

NONTRADITIONAL METHOD OF CHEMICAL MODIFICATION  
OF THE SURFACE OF POROUS SILICA

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The main results obtained in the study of the possibility of low-temperature chemical modification of porous silica, applying various nanodispersed substances to their surface are given. It has been shown that the use of the chemical transport reaction (CTR)  $\text{H}_2\text{O}_2/\text{ZnO}$  for this purpose with the participation of  $\text{H}_2\text{O}_2$  vapors at room temperature makes it possible to apply a number of oxides, sulfides and metal halides to the surface of various sorbents. An important advantage of the proposed modification method is that changes in the original texture parameters of the substrate are minimized. Using the example of modifying the behavior of highly pure  $\text{SiO}_2$  with zinc oxide, it was shown that the decomposition of gaseous intermediate products of CTR  $\text{H}_2\text{O}_2/\text{ZnO}$  occurs mainly in pores with a diameter of more than 6 nm.

**Keywords:** surface-modification, zinc oxide, chemical transport reaction, sorbents.

**Introduction.** The problems of chemical modification of the surfaces of various sorbents with the purpose of giving their surfaces this or that desirable property have recently been in the centre of attention of many researchers [1–4]. This is explained by the fact that the need for effective sorbents used in sorption, chromatography, contact catalysis and other fields, where strict requirements are set on the mentioned materials, has increased. First of all, it is a high sorption selectivity and capacity, temperature and chemical stability, unwashability of the modification layer, that is especially important when using these materials as chromatographically stationary phases and also availability of modification process and its controllability.

Among the sorbents used as initial substrates for obtaining surface-modified materials, silicon dioxides of various genesis take a special standing. According to some estimations, 60 to 80% publications on the chemical modification of surfaces are devoted to silicagels as materials, satisfying the indicated requirements to the greatest degree [5].

It is known, that chemical modification of a surface, especially if it is carried out with the replacement of surface silanol groups by various organic fragments, results in essential changes in its texture parameters: specific surface, specific volume of pores and pore size distribution, that is basically connected with a major

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change of the surface chemistry [6–8]. In addition, it is often difficult to track the course of the modification and, therefore, to obtain repeatable effects at transition from one batch of sorbents to another. That is why the search for new methods of chemical modification of sorbents surfaces is a problem of current importance.

In the present work the results of investigations of the possibility of chemical modification of the surface of special purity  $\text{SiO}_2$  by zinc oxide with the help of chemical transport reaction (CTR) with the involvement of  $\text{H}_2\text{O}_2$  vapours, described in [9, 10] for the first time, and studies of the influence of modification on the texture parameters of the initial sorbent are presented. The essence of this CTR is that at contiguity of  $\text{H}_2\text{O}_2$  vapors with metal oxides, halogenides and sulfides, gaseous complexes are formed, which transporting from one site of the system to another and at contiguity with a solid contact decompose, forming the mother substance.

An important feature of this reaction is that it proceeds at room temperature, and, no less important, it can be controlled by varying the rate of  $\text{H}_2\text{O}_2$  vapor supply, and it is possible to regulate the degree of sorbent surface modification, where the decomposition of the gaseous complex takes place by changing the sorbent maintenance time.

**Materials and Methods.** Experiments were carried out in a low-pressure flow setup providing gravimetric measurements during the course of the process. The setup is depicted schematically in Fig. 1. The mixture of hydrogen peroxide and water vapors ( $\text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1$ ) from ampoule 1 was passed under a pressure of  $\sim 80 \text{ Pa}$  through reactor 2 with a pellet of fine disperse powder of zinc oxide 99,999% pure (“Aldrich”). The ratio of the outer geometrical surface of the pellets to the free volume of the reactor was equal to  $\sim 2 \text{ cm}^{-1}$ . The gas flow from the reactor was supplied to the gravimetric unit (a McBain balance) with silica gel pellet 4 mounted on thin quartz helix 5 (sensitivity  $0.55 \cdot 10^{-2} \text{ g/cm}$ ). Silica gel pellets ( $\sim 0.1 \text{ g}$ ;  $1 \times 1 \times 0.1 \text{ cm}^3$ ) were prepared by pressing special purity  $\text{SiO}_2$  under a pressure of  $1500 \text{ kg/cm}^2$ . The specific surface area of silica gel was equal to  $240 \text{ m}^2/\text{g}$  and the specific pore volume was equal to  $0.690 \text{ cm}^3/\text{g}$ .

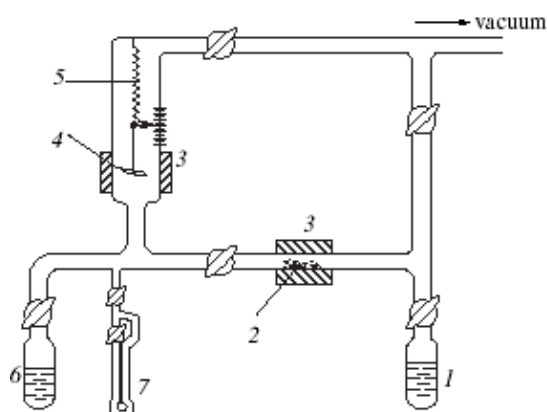


Fig. 1. Schematic representation of true low-pressure flow setup:

- 1 –  $\text{H}_2\text{O}_2$  vapor supply unit;
- 2 – reactor with a ZnO pellet;
- 3 – heater;
- 4 – silica gel pellet;
- 5 – quartz spring;
- 6 – ampoule with the adsorptive;
- 7 – oil-column manometer.

In the setup, provision was made for the regulation of pressure, flow rate, and temperature of the reactor and  $\text{SiO}_2$  pellet. The concentration of ZnO in the flow was determined using an atomic absorption spectrometer AAS-30 as follows. After 1 h of condensation of the gas flow at 77 K, the complex of ZnO with  $\text{H}_2\text{O}_2$  ( $\sim 10^{-9} \text{ mol}$ ) was accumulated in amounts sufficient for its analysis. Then the

condensate was heated to room temperature. Under these conditions the condensate transformed into a liquid, and the complex decomposed ready to yield initial ZnO. Since zinc oxide is poorly soluble in water, using a chemical reaction it was transformed into a soluble salt, which was then analyzed. This was accomplished as follows. A dilute hydrochloric acid aqueous solution of known concentration was added to the receiving flask with the accumulated solution to a combined volume of 3 mL. Accumulated ZnO reacted with HCl to yield ZnCl<sub>2</sub> readily soluble in water. The amount of substance transported in the course of the experiment was determined from the concentration of Zn in the obtained solution measured using an AAS-30 spectrometer. Then, given the gas flow rate and the gas pressure, the concentration of the complex in the gas flow was calculated.

**Results and Discussion.** The chemical transport of ZnO was carried out under conditions required in modifying the silica gel surface with zinc oxide. The contact time was equal to  $\sim 10^{-2}$  s, the vapor pressure of an equimolar mixture of hydrogen peroxide and water was equal to 80 Pa, the temperature of reactor was equal to 373 K, and  $s/V = 2 \text{ cm}^{-1}$ . In the steady-state chemical transport, the concentration of the intermediate (substance carrier) in the gas mixture was equal to  $\sim 3 \cdot 10^{10}$  molecule/cm<sup>3</sup>, and the transport rate was equal to  $4 \cdot 10^{12}$  molecule/cm<sup>3</sup>·s. In this case, the amount of substance transported with the gas flow for 1 h was as large as  $\sim 10^{-9}$  mol. Under these conditions, the gas flow containing the intermediate was passed over the silica gel pellet. As a result, the silicagel surface was modified. The adsorption properties of silica gel surface modified with zinc oxide were studied by measuring adsorption isotherms of benzene. Benzene vapors from ampoule 6 were supplied at a given pressure to the modified surface of SiO<sub>2</sub>. The adsorbed amount of benzene on the SiO<sub>2</sub> pellet was determined using a McBain balance.

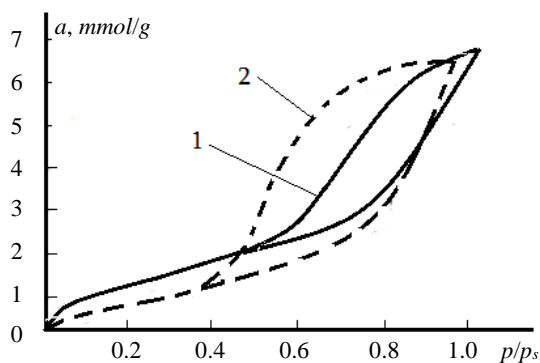


Fig. 2. Isotherms of adsorptions of benzene:  
1 – the initial SiO<sub>2</sub> sample;  
2 – the sample modified with gaseous products of the CTR H<sub>2</sub>O<sub>2</sub>/ZnO.

The adsorption of gaseous products of CTR H<sub>2</sub>O<sub>2</sub>/ZnO with their subsequent decomposition on the surface of SiO<sub>2</sub>, preliminarily thermovacuumated at 300°C for 2 h, results in changes in the sorbent texture parameters to which the isotherms of benzene adsorption testify (Fig. 2).

Thus, if on the first stages of modification (up to 20 h) the specific surface ( $s$ ) noticeably increases (up to 280 m<sup>2</sup>/g), later on it gradually decreases reaching up to 240 m<sup>2</sup>/g after 40 h of modification (Fig. 3, a).

As can be seen in Fig. 3, b, the position of the maximum on the pores distribution curve by sizes essentially shifts to the side of smaller sizes on the first stages of modification, and then this change almost stops.

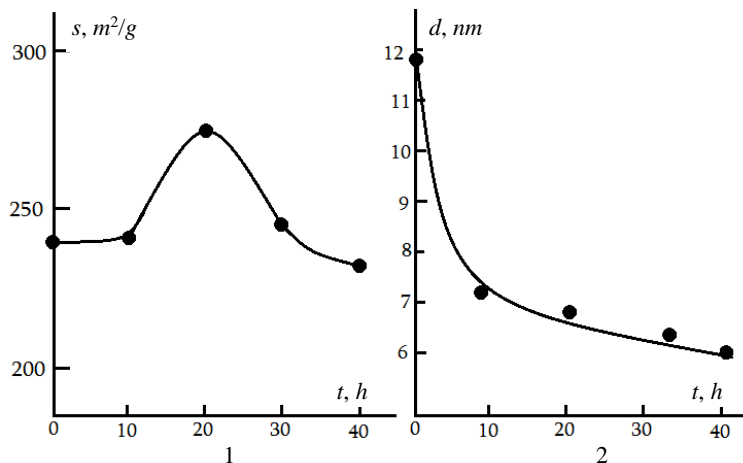


Fig. 3. Dependence of specific surface area (1) and position of maximum in pore size distribution curve by diameters  $d$  (2) from modification time of  $SiO_2$ , CTR  $H_2O_2/ZnO$ .

Fig. 4 shows the pores distribution curves by the sizes of initial and modified for 40 h  $SiO_2$ . From this it is evident that the processing of  $SiO_2$  surface by gaseous products of CTR  $H_2O_2/ZnO$  results in a shift in the maximum of pores distribution by diameters from 120 to 60 Å. It is worth mentioning that a remarkable change in both the specific surface and distribution of pores by sizes is observed in the first stages of modification. Then these changes take place more smoothly, and further on they stop at all.

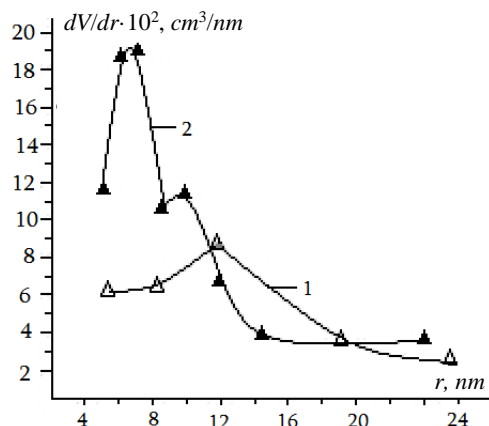


Fig. 4. Pore size distribution curves for:  
1 – the initial silica gel sample;  
2 – the sample modified with zinc oxide.

From the obtained results it is possible to conclude that the decomposition of intermediate compound of CTR  $H_2O_2/ZnO$  happens mainly in the pores with  $d > 60$  Å, and the increase in the specific surface in the first stages of modification is a consequence of formation of a secondary texture on the surface of large pores at the expense of ZnO, formed by the decomposition of intermediate compound of CTR  $H_2O_2/ZnO$  on their surface. In the favor of such a conclusion testifies also the fact, that despite the circumstance that the increase in modification time does not essentially affect the distribution of pores by sizes, it results in a decrease in the specific surface, which is probably a consequence of the subsequent “smoothing” of the surface.

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ԾԱԿՈՏԿԵՆ ՍԻԼԻԿԱԶՆՈՂԻ ՄԱԿԵՐԵՎՈՒՅԹԻ  
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Ներկայացված են ցածր ջերմաստիճաններում ծակոտկեն սիլիկահողի մակերևութին ոչ ավանդական մեթոդով տարբեր նյութերի նանոդիսպերս համակարգերի նստեցման հնարավորության ուսումնասիրությունների արդյունքները: Յույց է տրված, որ այդ նպատակով H<sub>2</sub>O<sub>2</sub>-ի գոլորշիների մասնակցությամբ ընթացող ցածրջերմաստիճանային քիմիական տրանսպորտային ռեակցիաների (ՔՏՈ) միջոցով կարելի է սորբենտների մակերևութին նստեցնել մի շարք նանոդիսպերս օքսիդներ, սուլֆիդներ և քլորիդներ՝ սենյակային ջերմաստիճանում: Հատուկ մաքրության SiO<sub>2</sub>-ի մակերևութին ցինկի օքսիդի նստեցման օրինակով ցույց է տրվել, որ H<sub>2</sub>O<sub>2</sub>/ZnO ՔՏՈ-ի միջանկյալ արգասիքների քայքայումը, որի արդյունքում ստացվում են ZnO-ի նանոդիսպերս մասնիկներ, տեղի է ունենում հիմնականում 6 մմ-ից մեծ չափսերով ծակոտիներում:

T. O. КАМАЛЯН

НЕТРАДИЦИОННЫЙ МЕТОД ХИМИЧЕСКОГО  
МОДИФИЦИРОВАНИЯ ПОРИСТОГО КРЕМНЕЗЕМА

Резюме

Приведены основные результаты, полученные при изучении возможности низкотемпературного химического модифицирования пористого диоксида кремния с нанесением на его поверхность различных нанодисперсных веществ. Было показано, что использование для этой цели низкотемпературной химической транспортной реакции (ХТР) H<sub>2</sub>O<sub>2</sub>/ZnO позволяет наносить ряд оксидов, сульфидов и галогенидов металлов на поверхность различных сорбентов при комнатной температуре. На примере нанесения ZnO на поверхность особо чистого SiO<sub>2</sub> выяснено, что разложение газообразных промежуточных продуктов ХТР H<sub>2</sub>O<sub>2</sub>/ZnO с образованием нанодисперсного ZnO происходит в основном в порах диаметром более 6 нм.