

TEXTURAL AND CATALYTIC FEATURES OF SILICON SURFACE
MODIFIED WITH ZnO IN THE REACTION OF HOMOGENOUS-
HETEROGENEOUS ACTIVATION OF PROPANE-OXYGEN
MIXTURES AT LOW PRESSURES

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The textural and catalytic characteristics of the surface of silica gel modified with zinc oxide by the sol-gel method and by means of a chemical transport reaction (CTR) have been studied. It was found that catalytic activity of the obtained contacts depends on both the nature and the structural and textural characteristics of the supported ZnO. Using the example of the reaction of low-temperature oxidation of propane, it was found that lower limit of the release of radicals from the surface into the volume with the CTR modification method is lower by 15–20 degrees than in the case of the sol-gel method. It was shown that the catalyst obtained by applying the active phase on the surface of the support by the CTR method is more efficient due to the energy homogeneity of its active centers and the texture characteristics of the surface.

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Introduction. The choice of optimal conditions for the deposition of ultrafine particles of metals or their oxides on the surface of solid porous supports is one of the urgent problems of heterogeneous catalysis [1, 2]. This is mainly due to the fact, that often the catalytic activity of the active phase deposited on a porous base, along with its chemical nature, is also a function of its structural and textural characteristics. Therefore, the search for new ways to obtain highly efficient heterogeneous catalysts does not lose its relevance for a long time [3].

It is known that ZnO is widely and successfully used in catalytic processes such as dehydrogenation, dehydration, addition and decomposition of substances that pollute the environment. Unique piezo- and pyroelectric effects, adsorption and reactions of gases on the surface of sorbents with deposited ZnO occupy a special place [4, 5]. Due to these properties, special attention is paid to the study of the

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properties of ZnO deposited on the surface of various porous carriers by various methods: aerosol pyrolysis, gas deposition, sol-gel, etc. [6].

One of the new and highly effective methods for modifying the surface of aerosil [7] and silica gel [8] with metal oxides is the chemical transport reaction (CTR). For example, the high catalytic activity of copper oxide deposited on the surface of solid supports by the CTR method was demonstrated in [8]. It was shown in [7, 9] that, when the surface of silica gel is modified by ZnO using the CTR method, the active component ZnO is predominantly deposited in the pores of the support with sizes of 80–100 Å.

This work presents some results of studying the structural, textural and heterogeneous catalytic characteristics of zinc oxide deposited on the surface of porous silica by the sol-gel and CTR methods. By the example of low-temperature oxidation of propane, the process of peroxide radicals release from the surface of solid contacts into the bulk is studied, depending on the structural and textural characteristics of the deposited ZnO.

Experimental Part. Highly dispersed ultrapure silica SiO₂ («Sigma Aldrich» trademark), 40% aqueous solution of hydrogen peroxide (chemically pure grade), surfactant dodecyl chloride, propane and oxygen with purity of 98.5% and 99%, respectively, were used as carriers of the active phase. Chromatographic analysis was carried out on a column packed with Chromaton with an OV-17 applied liquid phase. Column length is 2 m, diameter is 2 mm, carrier gas is nitrogen, carrier gas velocity is 25 mL/s, temperature is 433 K, flame ionization detector. The texture parameters and surface morphology of the initial and obtained by different methods samples were studied both directly by adsorption gravimetric methods and by means of scanning electron microscopy (SEM) analysis.

Preparation of Catalysts. A tablet of samples weighing about 0.1 g and dimensions 1×1×0.1 cm³ was prepared by pressing high-purity silica gel under a pressure of 1500 kg/cm². Then, zinc oxide was applied to the obtained tablets by two methods. In the first case (catalyst 1), ZnO fine powder was mixed with a 40% aqueous solution of hydrogen peroxide and kept at a temperature of 40°C for 8 h, that yielded ZnO₂. Then, according to the method described in [9], the surface of preliminarily prepared SiO₂ tablets was treated with an alcohol suspension in the presence of dodecyl chloride surfactant. The tablets were dried at a temperature of 600 K in a nitrogen flow. In this case ZnO₂ decomposes into ZnO on the surface.

The catalyst 2 was obtained by low-temperature deposition of ZnO on the surface of silica pellets using CTR of the ZnO/H₂O₂ complex according to the procedure described in [7]. In both cases described the content of the active ZnO phase deposited on the silica surface was about 5 mg/g.

Experiments to detect and study the qualitative and quantitative characteristics of radicals were carried out on a flow-through vacuum installation. A cylindrical quartz reactor 16 cm long and 1.5 cm in diameter was installed in an electric furnace, the temperature of which was controlled with a KVP-503 thermostat. The accuracy of maintaining the temperature was 0.5 degrees. The radicals released into the bulk were studied by the kinetic method of freezing radicals on an SE/X-2543 radio spectrometer in the range of 3000–4000 Oe at a frequency of $\nu = 9.39$ GHz, according to the method described in [10].

Two tablets of the test sample were placed vertically on a quartz grid parallel to each other at a distance of 5 mm. The reaction mixture passed through the reactor with the catalyst and was directed to the finger-like branch of the Dewar vessel with liquid nitrogen. The latter was in the resonator of the EPR radio spectrometer. The experiments were carried out with mixtures $P_{C_3H_8}:P_{CO_2}:P_{O_2} = 1:1:0.1$. The pressure of the mixture in the reaction zone was 0.05 Torr.

Results and Discussion. The treatment of the surface of silica with gaseous products of CTR ZnO/H₂O₂ leads to a significant change in its structural parameters, which is due to the formation of a secondary texture on the surface of the initial sorbent [7]. As a result, the specific surface area decreases by 15 m²/g, while the specific pore volume, on the contrary, increases by 0.042 cm³/g. In addition to changes in these basic texture parameters, there is also a significant change in the fractal dimension of the surface, which was determined based on calculations of the adsorption isotherms of N₂, CHCl₃, C₆H₆, *n*-hexane and cumene on the corresponding samples, using the Brunauer–Emmett–Teller multilayer adsorption equation.

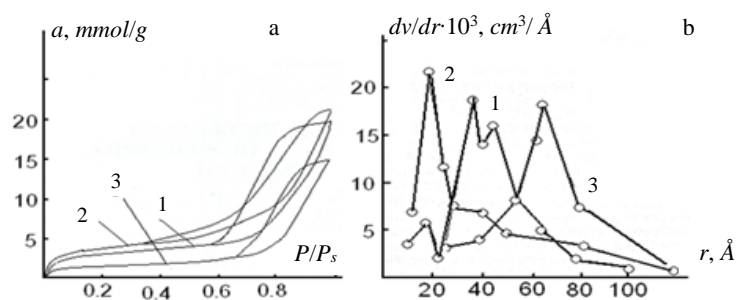


Fig. 1. Isotherms of low-temperature nitrogen adsorption (a) and pore distribution curves (b) by size for the initial (1) and treated with gaseous products of CTR ZnO/H₂O₂ of silica samples for 6 h (2) and 30 h (3).

Fig. 1 shows nitrogen adsorption isotherms (a) and pore size distribution curves (b) for the initial silica and that of obtained after treatment with gaseous ZnO/H₂O₂ by the CTR method. It follows from these data that as a result of modification, the surface texture of the initial silica changes greatly. This is expressed not only in a decrease in the value of the relative vapor pressure of the adsorptive, corresponding to the onset of capillary condensation, but also in a change in the type of the hysteresis loop. Moreover, at the initial stages of modification a decrease in the pressure of the onset of capillary condensation is observed, which indicates the decomposition of the modifier in relatively large pores. Further increase in the treatment time of the CTR with gaseous ZnO/H₂O₂ leads to the opposite picture – a shift of the onset of capillary condensation towards higher adsorptive pressures. Apparently, this is due to the fact that during long-term CTR-processing of silica, some pores are closed, while the size of others decreases or they change their shape, i.e. the surface is structurally modified. This is also evidenced by data on the pore size distribution (Fig. 1, b). At the first stage of treatment (6 h), a shift in the distribution maximum from 40 to 20 Å is observed. Further increase in the time of modeling (up to 30 h) leads to a shift of this maximum towards larger pore sizes (70 Å). Based on the pore size distribution curves, it can be concluded that, as a result

of the decomposition of the gaseous products of ZnO/H₂O₂ on the silica surface, the texture parameters change not only due to a change in the pore morphology, but also due to the formation of a new ZnO texture to the top. However, given the small amounts of ZnO deposited on the silica surface, it can be assumed that structural changes on the silica surface are mainly due to the blocking of some slot-like and bottle-shaped pores, which is the main reason for the decrease in the specific surface area. Apparently, a change in the chemical nature of the surface also plays a certain role in this process. This assumption may be evidenced by the change in the sorption capacity (S_{ssa} , specific surface area) of silicon-earth sorbent during its modification (Tab. 1).

Table 1

Time dependence of changes in texture parameters of treatment with gaseous products of ZnO/H₂O₂

t, h	$S_{\text{ssa}}, m^2/g$, for different adsorptives					$V_{\text{sp}}, cm^3/g$, by N ₂	D , fractal dimension
	N ₂ , 16.2 Å ²	CHCl ₃ , 28.5 Å ²	C ₆ H ₆ , 41 Å ²	C ₆ H ₁₄ , 51.5 Å ²	C ₉ H ₁₂ , 62.3 Å ²		
0	250	220	208	200	190	0.69	2.14±0.091
6	270	220	200	190	180	0.71	2.59±0.095
10	230	190	178	165	165	0.74	2.51±0.056
15	215	209	200	190	188	0.70	2.25±0.047
20	205	200	195	190	195	0.58	2.10±0.060
30	158	156	150	145	150	0.52	2.07±0.024

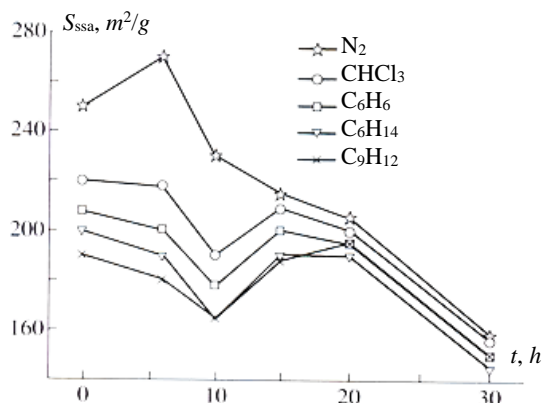


Fig. 2. Dependence of the change in the specific surface S_{ssa} of silica on the time of treatment with gaseous products of chemically-treated ZnO/H₂O₂.

In the initial period of modification (up to 10 h), an increase in the specific adsorption volume from 0.69 to 0.75 cm^3/g was observed. Subsequently, this volume decreased, and after 30 h of treatment it has a magnitude of 0.52 cm^3/g . A more reliable proof of the above can be the change in the specific surface area of silica (measured using different sorbents) with time depending on the treatment with gaseous products of CTR of ZnO/H₂O₂ shown in Fig. 2. After processing for 6 h, an increase in the specific surface area from 250 to 270 m^2/g was observed. Then it decreased and after 30 h of treatment it was only 158 m^2/g . This phenomenon was observed regardless of the size of the adsorptive molecules, but they have different dynamics. It follows from this that during the modification, in parallel with the changes in the specific surface area and adsorption volume, also the fractal

dimension of the surface was changed. Moreover, if an increase in the fractal dimension was observed at the initial stage, later it decreased due to the partial leveling of the surface due to the zinc oxide deposition.

Thus, based on the results of studying the process of treating the surface of silica by the CTR method, it was found that the proposed method of chemical modification can be quite effective not only for applying nanofilms, active components of heterogeneous catalysts on the surface of solid carriers, and obtaining new stationary phases for chromatography, but also to increase the temperature of the onset of intense sintering of silicas. This, in turn, makes it possible to increase significantly the regeneration temperature of sorbents and heterogeneous catalysts based on silica without significantly changing the textural parameters of their surfaces.

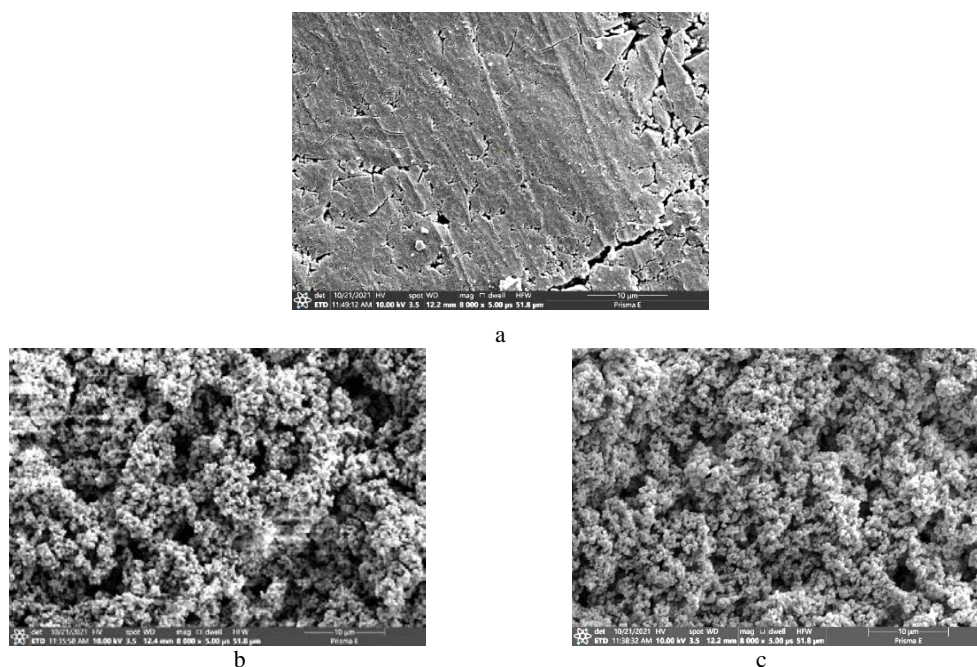


Fig. 3. SEM images of the surface of different silica gel samples: initial SiO_2 (a), modified with ZnO by the sol-gel (b) and CTR (c) methods.

Fig. 3 shows the data on the microstructure of the surfaces of solid contacts SiO_2/ZnO for samples, obtained using sol-gel and CTR methods. As evidenced, there are no significant local accumulations of the active phase on the surface of both catalysts: the surface is covered with ZnO particles evenly.

Using the example of the reaction of low-temperature oxidation of propane, the process of the release of radicals from the surface into the bulk was studied under various experimental conditions. The following series of experiments were carried out: 1 – without a catalyst; 2 – using silica without an active phase; 3 – silica with a catalyst 1; 4 – silica with a catalyst 2. EPR spectra of frozen-out radicals obtained at $T = 680\text{ K}$ and identical experimental conditions, depending on the nature of the catalyst, are shown in Fig. 4. In all experiments radicals were detected, which, in terms of the number of lines and the width of splitting, belong to alkyl peroxide radicals, RO_2 [10].

In the absence of a catalyst, radicals were not detected. At these temperatures without catalysts, radicals were not detected too. This means that radicals are formed due to the activation of propane and oxygen on the surface of solid contacts.

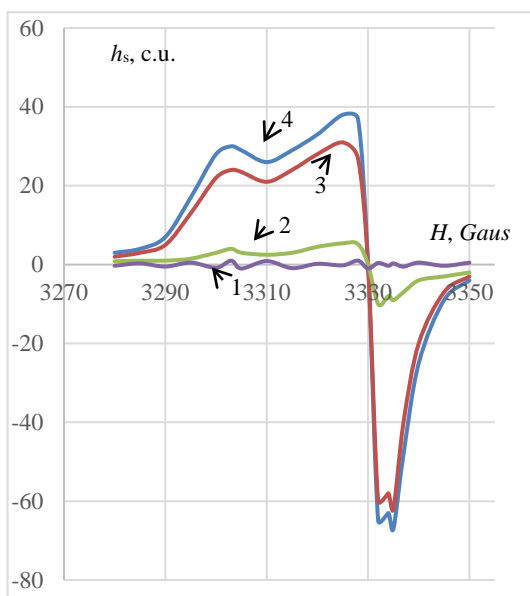


Fig. 4. EPR spectra of frozen RO_2 radicals at $\nu = 9.39 \text{ GHz}$, formed in the reactor at $P_{C_3H_8} : P_{CO_2} : P_{O_2} = 1 : 1 : 0.1$; $T = 680 \text{ K}$; total pressure of the mixture in the reaction zone 0.05 Torr :

- 1 – without a catalyst;
- 2 – with an untreated tablet;
- 3 – with a catalyst 1;
- 4 – with a catalyst 2.

Table 2

The amount of frozen-out peroxide radicals

Experiment No	Amount of radicals, $N/10^{-14}$, at T, K			
	620	640	660	680
1. Empty reactor	–	–	–	–
2. SiO_2 without an active phase	–	–	–	0.6
3. Catalyst 1	0.9	2.8	5.1	8.7
4. Catalyst 2	2.4	4.8	7.3	9.8

The amount of frozen-out peroxide radicals, $N/10^{-14}$, accumulated from the reaction zone ($P_{C_3H_8} : P_{CO_2} : P_{O_2} = 1 : 1 : 0.1$) within 30 min and at different temperatures are presented in Tab. 2. The data presented indicate that the amount of frozen-out radicals at all temperatures and identical experimental conditions strongly depends on the nature of the surface of the active phase of the catalyst, i.e. on the nature of the coating. No radicals are detected in an empty reactor at all temperatures. In a reactor with SiO_2 pellet without a deposited active phase, only traces of radicals were found at a temperature of 680 K . In the reactor with catalysts 1 and 2, radicals were found at all temperatures studied. However, in the presence of catalyst 2 their amount was noticeably higher at all temperatures. This was especially evident at relatively low temperatures. Thus, at $T = 620 \text{ K}$, the ratio of the content of radicals on the catalysts 2 : catalysts 1 was 2.66, while at $T = 680 \text{ K}$ it was only 1.26. According to [11], when the reaction particles interact with the catalyst surface, energy is

accumulated on the active centers of the latter, which leads to nonstationary surface state and the release of active particles from the surface into the bulk. Obviously, this is also influenced by the textural characteristics of the active phase. This is the reason for the high sensitivity of the gas-phase oxidation reactions of hydrocarbons to the state of solid contact of the surface.

Conclusion. Based on the results obtained, it can be stated that ZnO/SiO₂ catalysts activate propane and can be successfully used for low-temperature generation of active radicals in hydrocarbon oxidation processes. However, the activity of such catalysts depends on the textural characteristics of their surfaces, which, in turn, strongly depend on the method of applying the active phase to the surface of the inert support. Low-temperature deposition of the active phase of the catalyst using the CTR of the MeO/H₂O₂ system can help solve the problem of obtaining new highly selective and active heterogeneous catalysts, in particular, catalysts for the low-temperature oxidation of hydrocarbons.

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ՑԱԾՐ ԾՆՇՈՒՄՆԵՐԻ ԴԵՊՋՈՒՄ ՊՐՈՊԱՆ-ԹԹՎԱԾՆԱՅԻՆ
ԽԱՆՆՈՒՐԴՆԵՐԻ ՀՈՄՈԳԵՆ-ՀԵՏԵՐՈԳԵՆ ԱԿՏԻՎԱՑՄԱՆ
ՌԵԱԿՑԻՎԱՑՈՒՄ ZnO -ՈՎ ՄՈԴԻՖԻԿԱՑՎԱԾ ՍԻԼԻԿԱԶՆՈՂԻ
ՍԱԿԵՐԵՎՈՒՅԹԻ ՏԵՔՍՏՈՒՐԱՅԻՆ ԵՎ ԿԱՏԱԼԻՏԻԿ
ԱՌԱՆՁՆԱՀԱՏԿՈՒԹՅՈՒՆՆԵՐԸ

Ուսումնասիրվել են զոլ-գել և քիմիական տրանսպորտային ռեակցիայի (ՔՏՌ) միջոցով ցինկի օքսիդով մոդիֆիկացված սիլիկահողի մակերևույթի տեքստուրային և կատալիտիկ առանձնահատկությունները: Ցույց է տրվել, որ ստացված կոնտակտների կատալիտիկ ակտիվությունը կախված է ինչպես նստեցված ZnO -ի բնույթից, այնպես էլ դրա կառուցվածքային և տեքստուրային բնութագրերից: Պրոպանի ցածրջերմաստիճանային օքսիդացման օրինակով պարզվել է, որ ՔՏՌ եղանակով ստացված կատալիզատորի դեպքում մակերևույթից ծավալ ռադիկալների ելքի ջերմաստիճանային շեմը 15–20 աստիճանով ցածր է մոդիֆիկացման զոլ-գել եղանակով ստացված կատալիզատորի համեմատությամբ: Ցույց է տրվել, որ ՔՏՌ եղանակով սիլիկահողային կրիչի մակերևույթին ակտիվ ֆազի նստեցմամբ ստացված կատալիզատորն առավել արդյունավետ է շնորհիվ դրա մակերևույթի ակտիվ կենտրոնների էներգիական և տեքստուրային բնութագրերի համասեռության:

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ТЕКСТУРНЫЕ И КАТАЛИТИЧЕСКИЕ ОСОБЕННОСТИ
ПОВЕРХНОСТИ КРЕМНЕЗЕМА, МОДИФИЦИРОВАННОГО ZnO ,
В РЕАКЦИИ ГОМОГЕННО-ГЕТЕРОГЕННОЙ АКТИВАЦИИ
ПРОПАН-КИСЛОРОДНЫХ СМЕСЕЙ ПРИ НИЗКИХ ДАВЛЕНИЯХ

Изучены текстурные и каталитические характеристики поверхности силикагеля, модифицированного оксидом цинка золь-гель методом и при помощи химической транспортной реакции (ХТР). Установлено, что каталитическая активность полученных контактов зависит как от природы, так и от структурных и текстурных характеристик нанесенного ZnO . На примере реакции низкотемпературного окисления пропана выяснено, что нижний предел выхода радикалов с поверхности в объем при модифицировании с помощью ХТР на 15–20 градусов ниже, чем в случае золь-гель метода. Показано, что катализатор, полученный нанесением активной фазы на поверхность носителя методом ХТР, более эффективен благодаря энергетической однородности его активных центров и текстурных характеристик поверхности.