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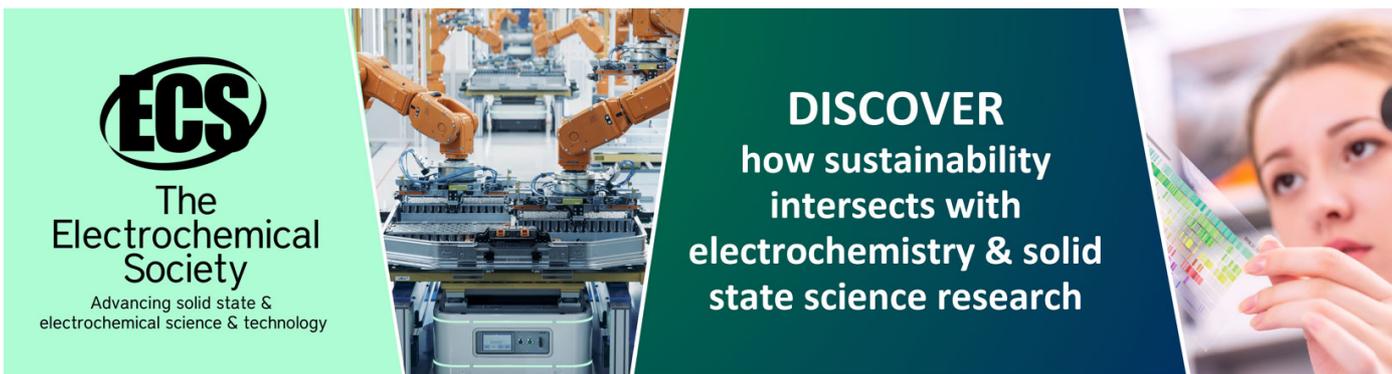
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Structural features and production of high purity porous supports from silicon dioxide by gas-phase deposition of silicon tetrachloride

V M Vorotyntsev*, A V Vorotyntsev, T S Sazanova, A N Markov and A D Kulikov

Nizhny Novgorod State Technical University n.a. R.E. Alekseev, Nanotechnology and Biotechnology Department, Nizhny Novgorod, Russian Federation, 603950

*e-mail: chemistry_lab@mail.ru

Abstract. One of the most interesting cases of the appearance of a porous material is gas-phase deposition of silicon dioxide. Silicon tetrachloride, oxidized in the gas phase at a temperature of the order of 1500 K (in the flame of an oxygen burner), forms silica particles with a diameter of about 100 nm. In this work, supports were obtained consisting of particles of high purity silicon dioxide. When silicon tetrachloride is oxidized in the gas phase, parts of SiO₂ with a diameter of about 0.1 μm are formed. Particle sizes and dispersion of their distribution were statistically evaluated. The purity of the obtained samples, for a number of metals, was determined on an inductively coupled plasma mass spectrometer with a detection limit of 10⁻¹⁰ wt.%. To change the porous structure, the supports were annealed in an inert gas flow.

1. Introduction

Mesoporous molecular sieves (MMS) based on silicon oxide were first obtained by a team of Mobil researchers in 1992 [1, 2]. To date, a number of MMS have been obtained both on the basis of silica and containing heteroatoms [3]. Mesoporous materials are most often used as catalytic materials [4, 5]. All MMS are united by a number of common properties, which cause so much interest in them. First of all, this is a high specific surface area (up to 1500 m²/g), a spatially ordered pore system of strictly the same size in the range from 2 to 10 nm (mesoporous according to the IUPAC classification [5]), and also thermal stability up to 800 °C, such materials for carrying out reactions at sufficiently high temperatures.

Mesoporous materials, with a pore diameter up to 10 nm, are widely used for immobilization and functionalization with ionic liquids. One of the most interesting cases of the appearance of a porous material is the gas-phase deposition of quartz glass. Silicon tetrachloride, oxidized in the gas phase at a temperature of the order of 1300 °C, forms silicon dioxide particles with a diameter of about 100 nm, which under the action of thermophoretic forces precipitate, forming a bulk phase [6]. This method produces blanks of optical fibers [6] and quartz filters [7]. The porosity of silicon dioxide resulting from gas-phase precipitation can vary over a wide range [7], reaching 0.98 in the MSWM method [8]. Porosity belongs to one of the important characteristics of porous media. By its magnitude, other characteristics can be estimated [9]. It is also important for understanding the processes of annealing porous materials, for example, to estimate the annealing rate of a billet [9-13].

The reason for the increased interest in mesoporous carriers is understandable: it is their highly developed surface combined with a large pore volume and the possibility of chemical modification of their surface. In addition, varying the conditions for the synthesis of mesoporous carriers allows one to



regulate their characteristics in a directed manner. The main synthetic approaches in the development of such systems are the described methods of covalent binding of IL with a silicate carrier due to interaction with its surface OH-groups, and also the simple application of IL by impregnation.

Modification of the surface of mesoporous silicate can also be carried out directly in the process of its synthesis. Thus, the authors of Ref. [14] first obtained the functionalized material MCM-41 by adding 3-chloropropyltriethoxysilane to the initial reaction mixture, and then adsorbed trialkylamines with different lengths of alkyl radicals were quaternized with this reagent grafted to the pore wall of the carrier. This last factor exerted a significant influence on the activity of the catalyst in the reaction of obtaining cyclic carbonates by binding of eco-oxides and carbon dioxide: it decreased with increasing length of the alkyl amine radical. Methods for preparing catalysts containing active metal complexes in the immobilized IL layer are described in [15, 16]. The simplest method is described in [15], where the authors first synthesized an individual metal complex Rh in a solution of methanol, and silicate MCM-41 or amorphous SiO₂ was added to it.

Thus, the use of any of the types of carriers described in the scientific and patent literature for IL immobilization makes it possible to obtain an active catalytic system. The choice of a carrier is determined by the specific tasks and reaction conditions in which this catalyst will be used.

In the present work, supports consisting of high-purity silicon dioxide particles that are formed by burning high-purity silicon chlorides in the flame of an oxygen-hydrogen burner are investigated.

2. Experimental

2.1. Materials

To obtain porous silica-based supports, silicon tetrachloride (99.9995%) from Firm HORST Ltd. was used. (Russia). Oxygen (99.999%) from Monitoring Ltd. (Russia) was used as an oxidizing agent. The samples were annealed in a nitrogen atmosphere (99.9999%), helium and hydrogen (99.99999 %) from Monitoring Ltd. (Russia).

2.2. Preparation and functionalization catalyst

In the flame of the oxygen-hydrogen (FOHB) burner of external mixing, pairs of silicon tetrachloride are fed in an amount of 100 g/h in a mixture with helium. The average temperature of the heated part of the substrate from coarse quartz is 900 °C. At the deposition stage, the heat treatment time of the particles is 2.5 min. In addition, annealing of particles already deposited on the substrate in an electric tube furnace at a temperature of 900 °C is conducted so that the total heat treatment time in the precipitation and annealing steps is 100 min. The porosity of the resulting support is 60% of its total volume. The pore sizes are 0.2 μm.

2.3. Characterization SiO₂ porous support

2.3.1 SEM, AFM. The morphological and visual appearance characteristics were observed by scanning electron microscopy Vega II (Tescan, Czech Republic) at the voltage of 20 kV with backscattered electron (BSE) detector and detector of reflected electrons (RE detector) with different zooming from. The use of BSE and RE detectors produces higher-contrast images in comparison to the SE detector.

Porous samples surface and its roughness were studied by atomic force microscopy (AFM) with a scanning probe microscope SPM-9700 (Shimadzu, Japan). AFM scanning was performed using a tapping mode by silicon vibrating cantilevers PointProbe FMR-20 (Nano World Innovative Technologies, USA) with a stiffness coefficient of 1.3 N/m and a typical tip radius of no more than 8 nm (guaranteed - no more than 12 nm), a tip height was 15 μm.

The experiments were carried out under ambient conditions. Automatic correction of linear noise was applied during scanning. For checking purposes reproducibility, AFM scanning was carried out on different surface sites. Processing of the obtained AFM images and their analysis were performed by a software SPM Manager ver. 4.02 (Shimadzu, Japan).

2.3.2 Specific surface area and pore size distribution. Specific surface area and pore size distribution were determined from absorption/desorption isotherms recorded on SorbiMS (META, Russia) with advanced term training of samples. The study of solids is closely related to the interpretation of the IV type of adsorption isotherms, where there is a hysteresis loop. By interpreting this type of isotherms, it is possible to estimate the specific surface area by BET and STSA with acceptable accuracy, as well as to obtain an approximate characteristic of pore size distribution and full pore volume.

3. Results and discussion

3.1. Synthesis and characterization

In the present work, supports consisting of high-purity silicon dioxide particles that are formed by burning high-purity silicon chlorides in the flame of an oxygen-hydrogen burner are investigated. When silicon tetrachloride is oxidized in the gas phase, it forms SiO_2 particles with a diameter of about $0.1 \mu\text{m}$ in figure 1.

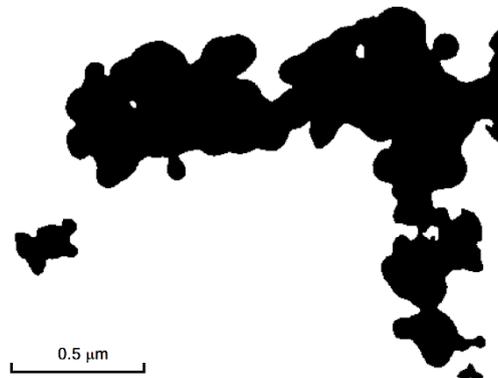


Figure 1. SiO_2 particles formed in the flame of an oxygen-hydrogen burner.

The average particle size and the dispersion of their distribution in size are close to those described in [5]. Under the action of thermophoresis forces, the particles are deposited on the outer surface of the substrate, forming a layer of porous (up to 90%) silicon dioxide. Photomicrographs of the porous layer were obtained with the help of Auger Electron Spectroscopy (AES) PHI 710. The shading of the samples for viewing on the instrument was carried out with the help of an organometallic bis-ethylbenzene-chromium compound (BEBC). A sample of porous silicon dioxide was placed in a quartz ampoule, after which the system was pumped. The required quantity of BEBC was added to the pumped ampoule, then the system was closed and slowly heated to a temperature below the decomposition temperature of the compound. Further, it was quickly raised to the thermal decomposition temperature of the BEBC, as a result of which the sample was covered with a conductive layer sufficient for viewing on the instrument.

According to the SEM micrographs in figure 2a, SiO_2 porous sample has a layered structure in cross-section. The observed layers were determined by the SEM images (sample size was 20). Then an intervallic ordered sample was formed from a range of values. An optimum quantity of intervals k was measured by Sturges' formula:

$$k = \log_2 n + 1, \quad (1)$$

where n is a sample size. For the selected sample size, the optimum quantity of intervals was about four. Then a number of values falling into each interval were counted, and a histogram was constructed in figure 2b.

The SEM micrographs of the porous sample surface in figure 3a illustrate a loose porous structure. The cross-sectional dimensions of these pores were determined (sample size was 50) and statistically analyzed in figure 3b.

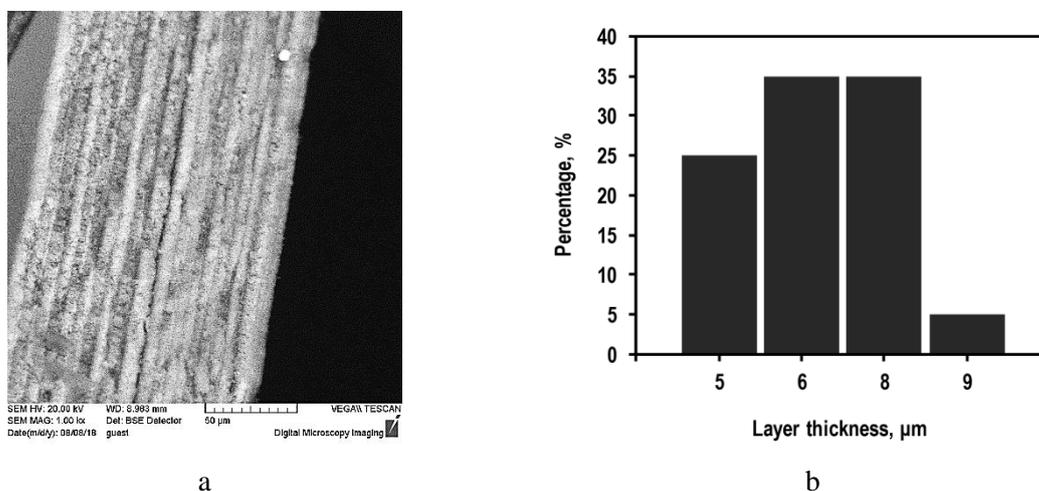


Figure 2. SEM microphotographs of the porous support layer (a - face at 1000-fold magnification, b - histogram of layer thickness distribution).

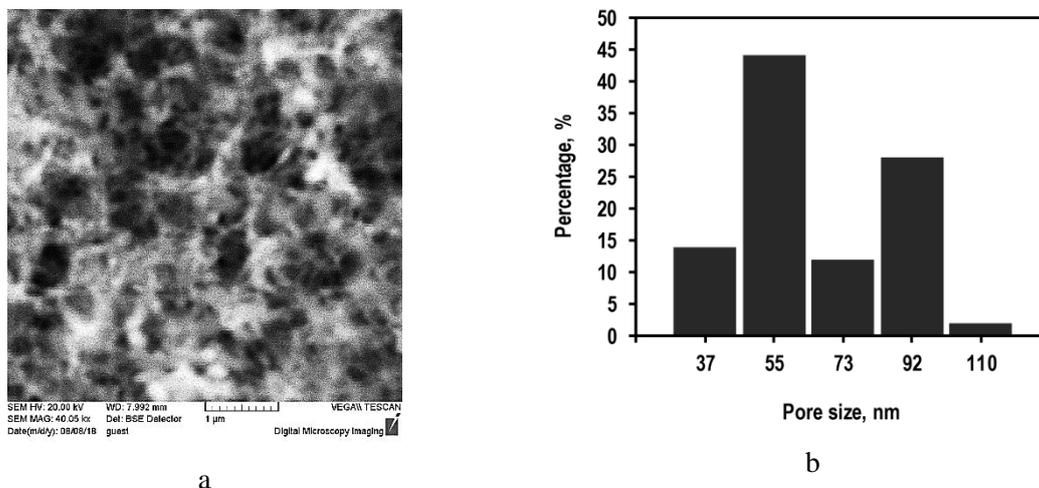


Figure 3. SEM microphotographs of the porous support surface (a - surface at 40050 times magnification, b - histogram of pore size distribution).

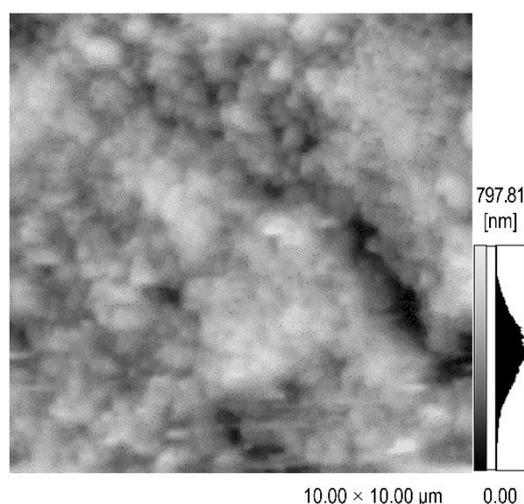
The obtained topographic map in figure 4 of the porous sample surface shows a loosely packed structure like the SEM micrograph in figure 3.

To estimate the mesoporous structure of the porous support low-temperature nitrogen adsorption was performed. Results are shown in table 1. We used two measurement methods (BET and STSA) as BET method allows to measure micropores and mesopores using mono-layer model and STSA (or t-plot) method is appropriate to calculate mesopores, macropores and outside surface specific surface area (but not micropores one as micropores are already field in the range of relative pressures from 0.1 to 0.5 in which STSA operates) using multi-layer model. So, for resins containing predominantly mesopores and macropores STSA specific surface area is always greater than BET one. As it is shown in table 1 our samples have mesoporous and macroporous morphology.

Table 1. Loading of the functional fragment (FF) and textural properties of the SILLPs.

Entry	Sample	S^{BET} (m^2/g)	S^{STSA} (m^2/g)	Cumulative pore volume (cm^3/g)	$dV_{\text{nm}}/V_{\text{sum}}$ (%)
1	Porous support (after <i>FOHB</i>)	22.12	30.46	0.556	4 nm – 76.4
2	Porous support (after <i>annealing in nitrogen atmosphere</i>)	48.73	54.83	0.749	14 nm – 32.1

According to AFM results, an arithmetic average roughness height (R_a) and a mean roughness depth (R_z) were obtained. A base length was 10 μm . Since the function of high distribution (according to surface profile) is unimodal, R_a and R_z could be used as quantitative parameters of the surface irregularities. Wherein R_a (about 90 nm) correlates with an amplitude of the small-scale roughness, and R_z (about 390 nm) correlates with the large-scale one.

**Figure 4.** AFM image of the SiO_2 porous sample.

The nature of the packing of the particles that create the support cage is different from those described in the literature. Apparently, this is due to the formation of the structure of the support by the principle of "touching-sticking", i.e., when the particles are first touched to the support framework, it sticks and remains in this place without moving anywhere. Similar structures can have fractal properties.

The content of metal impurities in the support material was determined by ICP-MS. To pre-concentrate, the impurities, distillation after chemical conversion of the base material to a volatile compound, silicon tetrafluoride, was used. In order to reduce the level of background contamination, the sample was treated with hydrofluoric acid vapor at elevated pressure and temperature. The limit of detection of impurities from a gram sample was 10^{-6} - 10^{-8} wt.%. The results of the analysis of high-purity silicon dioxide are given in table 2. For comparison, data on the content of metal impurities in some polymer filters are given. From the data presented, it can be seen that the total concentration of metal impurities in supports from high purity silicon dioxide is at the level of $7 \cdot 10^{-6}$ wt.%, which is two to three orders of magnitude lower than in polymer membranes. The obtained data testify to the

potential possibility of using them as catalytic substrates in the chemistry of high-purity substances, in particular, in the production of MS and silicon tetrachloride recovery.

Table 2. Comparative analysis of the concentration of metal impurities in the obtained support from SiO₂ and commercial Millipore MF-NA.

Element Sample	The concentration of metal impurities (wt. % · 10 ⁻⁷)								
	Al	Fe	Co	Cr	Mg	Cu	Ni	Sn	Pb
SiO ₂	5	30	8	6	3	2	2	9	4
Millipore MF-NA	3000	6000	20	3000	20000	5000	300	50	400

3.2 Dependence of structural characteristics and methods of influence

Important characteristics of porous materials, which determine their catalytic activity and productivity, are the pore diameter d and porosity E . Total porosity E_{Σ} is equal to the ratio V_{pore}/V , where V_{pore} and V are the total volume of the pores in the sample and the volume of the sample. Its value was determined from the difference in support density ρ and quartz density $\rho_{\text{quartz}} = 2.202 \text{ g/cm}^3$

$$E_{\Sigma} = 1 - \rho/\rho_{\text{quartz}} \quad (2)$$

The open porosity E_0 , responsible for the catalytic activity of the porous material and ultimately the productivity, was determined by the method of impregnation with a wetting liquid

$$E_0 = (M_{\text{impr}} - M)/(V\rho_{\text{liquid}}), \quad (3)$$

where M , M_{impr} – mass of dry and liquid-impregnated support, ρ_{liquid} – density of a liquid.

To evaluate the reproducibility of the characteristics of the supports, 3 supports were obtained at fixed values of the parameters of the deposition process. The porosity is reproduced with an error of not more than 0.02. The reproducibility of the porosity and its uniformity along the length of the support practically coincide.

In the range of porosity values greater than 0.7, the value of E_0 does not significantly differ from E_{Σ} . When the porosity decreases, an increase in the difference in the open and total porosity is observed. Figure 5 shows the dependence of porosity on the temperature of the preparation of the support. The amount of porosity decreases linearly with increasing temperature:

$$E_0 = (2.02 \pm 0.02) - (1.67 \pm 0.02) \cdot T^*, \quad (4)$$

where T^* – reduced deposition temperature.

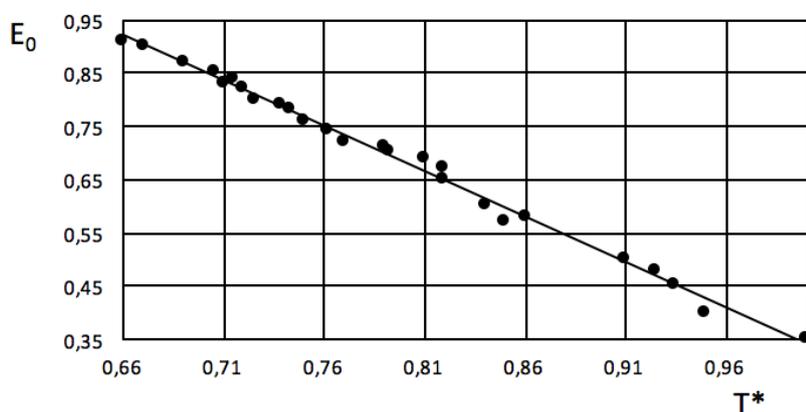


Figure 5. Dependence of the open porosity of the supports on the reduced temperature of the preparation of the SiO₂ support.

To measure the size of macropores, the Borruso-Behold method was most widely used, based on measuring the pressure necessary to press air bubbles (or another gas) through the pores of a material previously filled with a liquid with a known coefficient of surface tension, the "bubble point" method. To process the results obtained, use the Cantor formula:

$$d = 4q \cdot \cos(Q) / \Delta P, \quad (5)$$

where q - surface tension, Q - wetting contact angle, ΔP - pressure drop across the support. The formula (5) is valid only in the case when the pore has a cylindrical shape. In order to take into account the effect of deviations of the real form of the pores from the cylindrical shape on the measurement results, d correction is introduced in the form of a factor in the numerator of expression (5). However, not having its value for the obtained supports, it was assumed that the pores have a cylindrical shape. Isopropyl alcohol was used to determine the "bubble point", $q = 21.22$ dynes / cm, $\cos(Q) = 1$.

The results of measuring the pore sizes for supports with different porosities are shown in figure 6. It can be seen that the porosity of the support and the pore diameter vary in a consistent manner. This relationship is approximated by the equation:

$$E_0 = (180 \pm 30) \cdot d^{(2.04 \pm 0.06)} \quad (6)$$

with a correlation coefficient of 0.992, d is the pore diameter, μm .

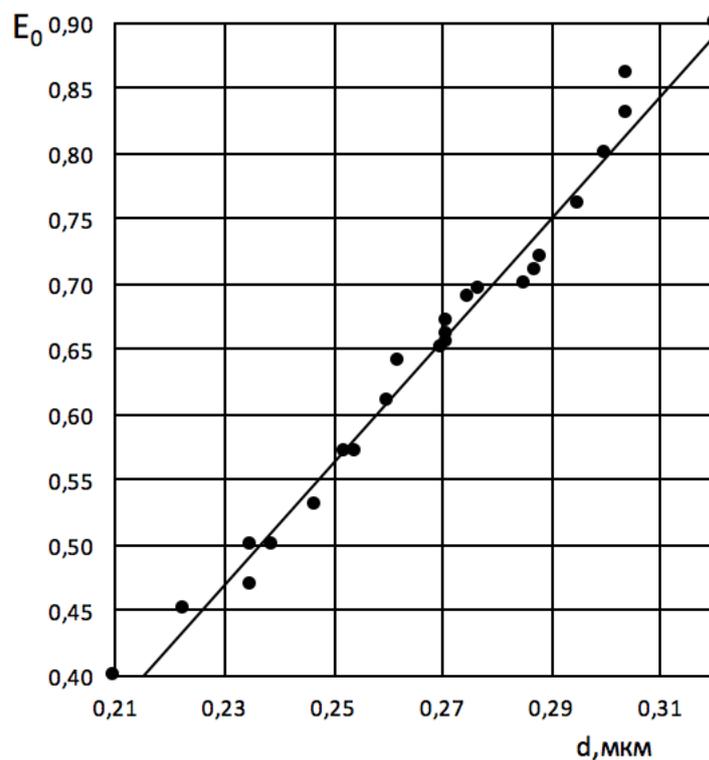


Figure 6. Dependence of the open porosity of the support on the pore diameter.

Calculation of the porosity of the supports versus the warm-up time was based on the Scherer model [17]. In the model, the real random structure of the support material is replaced by a lattice of intersecting cylinders. In the calculations, it was assumed that the energy dissipating in viscous friction is equal to the energy that arises from the decrease in the surface area.

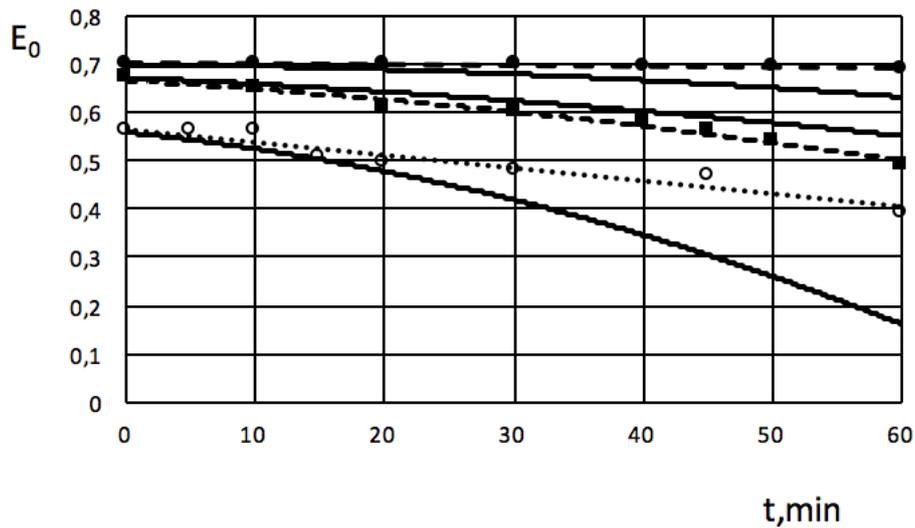


Figure 7. Dependence of the porosity of E_0 on the annealing time at T^* (from top to down): 1, 1' - 0.82; 2, 2' - 0.84; 3, 3' - 0.86. Solid lines - calculation by the equation (7), dotted lines - experimental values.

In reference [17], dependence is indicated that implicitly determines the porosity as a function of time

$$K(t - t_0) = \int_0^x [2(3\pi - 128x)^{-1/3} \cdot x^{-2/3}] dx, \quad (7)$$

where $k = (\gamma/\eta L_0) (\rho_s / \rho_0)$, $x = a/L$, $t-t_0$ – the annealing time from the fictitious moment t_0 , when $x = 0$, a – the particle diameter, γ – the surface tension coefficient [17], L_0 is the initial length of the cylinder, η is the viscosity of the glass, ρ_s , and ρ_0 are the density of solid and porous glass. The length of the cylinder L was determined from the porosity value E_0 , its diameter was assumed to equal to the particle diameter $a = 0.1 \mu\text{m}$.

In [17], the agreement between the calculated porosity vs. annealing time and experimental data was obtained for a certain selection of the viscosity of molten glass. In our case, it turned out to be necessary to increase the viscosity by 3 times in comparison with the used Scherer [17]. The figure shows the theoretical curves for three values of the annealing temperature $T^* = 0.82; 0.84; 0.86$ (T^* – the reduced temperature, equal to the ratio of the deposition temperature in the preparation of the support preform and the temperature of obtaining support blanks with porosity $E_0 = 0.4$).

Thus, during the annealing of supports made of high-purity silicon dioxide obtained by the flame hydrolysis of silicon chloride, it is possible to change their porosity from 0.9 to 0.4, and the pore size changes by a factor of 1.5-2, which was determined by the method "Bubble points".

In order to choose the optimum values of annealing time and temperature, a preliminary calculation of the porosity can be made with an error not exceeding the standard deviation of the calculated results from the experimental results estimated at 25 experimental points. This corresponds to 5% and the range of changes in E_0 values from 0.4 to 0.9.

Ultimately, varying the parameters of temperature, pressure, and annealing time made it possible to obtain a final material with different pore size distribution and total pore volume.

4. Conclusion

A method for obtaining supports consisting of particles of high-purity silicon dioxide, which are formed by burning high-purity chlorides in the flame of an oxygen-hydrogen burner, is developed. When silicon chlorides, in particular, silicon tetrachloride, are oxidized in the gas phase, parts of SiO_2 with a diameter of about $0.1 \mu\text{m}$ are formed. Statistically, there were limited particle sizes and dispersion of their distribution in size. Under the action of thermophoretic forces, the particles are

deposited on the outer surface of polycrystalline silicon (before the possibility of removing the resulting preform), forming a layer of porous (up to 90%) silicon dioxide. The purity of the samples was determined by the ICP-MS.

Acknowledgments

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