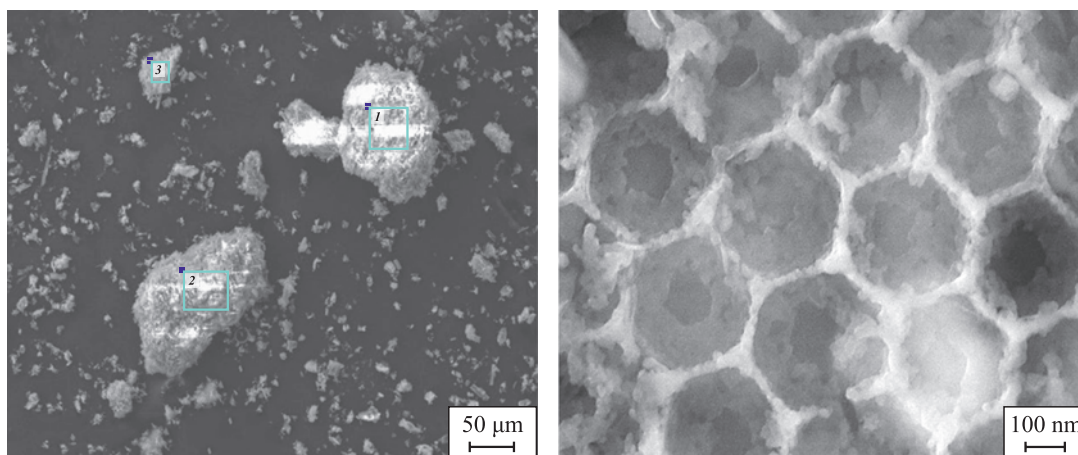
Fig. 3. XRD patterns of catalysts 5Co5Mn/opoka *I* (*a*), *II* (*b*), *III* (*c*), and *IV* (*d*)

Рис. 3. Результаты РФА образцов катализаторов 5Co5Mn/опока *I* (*a*), *II* (*b*), *III* (*c*), *IV* (*d*)

Area	Element content, wt. %						
	O	Na	Mg	Al	Si	K	Ca	Fe
1	58.18	0.14	0.83	8.68	28.18	1.29	0.42	2.30
2	57.39	0.10	0.82	8.50	28.71	1.59	0.14	2.77
3	65.16	0	0.66	6.31	25.61	0.88	0.08	1.32
Average	60.24	0.08	0.77	7.83	27.50	1.25	0.21	2.13

Fig. 4. Surface morphology of opoka *II* sample (SEM) and elemental composition at marked points

Рис. 4. Морфология поверхности образца опоки *II* (СЭМ) и элементный состав в отмеченных областях
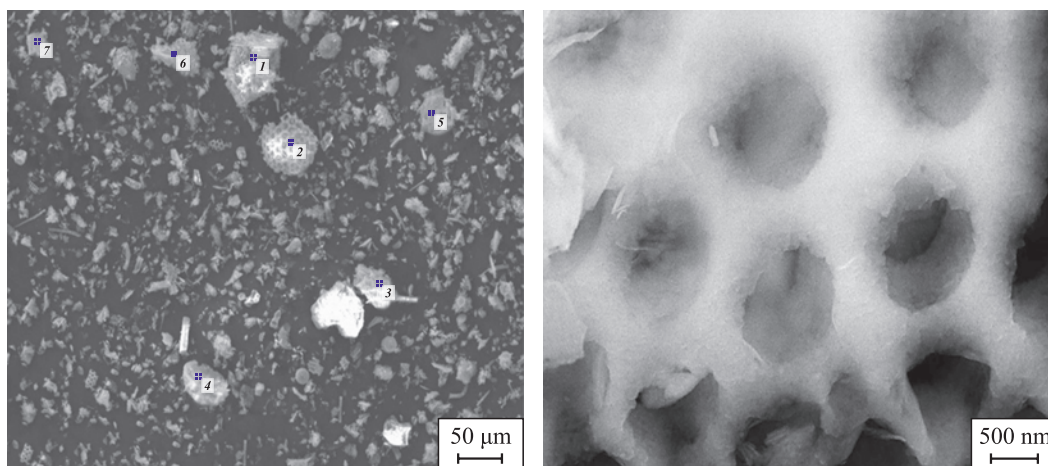
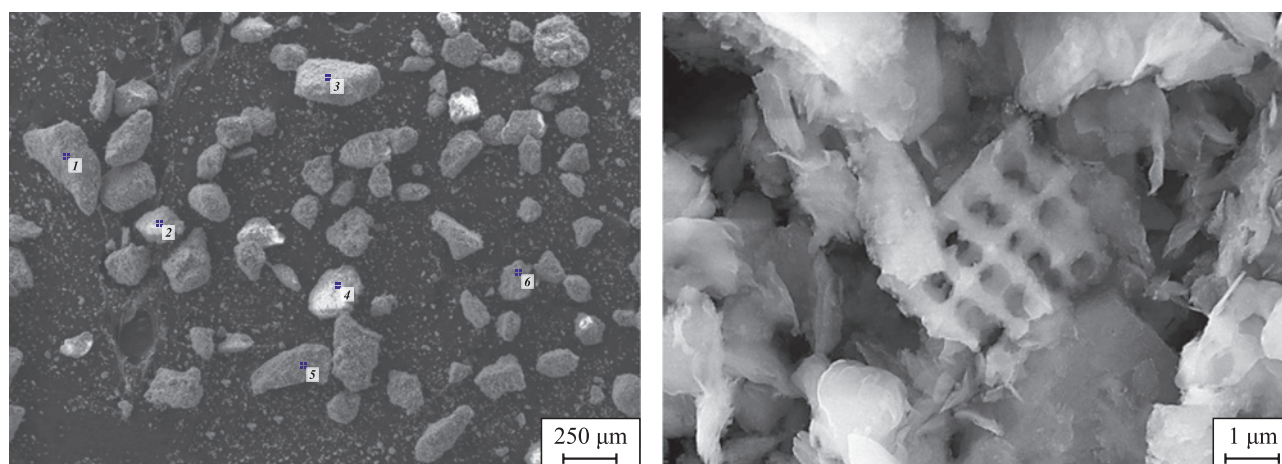| Point	Element content, wt. %						
	O	Mg	Al	Si	K	Ti	Fe
1	62.65	0.29	3.04	10.58	0.15	22.59	0.70
2	57.52	0.42	4.58	35.79	0.69	0.21	0.78
3	65.74	0.12	5.19	22.04	1.78	0.75	4.41
4	70.59	0.25	2.87	25.39	0.46	0.06	0.40
5	76.34	0.18	2.98	19.91	0.28	0.03	0.28
6	64.15	0.61	9.21	23.07	1.05	0.32	1.59
7	61.48	0.06	0.90	37.29	0.11	0	0.16
Average	65.50	0.28	4.11	24.87	0.64	3.42	1.19

Fig. 5. Surface morphology of opoka *IV* sample (SEM) and elemental composition at marked points

Рис. 5. Морфология поверхности образца опоки *IV* (СЭМ) и элементный состав в отмеченных точках

Point	Element content, wt. %								
	O	Mg	Al	Si	K	Ti	Mn	Fe	Co
1	64.39	0.50	4.56	26.05	0.34	0.07	1.50	0.84	1.73
2	38.39	0.99	0.35	35.77	1.86	0.57	5.55	3.39	5.12
3	14.66	0	21.22	3.54	0.19	0	17.19	21.98	21.23
4	5.05	0.83	3.66	47.53	1.61	3.20	16.08	5.90	16.15
5	36.58	0.74	7.40	30.93	1.63	0.17	9.03	4.46	9.05
6	55.00	0.89	7.40	24.52	0.79	0.23	4.38	1.63	5.14
Average	35.68	0.66	7.43	28.06	1.12	0.71	8.96	6.35	9.68

Fig. 6. Surface morphology of the 5Co5Mn/opoka *II* catalyst sample (SEM) and elemental composition at marked points

Рис. 6. Морфология поверхности образца катализатора 5Co5Mn/опока *II* (СЭМ) и элементный состав в отмеченных точках

amounts of titanium, which does not appear in XRD, likely due to its low concentration, even if present in compound form. Conversely, magnesium, which constitutes a fraction of a percent on the surface, is consistently detected in the form of magnesium silicate on diffractograms, particularly for the opoka *IV* sample (see Fig. 2, *d*). The application of AP to the opoka *II* sample resulted in a noticeable reduction in oxygen content on its surface (compare the data in the Tables in Figs. 4 and 6), even considering that the surface was stabilized with a hydrogen peroxide solution after synthesis. It can be assumed that a portion of weakly bonded oxygen on the support surface reacted during the combustion process when the AP was applied. Significant variations in Co and Mn concentrations on the catalyst granule surfaces are also observed, both in absolute terms and in their relative ratios. This variability likely stems from the structural heterogeneity noted earlier, especially in the number of open pores, where the AP precursor solution penetrates through capillary action prior to synthesis.

The specific surface area (S_{sp}) of certain support and catalyst samples, determined by the BET method, is shown below, in m²/g:

Opoka *I* 21.0
Opoka *II* 42.0
Opoka *IV* 64.1
5Co5Mn/opoka *I* 40.6
5Co5Mn/opoka *II* 29.5
5Co5Mn/opoka *IV* 62.8

A distinctive feature of the support treatment process is evident: as the treatment becomes more complex, the specific surface area of the samples increases, likely due to the exposure of an increasing number of fine pores. However, the application of the AP has varying effects on this value. As can be seen, the catalyst based on opoka *I* has twice the specific surface area S_{sp} of the initial support. Conversely, for the catalyst based on opoka *II*, this trend is reversed, while for the 5Co5Mn/opoka *IV* sample, there was almost no change. This may indicate differences in the dispersion of the AP formed during synthesis, depending on the surface morphology and, to some extent, the elemental composition of the different support samples.

A series of catalysts based on treated opoka was tested in the deep oxidation of propane and CO. The results are shown in Fig. 7. According to these data, the opoka-based catalysts demonstrated fairly high activity in both CO oxidation and propane deep oxidation. In the first case, 100 % CO conversion was achieved at 500 °C on the 5Co5Mn/opoka *I* catalyst (Fig. 7, *a*), with its activity being higher across
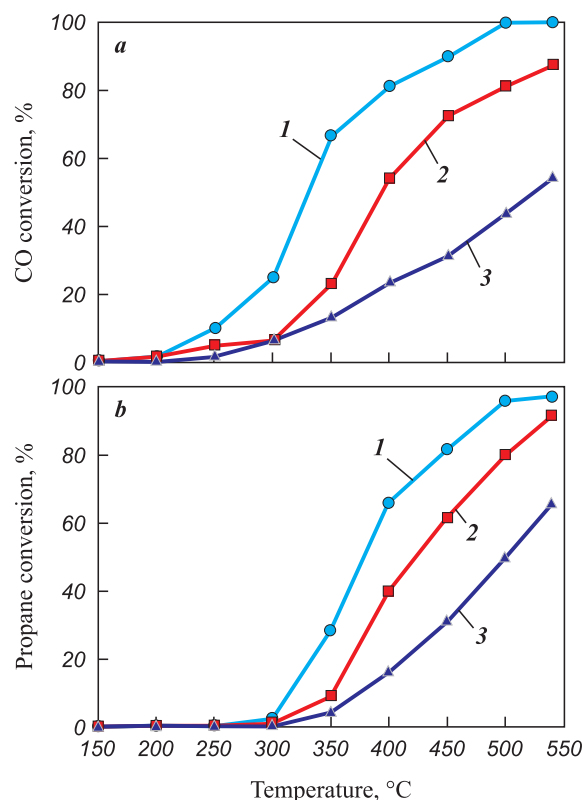

Fig. 7. Temperature dependences of CO (***a***) and propane (***b***) conversions on catalyst samples
1 – 5Co5Mn/opoka *I*, ***2*** – 5Co5Mn/opoka *II*, ***3*** – 5Co5Mn/opoka *IV*

Рис. 7. Зависимости конверсий СО (***a***) и пропана (***b***) от температуры на исследуемых образцах катализаторов
1 – 5Co5Mn/опока *I*, ***2*** – 5Co5Mn/опока *II*, ***3*** – 5Co5Mn/опока *IV*

the entire temperature range. In the second case, this same catalyst achieved a propane conversion of 97 % at 540 °C (Fig. 7, *b*). The sample based on opoka *IV* showed the lowest activity in these processes, despite having the highest specific surface area among the samples. It should be noted that for the 5Co5Mn/opoka *II* and 5Co5Mn/opoka *IV* samples, propane conversion in the high-temperature region (≥ 500 °C) exceeded CO conversion.

Conclusion

For the first time, catalysts with a CoMn active phase (5 % + 5 % based on metals) on differently treated opoka were obtained using the low-temperature combustion method with mixtures of Co and Mn nitrates and urea. XRD analysis showed that, following acid treatment and subsequent calcination, iron-magnesium complex oxide impurities are removed from the opoka samples, with the main phases being various modifications of silica, along with Na-, Ca-, and Mg-aluminosilicates, and a significant proportion of amorphous phases.

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SEM/EDS analysis of the morphology and surface elemental composition of the supports and catalyst revealed degradation of the initial nanoscale honeycomb structures as opoka processing became more complex, with further degradation upon AP application. A significant variability in elemental content among individual granules of both supports and catalysts was observed, likely due to the structural heterogeneity of this natural mineral.

The specific surface area of the support samples increased with more complex processing steps, but the surface area of the catalysts varied non-monotonically. Testing of several catalysts showed the activity order in the deep oxidation of both CO and propane as follows: 5Co5Mn/opoka *I* > 5Co5Mn/opoka *II* > 5Co5Mn/opoka *IV*, with CO conversion reaching 100 % at 500 °C and propane conversion reaching 97 % at 540 °C on the 5Co5Mn/opoka *I* sample. The sample based on opoka *IV* demonstrated the lowest activity in these processes, despite having the highest specific surface area among the catalysts studied (62.8 m^2/g).

Thus, natural opoka with minimal processing can serve as an effective support for deep oxidation catalysts for hydrocarbons and CO.

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