General and Inorganic Chemistry

Fractality of materials based on silica gel

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Based on the analysis of the isotherms of N_2 adsorption, the fractal dimension and other texture geometric parameters were determined for silica gel, modified silica gel, and relevant composite materials. The correlations between the texture parameters were found. A criterion for the estimation of the efficiency of using the composite adsorbent volume was proposed.

Key words: silica gel, composite materials, impregnation, adsorbents, texture, adsorption isotherms, determination of texture parameters, fractality, fractal dimension.

Quantitative characteristics of the texture of porous materials are important for examination of their properties. In particular, the fractal dimension of the internal surface of porous materials determines, perhaps, the transport and functional properties of adsorbents and catalysts.[1,2] Its estimation requires methods of calculation of the internal surface in some interval of linear scales. Presenting the internal surface obtained by one or another method as a function of the corresponding linear scale in the logarithmic coordinates, the fractal dimension of the internal surface of the porous material can be determined from the slope of the linear region (if any) in the scale interval with a linear approximation.

The experimental adsorption isotherms can be processed by two methods. First, this is the BET-based procedure of calculation of the internal surface of the porous material from experiments on adsorption of organic molecules differing in the length of the aliphatic radical.[3,4] In this case, the linear scale is the length of the aliphatic radical of the adsorbate. The specific surface found from the experiment with this adsorbate corresponds to each value of the length of the aliphatic radical. The second method is the procedure of calculation of the mesopore surface from the experimental isotherm of nitrogen adsorption in the region of capillary hysteresis and is based on the concept that the equilibrium configurations of the capillary condensate and polymolecular film coexist in pores.[5,6] In this case, the linear scale is the upper limit of the Kelvin radii of mesopores (ρ_K) filled with the capillary condensate at a specific value of the chemical potential of the adsorbate. Each Kelvin radius corresponds to the surface of mesopores free of the capillary condensate at the specific value of the chemical potential of the adsorbate.[7,8]

Experimental

Pre-washed (with distilled water) and dried silica gel (KSK trade mark) was evacuated for several hours at 200 °C. The silica gel was impregnated by the gradual dropwise addition of a solution of $CaCl_2$ (purity grade) with a specific concentration with continuous stirring of the sample. After the end of impregnation, the sample was rapidly washed on a filter and dried at 200 °C to a constant weight. The composition of the sample was found from the change in the silica gel weight. We obtained samples containing calcium chloride with the mass fraction (*m*)

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 781—785, May, 2000.

of the salt equal to 0.038, 0.054, 0.080, 0.116, 0.157, 0.230, 0.314, 0.360, 0.410, and 0.460 and one sample containing lithium bromide with the mass fraction of the salt equal to 0.480.

Isotherms of nitrogen adsorption—desorption were measured volumetrically at the boiling temperature of liquid nitrogen. Prior to measurement, the samples were evacuated for 5 h at 150 °C. Three parallel measurements were carried out for each sample.

Results and Discussion

Fractal dimension of silica gel. Let us consider the published data on silica gel. Figure 1 presents the porosity (ε) as a function of the internal surface (S) for xerogels obtained under different conditions.[9,10] Let us relate each value of the internal surface to some linear scale, which is introduced from the concepts of dimensionality as ε/S. Then presenting the corresponding data on the acidic (see Fig. 1, *1*) and neutral (see Fig. 1, *2*) media in the coordinates $\log S$—$\log(\varepsilon/S)$, we obtain a straight line (correlation coefficient $r^2 = 0.995$) in almost the whole interval (1—100 nm) of changing the linear scale ε/S (see insert in Fig. 1). The fractal dimension of silica gel equal to 2.71 is found from the slope of this straight line. For the data for an alkaline medium (see Fig. 1, *3*) and neutral aqueous solution (see Fig. 1, *4*), a similar procedure results in the fractal dimension of 2.66—2.73 in the scale interval of 1—10 nm. Therefore, the value of 2.7 can be accepted as the estimation characterizing the self-similarity of the texture of silica gel of a specific type.

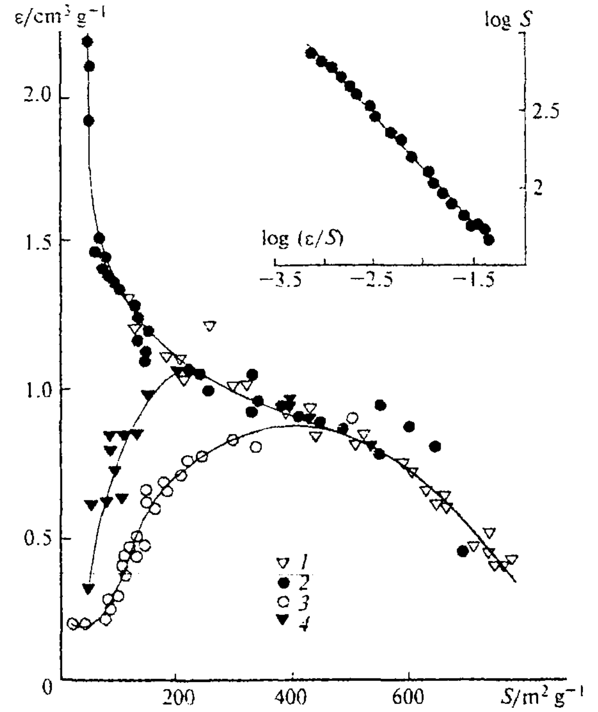

Fig. 1. Interrelation between the internal surface (S) and porosity (ε) of silica gels. Xerogels were prepared by the hydrothermal treatment of the gel in acidic (*1*), neutral (*2*), and alkaline (*3*) media and in a neutral aqueous solution (*4*). For experimental data, see Refs. 9 and 10. The dependence of the surface (S) on linear scale (ε/S) in logarithmic coordinates is presented in the inset.

The silica gel texture changes by various factors. The isotherms of low-temperature adsorption of nitrogen on silica gel subjected to intense mechanical pre-treatment in a centrifugal planetary-type mill are presented in the literature.[11,12] We processed these isotherms by the second procedure of those mentioned above. All samples in the interval of pore radii of 1—10 nm appear to have a pronounced linear region in the coordinates $\log S_{\text{meso}}$—$\log \rho_{\text{K}}$, from whose slope we found the fractal dimension of the internal surface of mesopores of the samples. Based on this analysis, we may conclude the following. The starting silica gel has the fractal dimension of ~2.70 at the pore radii from 1 to 10 nm. When the duration of mechanical treatment increases, the fractal dimension in this interval of pore radii increases rapidly to reach in several min the limiting value of ~3. For the sample subjected to a long mechanical treatment (for 45 min), the fractal dimension again decreases to ~2.65, *i.e.*, to almost the initial value (Fig. 2). Unlike other samples, silica gel after intense 45-min mechanical treatment becomes fractal in the whole interval of mesopore radii (1—100 nm). The change in the fractal dimension and fractality interval upon changing the duration of intense mechanical treatment indicates a deep internal rearrangement of the silica gel texture. This is also indicated by the dependence of the fractal dimension on the mesopore surface (see inset in Fig. 2).

Texture of silica gel-based composite adsorbents. Water-selective composite adsorbents prepared by the impregnation of the silica gel matrix with solutions of alkali and alkali-earth metal salts combine a high sorp-

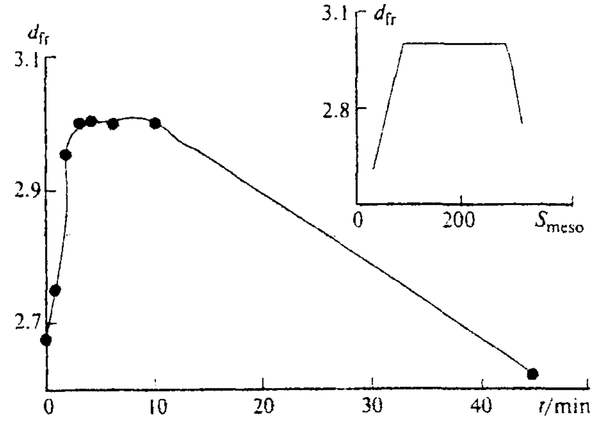

Fig. 2. Fractal dimension (d_{fr}) of silica gels as a function of the duration (t) of mechanical treatment (for processing of the nitrogen adsorption isotherms, see Refs. 11 and 12). The dependence of the fractal dimension on the surface area of mesopores (S_{meso}) is shown in the inset.

tion capacity with respect to water due to the presence of a hygroscopic salt with the physicomechanical properties of the silica gel matrix. They can be used in adsorption thermal pumps, for example, in refrigerators.[13]

The adsorbent texture is important for quantitative estimation of the parameters of an adsorption thermal pump, such as efficiency and intensity.[14] Since the texture of the porous matrix remains unchanged during the preparation of the composite adsorbent, the type and amount of the salt dispersed in pores of the supporting matrix are determining parameters in syntheses of adsorbents.[15]

We studied the texture of composite adsorbents by low-temperature nitrogen adsorption for the KSK coarse-pore silica gel containing different amounts of salts. A special software program package was used for processing of the experimental adsorption and desorption isotherms.[16]

Let us estimate the limiting amount (m_{lim}, in mass fractions) of solid calcium chloride, which can be introduced into the silica gel matrix. From the conditions of material balance, we obtain

$$(1 - m_{\text{lim}})\cdot\varepsilon_0 d = m_{\text{lim}}, \qquad (1)$$

where ε_0/cm^3 g^{-1} is the porosity of starting silica gel, and d/g cm^{-3} is the density of calcium chloride that changes with the amount of water per calcium chloride molecule from 1.68 for $CaCl_2\cdot 6H_2O$ to 2.51 for anhydrous $CaCl_2$.[17] According to our measurements, the porosity of starting silica gel is equal to 0.96 cm^3 g^{-1}. Therefore, the limiting filling value m_{lim} calculated by Eq. (1) ranges from 0.69 to 0.71, depending on the density of anhydrous $CaCl_2$ used in the calculation. The experimental dependence of the porosity on the mass fraction of calcium chloride introduced into the silica gel matrix is presented in Fig. 3. The straight line (correlation coefficient $r^2 = 0.98$) that approximates the experimental data crosses the axis m at the point ~0.62. Interpolation by third-power polynomials of the experimental values of the specific surface by BET and the mesopore surface at different mass fractions of $CaCl_2$ (Fig. 4, correlation coefficients r^2 = 0.98—0.99) results in almost the same value of limiting filling $m_{\text{lim}} \approx 0.63$. The difference between the estimation by formula (1) and experimental data can be attributed to the fact that the salt particles in pores of the silica gel matrix possess an intrinsic porosity.

Let us elucidate in which pores the salt is localized. It follows from processing of the nitrogen adsorption isotherms that the mesopore radii in the nonimpregnated silica gel range from 1 to 100 nm, and the micropore volume is ~0.1 cm^3 g^{-1}. After the salt was introduced into the silica gel pores, the interval of mesopore radii remained unchanged but the micropore volume virtually cannot be estimated. Let us determine the volume of pores (ε^*) occupied by the salt from the experimental values of porosity ε and the balance of pore volumes in the composite adsorbent with the mass fraction m of calcium chloride:

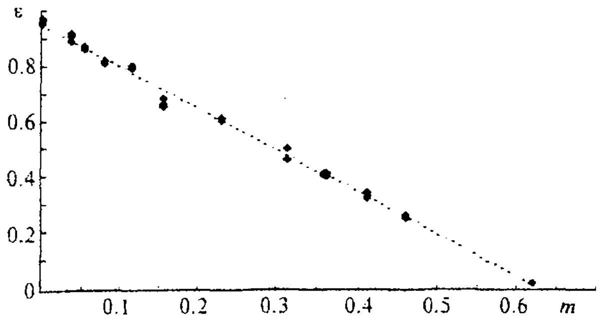

Fig. 3. Porosity (ε) of the composite adsorbent as a function of the mass fraction (m) of the salt.

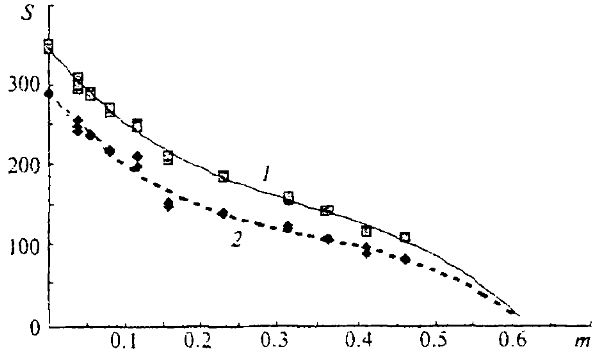

Fig. 4. Surface area (S) of the composite adsorbent as a function of the mass fraction (m) of salt: *1*, specific surface by the BET method; and *2*, mesopore surface.

$$\varepsilon^* = (1 - m)\varepsilon_0 - \varepsilon. \qquad (2)$$

The dependence of m on ε^* calculated by Eq. (2) taking into account the experimental data (see Fig. 3) is presented in Fig. 5. The correlation coefficient of the linear approximation is r^2 = 0.97. The density of the salt dispersed in pores is found from the slope of the straight line: d = 1.75 g cm^{-1}. It should be expected from the procedure used for the pretreatment of the samples (evacuation for 5 h at 150 °C) that the pores contain the almost anhydrous salt with a density of ~2.51 g cm^{-3}.[17] The difference can be attributed to the overestimation of the pore volume ε^* occupied by the salt if we assume that $CaCl_2$ particles do not penetrate into the micropores but only block them to some extent. The volume of "blocked" pores (ε_b) at different mass fractions of calcium chloride can easily be calculated from the correlation

$$\varepsilon_b = \varepsilon^* - m/d. \qquad (3)$$

We failed establish any correlation between the volume of blocked pores ε_b and the mass fraction m of the salt in silica gel, but the ε_b value appeared to be lower

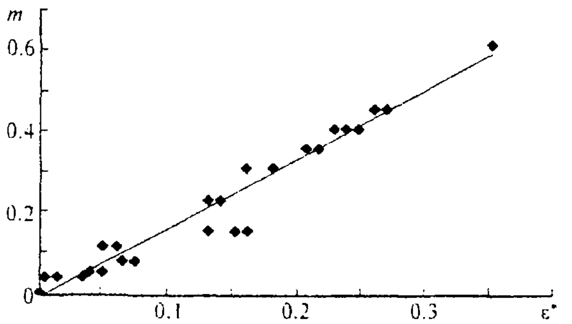

Fig. 5. Estimation of the density (ε^*) of the salt dispersed in silica gel pores.

than 0.06 $cm^3 g^{-1}$ in all cases, *i.e.*, it coincides with the micropore volume of the starting silica gel matrix. Thus, the salt introduced into the silica gel matrix does not penetrate into micropores and is present in mesopores.

Fractal dimension of composite adsorbents. The calculation of the fractal dimension (d_{fr}) from the experimental nitrogen adsorption isotherms showed that the interval of linear approximation in the coordinates "logarithm of mesopore surface—logarithm of the Kelvin radius" for all samples under study was the same and amounted to 1—10 nm. Thus, the interval of adsorbent fractality is mainly determined by the texture of the initial matrix. Meanwhile, the fractal dimension depends on the saturation of the porous matrix with a salt. For nonimpregnated silica gel, it is equal to ~2.70. Assuming that the completely impregnated sample has the fractal dimension corresponding to the fractal dimension of bulky $CaCl_2$, *i.e.*, ~3, we can plot a correlation function between the d_{fr} and m values with a minimum at the ~20% content of $CaCl_2$ (Fig. 6).

The dependence of the fractal dimension on the mass fraction of salt can be explained by the fact that an increase in the salt content in the silica gel matrix changes the character of filling of the pore volume with calcium chloride. In the samples with a low content of $CaCl_2$, the salt is localized predominantly in smaller mesopores, because under the capillary forces the solution of salt that impregnates silica gel is distributed in the regions with the maximum surface curvature, *i.e.*, in pores with the minimum radius. In the course of drying recrystallization occurs that is accompanied by local smoothening of the relief of the matrix surface up to the full filling of mesopores of some limiting radius with salt clusters (the left descending branch of the curve in Fig. 6). The point of a minimum corresponds to the sample in which the salt fills mesopores of radii that do not exceed the mentioned limiting value.

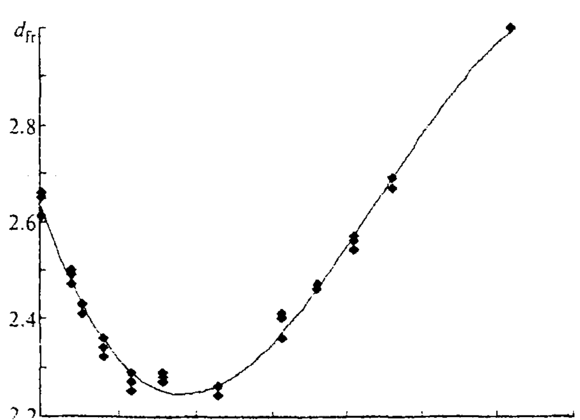

Fig. 6. Fractal dimension (d_{fr}) of the composite adsorbent as a function of the mass fraction (m) of the salt.

When the salt content in silica gel further increases, the salt fills mesopores of greater radii. In addition, individual $CaCl_2$ crystals are formed on the surface of large mesopores due to the energy surface inhomogeneity. The texture inhomogeneity of the salt crystals leads to the enhancement of the microrelief and, hence, to an increase in the fractal dimension of the internal surface (the right ascending branch of the curve in Fig. 6).

Peculiarities of mass transfer in a composite adsorbent particle. The character of "packing" of the internal surface in the porous particle bulk makes it accessible for mass transfer. It can be assumed that an increase in the fractal dimension decreases the effective diffusion coefficient to the same extent as the pore tortuosity (β). In fact, the fractality interval corresponds to the spectrum of diffusion times ρ_K^2/D (D is the molecular diffusion coefficient) that characterizes the distribution of local stagnant zones in an arbitrary point of the sorbent. In the first approximation, the fractality factor can be introduced into a known formula for the effective diffusion coefficient similarly to the tortuosity factor

$$D_{ef}/D_0 = \varepsilon/(d_{fr}\beta), \tag{4}$$

where D_0 is the molecular diffusion coefficient in the volume, and β is the tortuosity factor. From Eq. (4) using the data in Figs. 3 and 6, we obtain in the interval $0 < m < 0.62$ an approximation that takes into account the influence of the mass fraction of the salt introduced on the effective dimensionless diffusion coefficient $D_{ef}\beta/D_0$ (Fig. 7).

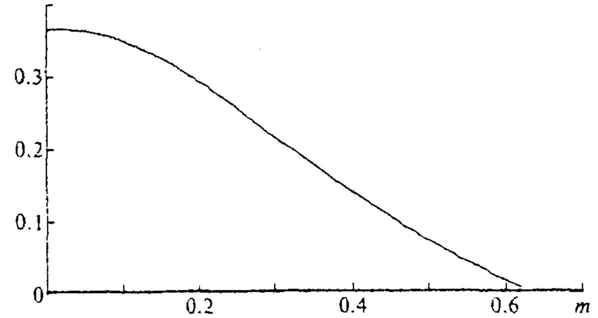

Fig. 7. Effective dimensionless diffusion coefficient ($D_{ef}\beta/D_0$) as a function of the mass fraction (m) of the salt.

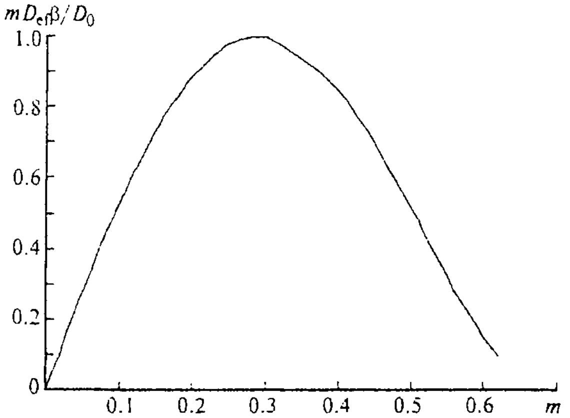

Fig. 8. Utilization efficiency of the adsorbent volume (in fractions of the maximum efficiency) as a function of the mass fraction (m) of the salt.

In adsorption heat pumps where water is used as the working body, under other equivalent conditions, the moisture capacity of the composite adsorbent is proportional to the amount of the salt introduced. By contrast, the effective diffusion coefficient of vapor decreases as the salt content in the adsorbent increases (see Fig. 7). The influence of both factors results in a substantially nonlinear dependence of the efficiency of the volume utilization of the adsorbent grain on the salt content. Therefore, an optimum composition of the composite adsorbent should exist for which the factor of utilization of the grain volume is maximum. The utilization efficiency of the adsorbent grain volume can qualitatively be characterized by the product of the effective diffusion coefficient and moisture capacity of the adsorbent ($mD_{ef}\beta/D_0$). The utilization efficiency of the adsorbent grain volume as a function of the mass fraction of the introduced salt calculated from the experimental data presented above is shown in Fig. 8. The adsorbent with the salt content of ~28 wt.% corresponds to the maximum efficiency.

Thus, based on the available experimental data, we may suggest the presence of fractal peculiarities in the silica gel texture and related composite materials in the radius interval of 1—10 nm. Taking into account these peculiarities in the synthesis of composite materials makes it possible to optimize their functional properties.

The authors thank the Director of the Laboratory at the G. K. Boreskov Institute of Catalysis (Siberian Branch of the Russian Academy of Sciences) Yu. I. Aristov for providing several samples for studying the texture.

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Received July 7, 1999