

Method of Discrimination of Surface Fractality

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Received August 31, 1992; accepted January 7, 1993

A simple method for the discrimination of surface fractality is proposed. This method is based on the comparison of the nitrogen adsorption isotherm on a given sample with the "standard" isotherm on a smooth surface. The proposed comparative method makes it possible to determine the lower limit of the scale range of surface fractality. A thermodynamic method is recommended as a complement to fractal analysis in the scale range of about 10–1000 Å. The results of the investigation of surface roughness are presented with examples of typical samples of silica gels, porous glasses, apatite, and coal. © 1993 Academic Press, Inc.

INTRODUCTION

After the pioneering works of Pfeifer and Avnir (1), who proposed an adsorption method for the determination of surface fractal dimension, numerous adsorbents have been claimed as fractals. Published data point toward the fractal properties of active carbons, coals, blacks, aerogels, porous glasses, silica gels, etc. By using adsorption data, one can analyze pore structure in the scale range from molecular sizes to 1000 Å. Different techniques and calculating procedures have been developed. Information about surface roughness in the scale range of molecular sizes (usually less than 10 Å) can be obtained by means of a method of molecular tiling (1), which uses adsorption data in the region of monolayer adsorption. The scale range from 10–20 Å to 1000 Å can be investigated by means of a thermodynamic method (2) and the methods based on the analysis of pore size distribution (1). These methods employ data in the region of capillary condensation. Different methods have been developed to analyze the intermediate region of polymolecular adsorption (3–6). All known methods do not give a definite answer to whether or not a given surface has fractal properties, but only point toward such a possibility. Moreover they are based on certain assumptions which are valid only within a certain scale range.

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We propose a simple method for the discrimination of surface fractality. This method is based on the nitrogen adsorption isotherm in the region of polymolecular adsorption and corresponds respectively to the scale range from molecular sizes to 100 Å. Employment of this method enables one to obtain information on a lower limit of scales of possible fractality. The thermodynamic method is a complement to testify for or against the fractal properties of adsorbents on larger scales up to 1000 Å. The conclusions obtained from nitrogen adsorption isotherms are important for a critical analysis of the results obtained by different adsorption methods and also nonadsorption methods such as small angle scattering techniques (7).

THEORY

It is well known (8) that low temperature (at 77 K) adsorption isotherms of nitrogen on numerous adsorbents of different origin obey a single empirical law in the region of polymolecular adsorption up to the beginning of capillary condensation. When this takes place, the isotherm measured on a porous solid is proportional to the so called "standard" isotherm or *t*-curve of de Boer, which corresponds to a nonporous smooth surface,

$$N(P/P_0) = N_{mi} + S_{me} N_{st}(P/P_0), \quad [1]$$

where $N(P/P_0)$ (mmol/g) is the adsorption on a given sample, $N_{st}(P/P_0)$ (mmol/m²) is the adsorption on a smooth surface of unit area at the same relative pressure (P/P_0), an excess N_{mi} (mmol/g) is the adsorption in micropores, and a factor of proportionality, S_{me} (m²/g), is the specific surface area of mesopores. Several comparative methods for calculating the specific surface area are based on this property of nitrogen isotherms. As we are considering here porous materials without any appreciable amount of micropores, the value of S_{me} does not differ significantly from the BET surface area. At the same time, the value of N_{mi} is negligible relative to the total adsorption as $P/P_0 \rightarrow 1$ and may be either positive or negative depending on the peculiarities of submonolayer adsorption.

A low sensitivity of the standard isotherm $N_{st}(P/P_0)$ to the origin of solid surface is the advantage of nitrogen as a probe gas. The universality of $N_{st}(P/P_0)$ implies that the adsorbate-adsorbent interactions as well as the chemical and geometrical surface heterogeneity on molecular level affect the nitrogen adsorption only in the early stages and are reduced during the monolayer filling. We are not in a position in this brief paper to discuss thoroughly why this remarkable feature of nitrogen adsorption isotherms occurs for a number of typical nonporous solids. A possible explanation proposed by Sing (9) is that the quadrupole-quadrupole interactions between adsorbed molecules of nitrogen predominate over the adsorbate-adsorbent interactions. This is one reason why the influence of the surface chemical origin on nitrogen adsorption is not so intrinsic as for other adsorbates and why nitrogen is an ideal adsorbate for an analysis of the geometrical structure of porous solids.

We propose to use nitrogen adsorption isotherms for the discrimination of surface irregularities, particularly fractal-type irregularities. The idea is as follows. The existence of surface irregularities of a size more than the molecular diameter of nitrogen ($\sim 4 \text{ \AA}$) should lead to a deviation from the linear relationship (Eq. [1]) in the region of polymolecular adsorption. On the other hand, if the adsorption isotherm on an explored surface obeys Eq. [1] over a certain range of relative pressures, then it can be concluded that in the corresponding range of scales the given surface is similar to a smooth surface and therefore not fractal. In the region where the experimental nitrogen isotherm does not fit the empirical law (Eq. [1]) it is possible to investigate fractal properties using corresponding models. When this occurs, the upper limit of validity of Eq. [1] is the lower limit of possible fractality.

To provide a quantitative comparison among surfaces, it is convenient to employ a certain algebraic equation for the standard isotherm. Because of its empirical nature, there is no reliable theoretical equation. The Frenkel-Halsey-Hill (FHH) equation for a standard nitrogen isotherm,

$$N_{st}(P/P_0) = K/(\ln(P_0/P))^{1/m}, \quad [2]$$

describes numerous experimental data quite well (8). Only in exceptional cases, e.g., for adsorption on Au(111) (10), does the exponent m equal 3, corresponding to the theoretical value for adsorption ruled by adsorbate-adsorbent dispersion interactions. For the most part, the empirical FHH equation with $2 < m < 3$ is used to fit experimental data. Dubinin *et al.* (11) recommend Eq. [2] with parameters $m = 2.24$, $K = 0.0157 \text{ mmol/m}^2$ as a standard nitrogen isotherm on various inorganic and carbon nonporous solids in the range of relative pressures from ~ 0.1 to ~ 0.9 . Our investigations also confirm satisfactory agreement between the FHH equation with these parameters and nitrogen isotherms on a number of mesoporous solids in the region of polymolecular

adsorption. The standard isotherm in this form is employed here.

The deviations from Eq. [1] are caused by the capillary condensation in mesopores of size more than $\sim 10 \text{ \AA}$. The fractal properties on the scales more than $10\text{--}20 \text{ \AA}$ can be investigated on the basis of nitrogen adsorption isotherms by means of a thermodynamic method. The thermodynamic method employs the following equation valid for capillary condensation on a fractal surface characterized by the fractal dimension d_{fs} (2):

$$\log[S_{lg}(P/P_0)] = \text{const} - (d_{fs} - 2)\log[a_c(P/P_0)]. \quad [3]$$

Here, $S_{lg}(P/P_0)$ is the area of condensed nitrogen-vapor equilibrium interface at a given value of relative pressure calculated by integrating the isotherm from the current value, $N(P/P_0)$, to the maximal value, N_{max} , available as $P/P_0 \rightarrow 1$ according to the Kiselev equation,

$$S(P/P_0) = (RT/\sigma) \int_{N(P/P_0)}^{N_{max}} \ln(P_0/P) dN, \quad [4]$$

where σ is the surface tension of liquid nitrogen, R is the universal gas constant, and T is the temperature. $a_c(P/P_0)$ is the mean radius of curvature of this interface calculated by the Kelvin equation,

$$a_c(P/P_0) = 2\sigma v_m / RT \ln(P_0/P), \quad [5]$$

where v_m is the molar volume of liquid nitrogen. In fact, Eq. [3] represents the common relationship for the area of a fractal surface; $S_{lg}(P/P_0)$ is interpreted as the area of solid surface measured by a yardstick of size equal to $a_c(P/P_0)$. For details of the thermodynamic method see (2).

The combination of the comparative method, based on Eq. [1], and the thermodynamic method, based on Eq. [3], makes it possible to discriminate the fractal properties of mesoporous materials in the range of scales from $\sim 4 \text{ \AA}$ (molecular diameter of nitrogen) to $\sim 1000 \text{ \AA}$ on the basis of one experimental nitrogen adsorption isotherm.

EXPERIMENTAL EXAMPLES

We will demonstrate the effectiveness of proposed methods for two different types of rough surfaces: (i) mesoporous solids with rough internal surface in the limited scale range (with particular examples of silica gel and porous glass); (ii) almost nonporous particles with rough external surface (with particular examples of natural apatite and coal). For these systems, it turns out to be possible not only to determine the lower scale limit of surface roughness by means of the comparative method but also to confirm the surface fractality by means of the thermodynamic method. Furthermore, for the sake of completeness, we will present the examples with

“negative” results, when the analysis of the nitrogen adsorption isotherm gives a reliable conclusion about the absence of surface fractal properties. This is why we regard our method as a method for discrimination of surface fractality.

Mesoporous Solids

LiChrospher Si 300 (supplied by E. Merck, Darmstadt, Germany) is a mesoporous support of a family of silica gels. Like most of the silica gels, the particles of LiChrospher Si 300 consist of the primary particles of size up to several hundreds of Å. The voids between primary particles are linked together and constitute a pore network available for the adsorbing species. The pore size distribution is relatively narrow with a nominal pore diameter of 300 Å (Si 300), specific (BET) surface area $S_{\text{BET}} = 111 \text{ m}^2/\text{g}$, and pore volume $V_0 = 0.996 \text{ cm}^3/\text{g}$ (12). The low temperature nitrogen adsorption isotherm on the sample of LiChrospher Si 300 employed is plotted in Fig. 1a by using traditional coordinates: adsorption (N , in mmol/g sample) versus relative pressure (P/P_0).

The adsorption and the desorption branches form well defined hysteresis loop of type H1 by the IUPAC classification (8). Such a hysteresis loop with clear boundaries is characteristic for a number of silica gels and other mesoporous solids and indicates a relatively narrow mesopores size distribution in a sample. The reversible part of the isotherm below the hysteresis corresponds to the mono- and polymolecular adsorption on the surface of mesopores and to reversible capillary condensation in the surface indentations.

In Fig. 1b the adsorption isotherm $N(P/P_0)$ is replotted employing standard coordinates of the comparative method (Eq. [1]) as a function of the standard nitrogen adsorption isotherm $N_{\text{st}}(P/P_0)$ (mmol/m²). The isotherm is a linear function of the standard isotherm $N_{\text{st}}(P/P_0)$ up to the relative pressure $P/P_0 = 0.42$, which corresponds to capillary condensation in pores of size $\sim 10 \text{ Å}$ in conformity with the Kelvin equation (Eq. [5]). In response to Eq. [1], this value is the upper limit of similarity of the adsorption process on the explored sample and on a smooth surface. The slope of the linear part of the plot is related to the value of mesopore surface area $S_{\text{me}} = 110 \text{ m}^2/\text{g}$, which is in close agreement with the BET specific surface area.

The departures of the comparative plot from linearity are observed long before the beginning of capillary hysteresis, which occurs at $P/P_0 = 0.85$. Such behavior suggests the existence of surface roughness on the scales more than 10 Å, which is quite less than the nominal pore diameter equal to 300 Å. In this region the process of capillary condensation in the surface indentations and pores predominates and to assess the surface fractal properties of the sample we have used the thermodynamic method (Eqs. [3]–[5]). In Fig. 1c the two plots, based on the adsorption and desorption branches of the isotherm, respectively, are drawn employing

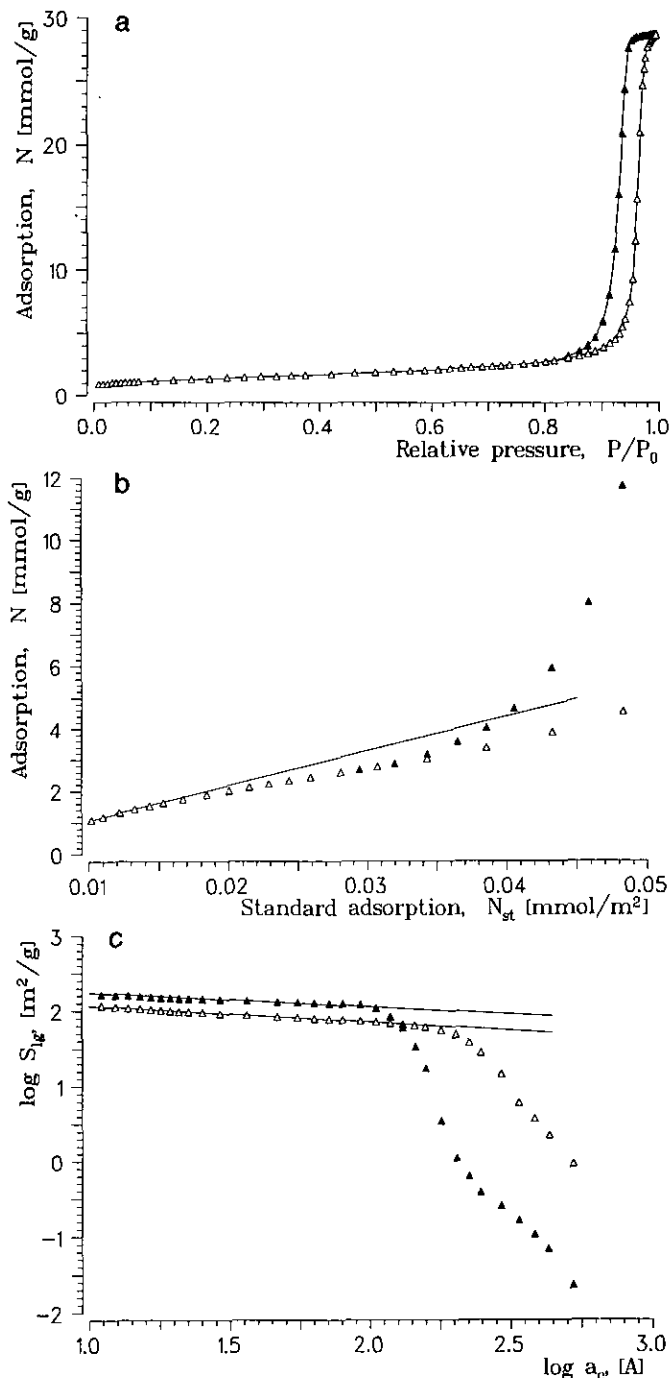


FIG. 1. Fractal analysis of a sample of silica gel LiChrospher 300. (a) Low temperature nitrogen adsorption isotherm, $N(P/P_0)$; (Δ) adsorption, (\blacktriangle) desorption. (b) comparative plot $N(P/P_0)$, experimental adsorption isotherm [(Δ) adsorption, (\blacktriangle) desorption]; $N_{\text{st}}(P/P_0)$, standard adsorption isotherm. The straight line corresponds to the linear regression of the initial part of the plot in the range of relative pressures 0.07–0.42 with the slope $S_{\text{me}} = 110 \text{ m}^2/\text{g}$. (c) Results of calculations, by means of the thermodynamic method, of the surface area, S_{fr} , of condensed nitrogen as a function of the current mean radius of curvature, a_c ; (Δ) calculated from adsorption data, (\blacktriangle) calculated from desorption data. The straight lines correspond to the linear regression in the scale range 15–150 Å for the adsorption plot with the surface fractal dimension $d_{\text{fs}} = 2.22$ and in the scale range 15–100 Å for the desorption plot with the surface fractal dimension $d_{\text{fs}} = 2.20$.

standard coordinates of the thermodynamic method, $\log S_{lg} - \log a_c$ (Eq. [3]).

The region of fractality corresponds to the linear part of the $\log S_{lg} - \log a_c$ plot. The plot, based on the adsorption branch, testifies to the fractal properties over the scale range from at least ~ 15 to ~ 150 Å, where it can be regarded as linear. The result of linear regression in this range is presented by a straight line. The slope corresponds to the surface fractal dimension $d_{fs} = 2.22$. The plot, based on the desorption branch, is linear in a slightly narrower scale range, up to ~ 100 Å, that can be related to the influence of the irreversible desorption from mesopores in the hysteresis region. Linear regression of the desorption plot gives $d_{fs} = 2.20$. The results obtained by using the adsorption and desorption data are quite close. However, because the adsorption branch in the given scale range corresponds to the reversible capillary condensation, we suppose the adsorption data more reliable.

We emphasize that the lower limit of fractality, $a_{min} = 15$ Å is related to the value of relative pressure $P/P_0 = 0.52$, which is a little bit more than the upper limit of linearity of the comparative plot. The upper limit of fractality, $a_{max} = 150$ Å, is comparable with the mean radius of mesopores. We would expect this type of fractality in such mesoporous materials as LiChrospher Si 300. Here the fractality reflects the roughness of primary particles of SiO_2 but not the geometry of the pore network. This is characteristic for a porous structure, where the pore network is constituted by channels with a relatively narrow size distribution but, at the same time, with rough walls. In this case, it is obvious that the mean radius of pore channels is the upper limit of possible fractality.

CPG-240 (supplied by Community Bureau of Reference, Brussels, Belgium) is a mesoporous adsorbent of a family of controlled porous glasses. The pore structure in controlled porous glasses is formed by channels which constitute a pore network in solid matrix. These materials are characterized by extremely narrow pore size distribution and are regarded as candidates to the reference materials. The notation "240" reflects the nominal pore diameter. For the considered sample of CPG-240 the specific (BET) surface area $S_{BET} = 92$ m^2/g and the pore volume $V_0 = 1.03$ cm^3/g . The low temperature nitrogen adsorption isotherm, N , is presented in Fig. 2a as a function of the relative pressure, P/P_0 , and in Fig. 2b as a function of standard isotherm, $N_{st}(P/P_0)$. The results of fractal analysis by means of the thermodynamic method are presented in Fig. 2c.

These results are quite similar to those for the sample of LiChrospher Si 300 (Fig. 1). The comparative plot, Fig. 2b, is linear in the range of relative pressures, P/P_0 , from 0.07 to 0.42 with a slope related to the value of mesopore surface area $S_{me} = 93$ m^2/g in close agreement with the BET surface area. The lower limit of surface roughness is about 10 Å.

The $\log S_{lg} - \log a_c$ plot (Fig. 2c) highlights the fractal properties over the scale range from ~ 10 to ~ 200 Å with

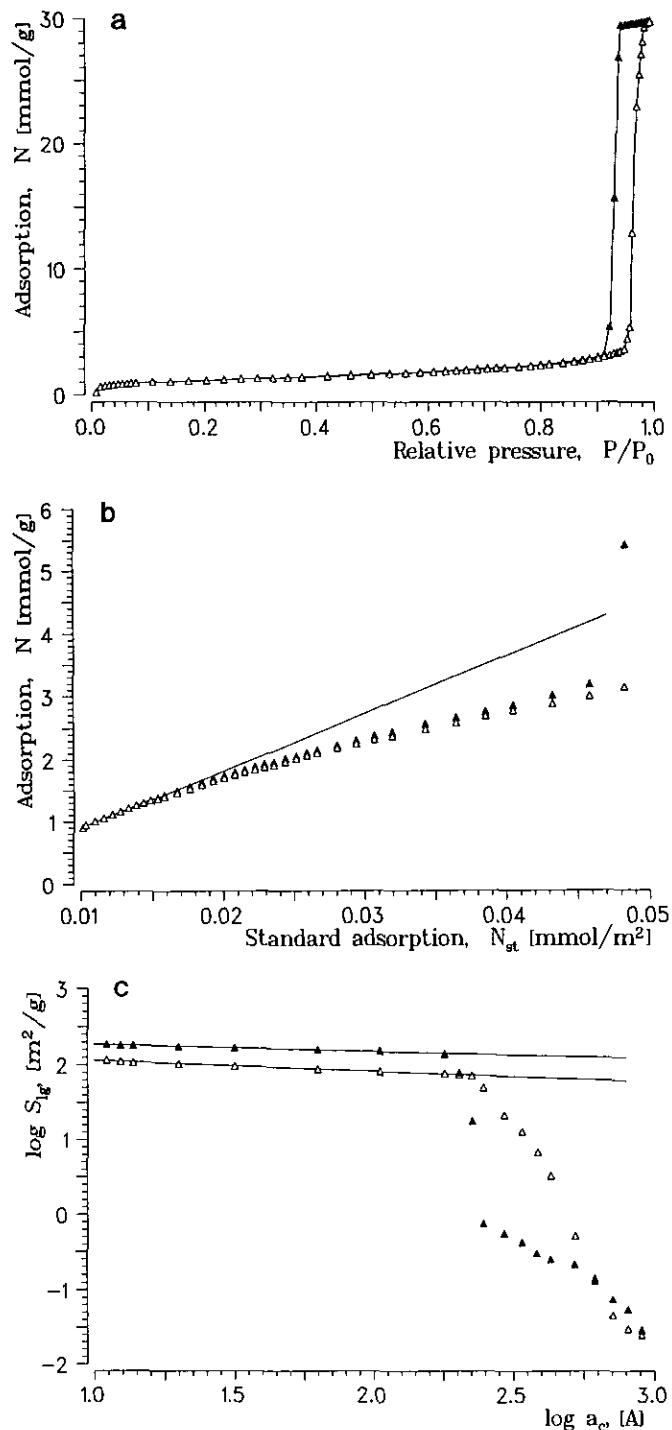


FIG. 2. Fractal analysis of a sample of controlled porous glass CPG-240. (a) Low temperature nitrogen adsorption isotherm [(Δ) adsorption, (\blacktriangle) desorption]. (b) Comparative plot [(Δ) adsorption, (\blacktriangle) desorption]. The straight line corresponds to the linear regression of the initial part of the plot in the range of relative pressures 0.07–0.42 with the slope $S_{me} = 93$ m^2/g . (c) Results of calculations, by means of the thermodynamic method [(Δ) calculated from adsorption data, (\blacktriangle) calculated from desorption data]. The straight lines correspond to the linear regression in the scale range 10–200 Å for the adsorption plot with the surface fractal dimension $d_{fs} = 2.14$ and in the scale range 10–120 Å for the desorption plot with the surface fractal dimension $d_{fs} = 2.10$.

the surface fractal dimension $d_{fs} = 2.14$. These parameters are related to the plot, based on the adsorption branch. The plot, based on the desorption branch, is linear over the scale range up to $\sim 120 \text{ \AA}$, and the corresponding value of $d_{fs} = 2.10$. Hence, we can conclude that the roughness of the internal surface of sample CPG-240 can be characterized by using the fractal dimension in the scale range up to the characteristic size of pore channels. Here, as well as for Li-Chrospher Si 300, the fractality reflects the roughness of the pore walls but not the geometry of pore network.

Similar results have been obtained for other mesoporous solids with relatively wide pores (hundreds of \AA), e.g., for polybutadiene coated silica (12). The surface of mesopores in such materials can demonstrate fractal properties in the scale range from the upper limit of linearity of the comparative plot up to the characteristic size of pore channels.

Particles with Rough External Surface

Natural apatite is a typical example of fine particles with very rough external surface and polydisperse pore size distribution but also with low specific surface area and low porosity. The low temperature nitrogen isotherm (supplied by S. Ostapenko, Mine Institute, Russian Academy of Sciences, Apatity, Russia) for a particular sample of apatite with the BET surface area of $0.11 \text{ m}^2/\text{g}$ is plotted in Fig. 3a as a function of relative pressure P/P_0 . The hysteresis loop, formed by the adsorption and desorption branches, is of type H3 by the IUPAC classification (8). It is relatively narrow and the boundaries of the hysteresis region cannot be clearly identified, as is characteristic for such materials.

In Fig. 3b the adsorption isotherm is plotted in the coordinates of the comparative method. The initial linear region shows that up to the relative pressure $P/P_0 = 0.49$ (that corresponds to the upper limit of linearity), the adsorption isotherms on a given sample and on a smooth surface are similar. The slope of the linear part of the plot corresponds to the value of mesopore surface area of $S_{mc} = 13 \text{ m}^2/\text{g}$. When $P/P_0 > 0.49$, the process of capillary condensation predominates; to assess the fractal properties of the surface under consideration we have used the thermodynamic method (Eqs. [3]–[5]).

The two plots ($\log S_{lg} - \log a_c$) in Fig. 3c based on adsorption and desorption isotherms testify to the fractal properties in the scale range from 17 to 800 \AA , where both plots can be regarded as linear. The value of fractal dimension can be estimated as $d_{fs} = 2.68 \pm 0.02$. We emphasize that for this sample the inner limit of fractality, $a_{min} = 17 \text{ \AA}$, is related to the value of relative pressure $P/P_0 = 0.57$, which is slightly higher than the upper limit of linearity of the comparative plot.

As another typical example of particles with low porosity, the low temperature nitrogen adsorption isotherm (supplied by P. Ravikovich, Research Institute of Chlorine Institute, Moscow, Russia) on a certain sample of natural coal with

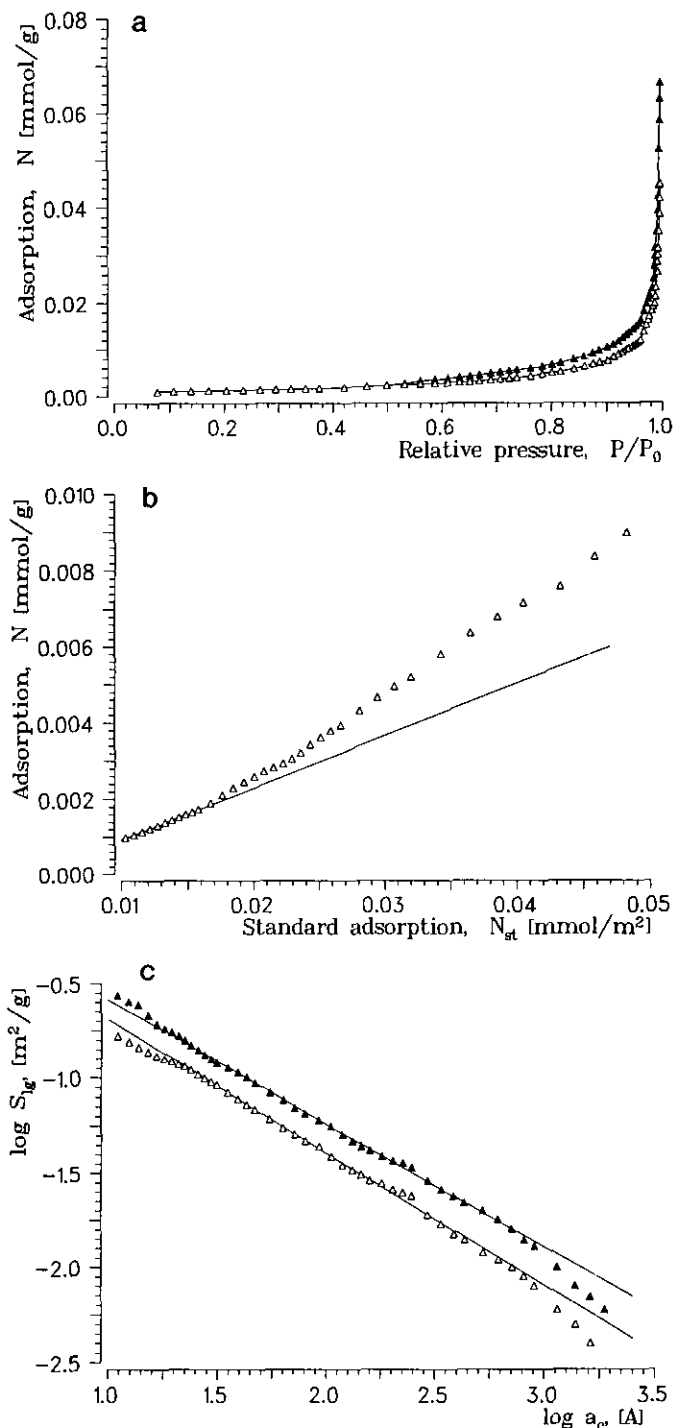


FIG. 3. Fractal analysis of a sample of natural apatite. (a) Low temperature nitrogen adsorption isotherm [(Δ) adsorption, (\blacktriangle) desorption]. (b) Comparative plot [(Δ) adsorption, (\blacktriangle) desorption]. The straight line corresponds to the linear regression of the initial part of the plot in the range of relative pressures 0.07–0.49 with the slope $S_{mc} = 0.13 \text{ m}^2/\text{g}$. (c) Results of calculations by means of the thermodynamic method [(Δ) calculated from adsorption data, (\blacktriangle) calculated from desorption data]. The straight lines correspond to the linear regression in the scale range 17–800 \AA for the adsorption plot with the surface fractal dimension $d_{fs} = 2.65$ and in the scale range 17–800 \AA for the desorption plot with the surface fractal dimension $d_{fs} = 2.70$.

specific BET surface area $S_{\text{BET}} = 4.63 \text{ m}^2/\text{g}$ and pore volume $V_0 = 0.035 \text{ cm}^3/\text{g}$ is presented in Fig. 4a.

The slope of the linear part of the comparative plot (Fig. 4b) corresponds to the mesopore surface area of $S_{\text{me}} = 4.88 \text{ m}^2/\text{g}$. The lower limit of the surface roughness estimated from the comparative plot equals 12 \AA . The fractal analysis by means of the thermodynamic method (Fig. 4c) leads to the value of surface fractal dimension $d_{\text{fs}} = 2.43 \pm 0.01$ in the scale range $25\text{--}500 \text{ \AA}$. Moreover, in this case the results based on the adsorption and desorption data nearly coincide.

Here the fractal dimension characterizes the roughness of the external surface of the particles in a relatively wide scale range. It is worth noting that the upper limits of fractality in these samples (especially in the case of apatite) tend to be close to the upper boundary of sensibility of the adsorption measurements. Therefore the real scale range of fractality may be still wider.

"Negative" Examples

The examples presented in Figs. 1–4 are "positive" ones: the similarity of the experimental low temperature nitrogen adsorption isotherm and the standard isotherm for a smooth surface is limited by a particular value of the relative pressure and this value corresponds to the lower scale limit of surface roughness which turns out to be a fractal type roughness. In Fig. 5 we present negative examples, when the comparative analysis highlights the smoothness of the explored surface and discriminates the fractal properties.

Three typical samples are considered: (i) a sample of the silica gel LiChrosorb Si 60 (Silica-60, research product of E. Merck) with specific BET surface area $S_{\text{BET}} = 504 \text{ m}^2/\text{g}$ and pore volume $V_0 = 0.77 \text{ cm}^3/\text{g}$; (ii) a sample of the controlled porous glass CPG-120 with specific BET surface area $S_{\text{BET}} = 120 \text{ m}^2/\text{g}$ and pore volume $V_0 = 0.63 \text{ cm}^3/\text{g}$ (supplied by Community Bureau of Reference, Brussels, Belgium); (iii) a sample of the porous glass Vycor 7930 with specific BET surface area $S_{\text{BET}} = 201 \text{ m}^2/\text{g}$ and pore volume $V_0 = 0.22 \text{ cm}^3/\text{g}$ (supplied by Community Bureau of Reference, Brussels, Belgium). These examples as well as the samples presented in Figs. 1 and 2 are of special interest because many similar samples of porous glasses and silica gels have been investigated by means of different adsorption, transmission electron microscopy, direct energy transfer, and small angle scattering measurements in several publications in order to characterize surface roughness [for detailed references see recent papers (13–16)].

For most silica gels and porous glasses the adsorption and desorption branches of the isotherm form a well-defined hysteresis loop either of type H1 as for LiChrospher 300 (Fig. 1a), CPG-240 (Fig. 2a), and CPG-120 (Fig. 5a) or of type H2 as for Silica-60 and Vycor (Fig. 5a). Such hysteresis loops are observed in mesoporous materials with a monomodal pore size distribution. The nominal pore diameters are 60 \AA for Silica-60, 40 \AA for Vycor, and 120 \AA for CPG-

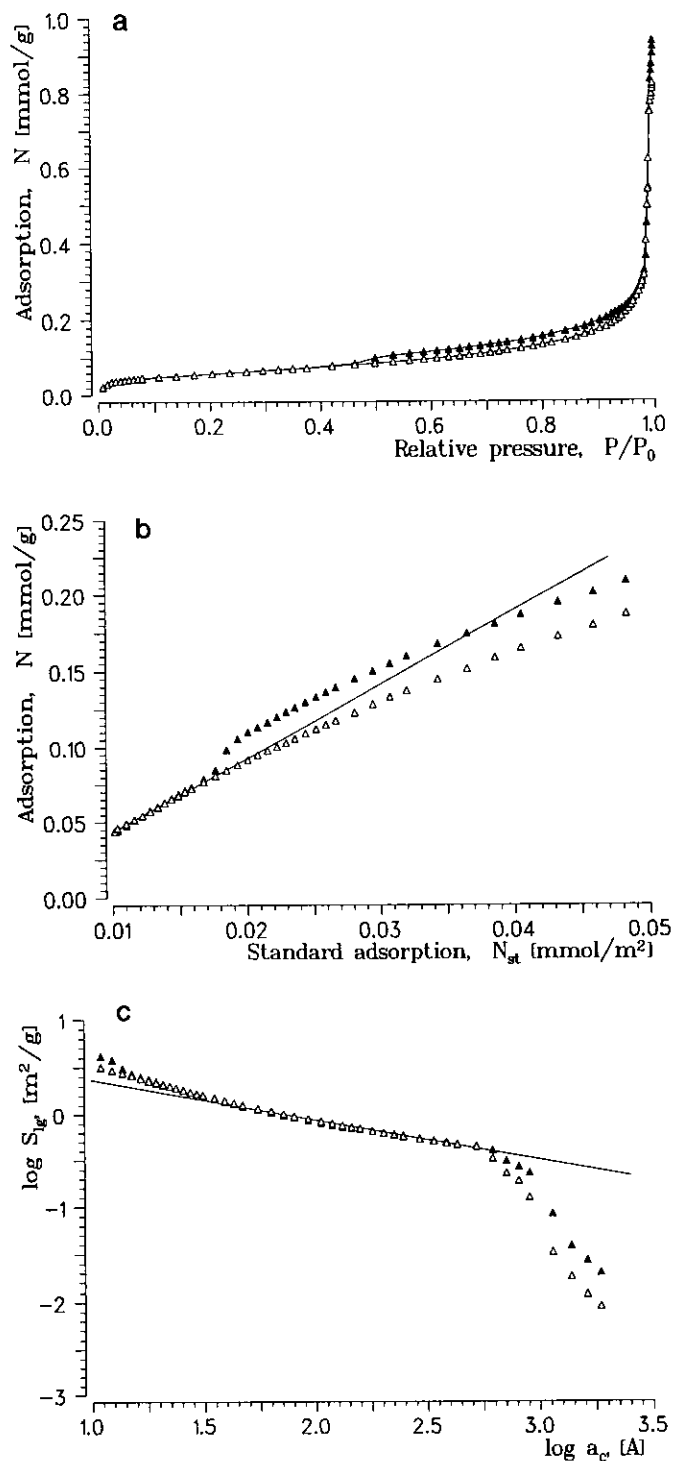


FIG. 4. Fractal analysis of a sample of natural coal. (a) Low temperature nitrogen adsorption isotherm [(Δ) adsorption, (\blacktriangle) desorption]. (b) Comparative plot [(Δ) adsorption, (\blacktriangle) desorption]. The straight line corresponds to the linear regression of the initial part of the plot in the range of relative pressures 0.07–0.46 with the slope $S_{\text{me}} = 4.88 \text{ m}^2/\text{g}$. (c) Results of calculations, by means of the thermodynamic method [(Δ) calculated from adsorption data, (\blacktriangle) calculated from desorption data]. The straight lines correspond to the linear regression in the scale range $25\text{--}500 \text{ \AA}$ for the both adsorption and the desorption plots with the surface fractal dimension $d_{\text{fs}} = 2.43$.

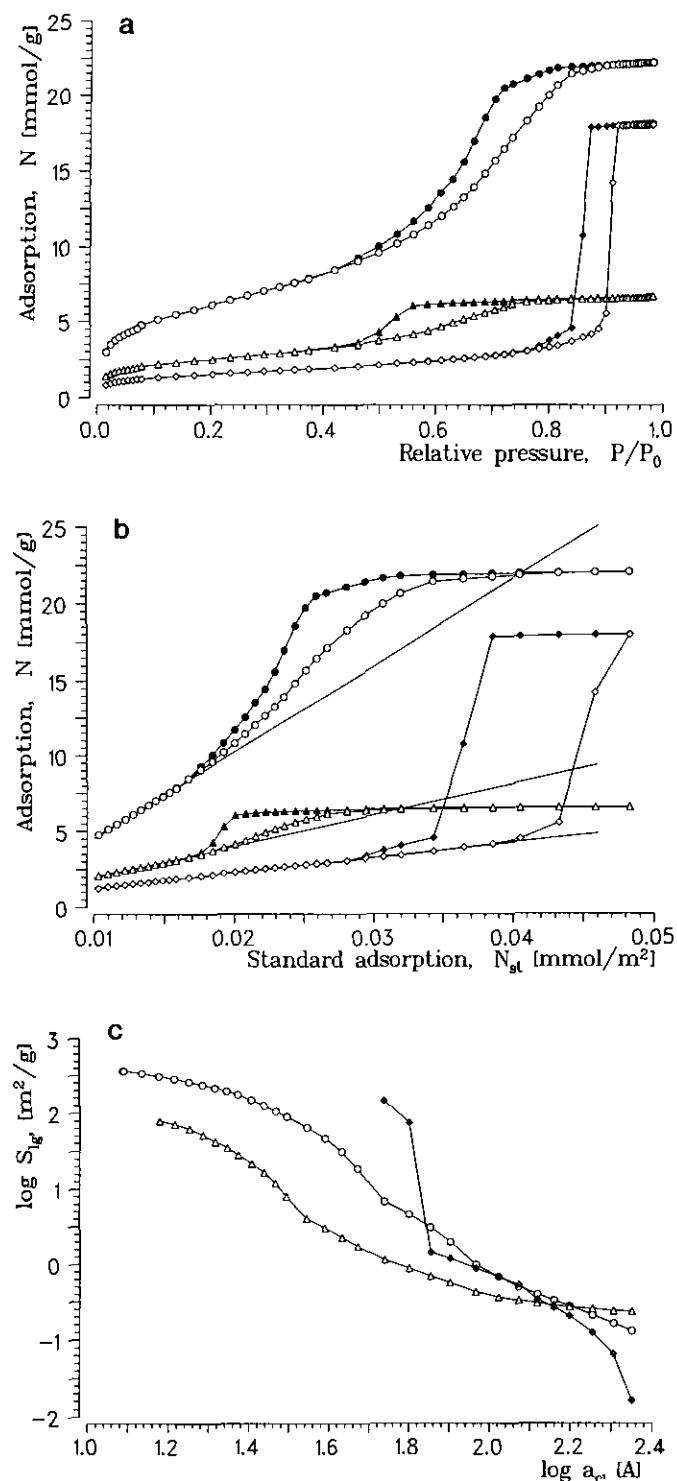


FIG. 5. Discrimination of surface fractality in the samples of silica gel LiChrosorb Si 60 [(○) adsorption, (●) desorption], controlled porous glass CPG-120 [(◇) adsorption, (◆) desorption], porous glass Vycor 7930 [(△) adsorption, (▲) desorption]. (a) The low temperature nitrogen adsorption isotherms. (b) Comparative plots. The straight lines correspond to the linear regression of the initial part of the adsorption plots with the slopes $S_{me} = 567 \text{ m}^2/\text{g}$ for Silica-60, $S_{me} = 205 \text{ m}^2/\text{g}$ for Vycor, and $S_{me} = 98 \text{ m}^2/\text{g}$ for CPG-120. (c) Results of calculations, by means of the thermodynamic method. The linearity is not observed in any appreciable scale range.

120. The reversible part of the isotherm below the hysteresis corresponds to the adsorption on the surface of mesopores and also to the reversible capillary condensation when this surface is rough.

From the comparative plots in Fig. 5b it follows that for all the given samples, the initial parts of the adsorption isotherms are linear functions of the standard adsorption isotherm at least in the whole region below the hysteresis. The departures of the comparative plots from the linearity are caused not by the reversible capillary condensation on a rough surface (as we have seen on examples of LiChrospher 300 and CPG-240) but by capillary condensation in the pore channels. The upper limits of linearity of the comparative plot are $P/P_0 = 0.46$ for Silica-60, $P/P_0 = 0.53$ for Vycor, and $P/P_0 = 0.86$ for CPG-120. Consequently, on a scale more than molecular size of nitrogen ($\sim 4 \text{ \AA}$) and less than the $\sim 12 \text{ \AA}$ for Silica-60, $\sim 15 \text{ \AA}$ for Vycor, and $\sim 60 \text{ \AA}$ for CPG-120, the surfaces under investigation are similar to a smooth surface and, therefore, cannot offer fractal properties. The thermodynamic method of Eqs. [3]–[5] also testifies to the absence of fractal properties of these samples in the scale range corresponding to capillary condensation, i.e., up to hundreds of \AA (Fig. 5c). Therefore we can discriminate the fractal properties for these samples. It seems likely that in materials with well-defined mesoporous structure, e.g., silica gels and porous glasses, the surface fractality can be observed only when the characteristic size of pores is sufficiently large.

DISCUSSION

We recommend the use of the comparative method based on low temperature nitrogen adsorption isotherms in combination with the thermodynamic method for the discrimination or for the confirmation of surface fractality. Low temperature nitrogen adsorption isotherms are readily available in a number of surface science laboratories by means of automated instruments. Moreover, most researchers dealing with porous materials employ nitrogen adsorption for calculations of standard structure parameters, namely porosity, BET specific surface area, and pore size distribution. Therefore, they can carry out the fractal analysis also using the same experimental data. These factors make nitrogen adsorption one of the most indicative methods of fractal analysis available for the comparison of different samples. This is quite essential, because in the literature there exist a number of investigations of the fractal properties of mesoporous solids, in particular of silica gels and porous glasses, and, at times, the conclusions for similar materials are in conflict. The samples from one family of porous materials can demonstrate varying structure properties. Porous glass Vycor is a typical example. The samples from different lots are significantly different (13). In response to this difference we cannot compare our results about the absence of fractal

properties for the given sample of porous glass Vycor of BET surface area $201 \text{ m}^2/\text{g}$ with the results published previously. One group (14) has found that for a sample of porous glass Vycor of BET surface area $103 \text{ m}^2/\text{g}$ the surface roughness had an upper scale limit of 20 \AA and that fractal properties were not observed at larger scales. However, another group (15) has found fractal properties with a fractal dimension equal to 2.3 in the scale range of about $20\text{--}100 \text{ \AA}$ for a sample of porous glass Vycor of BET surface area $159 \text{ m}^2/\text{g}$. This type of variability is characteristic for the samples of silica gels also.

In addition it is essential to make the following remarks concerning the relation between the method of analysis of nitrogen adsorption isotherms proposed here and the known methods proposed earlier. In view of the special form of "standard" nitrogen isotherm on a smooth surface (Eq. [2]), a formal application of known methods of calculating the fractal dimension from nitrogen isotherms in the region of polymolecular adsorption can lead, at times, to misleading conclusions. For example, all modifications of the FHH theory for fractal surface lead to the proportionality (6)

$$N(P/P_0) \propto 1/(\ln(P_0/P))^{(3-d_f)/3}, \quad [6]$$

which is quite similar to Eq. [2]. The only difference between these two equations, but a most important one, is that the parameter m in Eq. [2] is an empirical value obtained by fitting the numerous experimental data. Equation [6] is based on the usual FHH equation with exponent $m = 3$ for a flat surface, which is valid for nitrogen adsorption only in particular cases. The surface fractal dimension, d_{fs} , is supposed to be calculated from a comparison of Eq. [6] and an experimental isotherm. Formal application of Eq. [3] to the standard isotherm (Eq. [2]) with parameter $m = 2.24$ gives $d_{fs} = 1.66$. On the other hand, several approaches starting from different principles lead to another proportionality (17, 18),

$$N(P/P_0) \propto 1/(\ln(P_0/P))^{(3-d_{fs})}, \quad [7]$$

giving a value of $d_{fs} = 2.55$ for the standard isotherm, which is regarded as an empirical isotherm of nitrogen adsorption at 77 K , a smooth surface with $d_{fs} = 2$. This example does not discriminate between the theories leading to Eq. [6] or to Eq. [7] but indicates that these methods have to be applied taking into account all necessary limitations, especially in the case of nitrogen adsorption on mesoporous solids.

CONCLUSION

An analysis of low temperature nitrogen adsorption isotherms provides the capability to determine the surface frac-

tality. The comparative method, based on Eqs. [1] and [2], gives a definite negative answer or a "soft" positive answer as to whether or not the surface of a given mesoporous material may be considered as a fractal. In the scale range corresponding to the linear relationship between the nitrogen isotherm on a given sample and the standard isotherm on a smooth surface, the fractal properties do not exist definitely. The upper limit of similarity of these isotherms is the lower limit of the region of possible fractality. On the other hand, in the region of nonlinearity of the comparative plot, only additional study can confirm the existence of fractal properties. In this case the thermodynamic method, based on Eqs. [3]–[5], is useful. This conclusion is supported by our investigations of such materials as silica gels, porous glasses, natural apatite, and coal.

ACKNOWLEDGMENTS

The authors are thankful to K.S.W. Sing for helpful discussions and to anonymous referees for essential remarks. A.N. thanks the Humboldt-Stiftung and the Deutsche Forschungsgemeinschaft for support.

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