

Correlation Between the Fractal Dimension and the Microporous Structure of a Solid

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Summary. A theoretical description of gas adsorption on heterogeneous microporous solids is compared with that based on the fractal nature of these solids. It is shown that the structural parameters of a microporous solid correlate with the fractal dimension that characterizes the geometrical irregularities of microporous solids. Numerical studies performed for model solids with different degrees of microporosity show that the root-mean-square value of micropore size depends linearly on the fractal dimension.

Keywords. Gas adsorption; Fractal surfaces; Microporous solids.

Korrelation zwischen Bruchdimension und Mikroporenstruktur an Festkörpern

Zusammenfassung. Eine theoretische Beschreibung der Gasadsorption an heterogenen mikroporösen Feststoffen wird mit der auf der Bruchstruktur dieser Körper basierenden verglichen. Es wird gezeigt, daß die Strukturparameter eines mikroporösen Feststoffs mit den Bruchdimensionen, die die geometrischen Ungleichmäßigkeiten des mikroporösen Körpers charakterisieren, in Korrelation zu setzen sind. Numerische Untersuchungen an Modellfeststoffen mit verschiedenem Grad an Mikroporosität zeigen, daß die Wurzel aus den mittleren Quadraten der Mikroporengröße linear mit der Bruchdimension verknüpft ist.

Introduction

Almost all solid adsorbents are heterogeneous; in general, the adsorbent heterogeneity consists of the surface and structural heterogeneities of a porous solid [1, 2]. The source of surface heterogeneities are various irregularities of the solid surface (such as cracks, steps and flaws), surface imperfections of molecular dimensions (such as dislocations and vacancies), strongly-bound impurities, and the different atoms present on the surface [1–5]. Although the surface irregularities increase the geometrical nonuniformity of the solid surface, the most significant contribution to this nonuniformity is from very fine pores (micropores) of various sizes and shapes (structural heterogeneity) [1, 6]. The structural heterogeneity of a microporous solid may be characterized by the micropore-size distribution function [6,

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7–11]. This distribution function may be evaluated from adsorption measurements carried out at low concentrations of adsorbates [6, 11].

There is another possibility for characterizing the geometrical nonuniformity of a solid surface. Extensive experimental and theoretical studies [12–17] showed that fractal geometry may be applied in a natural way to adsorption because the number of adsorbed molecules of a definite size required to cover the surface measures the surface area of a fractal object. In terms of the fractal theory, the degree of the geometrical nonuniformity of the solid surface may be characterized by the fractal dimension D , which takes values between two and three [12]. Higher values of D correspond to surfaces with larger geometrical nonuniformities. Extensive experimental studies [14, 16] showed that the surface of most materials are fractals, and that the noninteger fractal dimension D is pertinent not only as an operative measure of the surface nonuniformity [14, 16], but useful also for studying surface phenomena in general [17].

In the case of a microporous solid, the contribution to the geometrical surface nonuniformity from surface irregularities is small in comparison to that from structural heterogeneities of the micropores. Because of this feature of microporous solids, there is a correlation between the fractal dimension D and the parameters that characterize the structural heterogeneities of the micropores. It is expected that this correlation will enrich our knowledge about the fractal nature of microporous solids and the adsorption process on fractal surfaces of heterogeneous microporous adsorbents.

Results and Discussion

Adsorption Isotherm for Fractal Surfaces of Microporous Heterogeneous Solids

The overall adsorption isotherm for a gas or vapor on a heterogeneous microporous solid may be represented by the following integral [7]

$$\Theta = \int_{x_{\min}}^{x_{\max}} \exp(-m^2 A^2) J(x) dx, \quad (1)$$

where

$$A = RT \ln(p_s/p). \quad (2)$$

Here $\Theta = n/n_0$ is the relative adsorption in the micropores defined as the ratio of adsorbed amount n to the maximum adsorbed amount n_0 , A is the adsorption potential defined by equation (2), $J(x)$ is the micropore-size distribution, x is the linear micropore dimension, x_{\min} and x_{\max} are respectively the minimum and maximum values of x , p is the equilibrium pressure of the adsorbate, p_s is the saturation vapor pressure, T is the absolute temperature, R is the universal gas constant, and m is a constant that depends on the adsorbate and the type of microporous structure [7]. The exponential factor in the integral Eq. (1) is obtained by assuming that the characteristic energy E_0 is inversely proportional to the half-width of slit-like micropores [7]. The micropore-size distribution $J(x)$ fulfills the following normalization condition

$$\int_{x_{\min}}^{x_{\max}} J(x) dx = 1. \quad (3)$$

Pfeifer and Avnir [12] proposed a theory of adsorption on fractal objects that leads to the following equation for the pore-size distribution,

$$J(x) = \rho x^{2-D} \quad (x_{\min} < x < x_{\max}), \quad (4)$$

where

$$\rho = \frac{3-D}{x_{\max}^{3-D} - x_{\min}^{3-D}}. \quad (5)$$

If D in Eq. (4) is a number between two and three, then it denotes the fractal dimension of the surface accessible for adsorption. For microporous solids, the fractal dimension D can be estimated from that of the adsorption isotherm associated with the formation of one or two opposite monolayers in the micropores, or from the corrected isotherm describing only adsorption on the micropore walls [18].

Substitution of Eq. (4) into Eq. (1) gives the following expression for adsorption on fractal surfaces of heterogeneous microporous solids [18],

$$\Theta(A) = \int_{x_{\min}}^{x_{\max}} \rho x^{2-D} \exp(-mx^2 A^2) dx, \quad (6)$$

where ρ is given by Eq. (5).

Isotherm Equation for Adsorption on Heterogeneous Microporous Solids

Jaroniec and Choma [6, 9] proposed the following gamma distribution function to represent the micropore-size distribution $J(x)$:

$$J(x) = 2 \frac{(qc)^{\nu+1}}{\Gamma(\nu+1)} x(x^2 - x_{\min}^2)^\nu \exp[-qc(x^2 - x_{\min}^2)]. \quad (7)$$

Here c is the structural parameter [6, 7, 9], q and ν are parameters of the gamma distribution function, and Γ denotes the gamma function; c is greater than zero, and ν is greater than minus unity. To simplify integration of Eq. (1) with the gamma micropore-size distribution given by Eq. (7), Jaroniec and Choma [6] approximated x_{\max} by infinity; then Eqs. (1) and (7) give

$$\Theta = \exp(-mx_{\min}^2 A^2) \left(\frac{q\beta^2}{q\beta^2 + A^2} \right)^{\nu+1}, \quad (8)$$

where $m = c/\beta^2$ and β is the similarity coefficient which depends on the adsorbate only [19]. For strongly microporous solids, a simplified version of Eq. (8) is used for analyzing the gas adsorption isotherm [6, 9, 20]. This simplified equation is obtained by assuming in Eq. (8) that $x_{\min} = 0$; then the exponential term in Eq. (8) becomes unity. Experimental verification of Eq. (8) showed its great utility for characterizing gas adsorption isotherms measured on heterogeneous microporous solids [6, 9, 20].

The parameters q and ν are useful for calculating various quantities that provide information about the microporous structure of a solid [6, 21]; for instance, the

square root of the mean value $\overline{x^2}$ (which is analogous to the average value of x) is expressed in terms of the parameters q and v by a simple analytical equation

$$\tilde{x} = (\overline{x^2})^{1/2} = \left(\int_{x_{\min}}^{\infty} x^2 J(x) dx \right)^{1/2} = \left(x_{\min}^2 + \frac{v+1}{cq} \right)^{1/2}. \quad (9)$$

A simple analytical equation for the dispersion σ_{x^2} associated with the micropore-size distribution $J(x)$,

$$\sigma_{x^2} = \left(\int_{x_{\min}}^{\infty} (x^2 - \overline{x^2})^2 J(x) dx \right)^{1/2} = \frac{(v+1)^{1/2}}{cq}. \quad (10)$$

The quantities \tilde{x} and σ_{x^2} characterize the microporous structure of a solid. For strongly heterogeneous solids, when x_{\min} may be approximated by zero, the average value x and the dispersion σ_x are also expressed by simple analytical equations [21].

Model Studies

The aim of the model studies is to show that the isotherm Eq. (8) is useful for describing gas adsorption on fractal surfaces of heterogeneous microporous solids, and that the parameters of this equation correlate with the fractal dimension. To study the correlation between the fractal dimension D and the parameter \tilde{x} defined by Eq. (9), we calculated the theoretical adsorption isotherms according to Eq. (6) for different values of the fractal dimension $D=2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8,$ and 2.9 and three sets of the parameters $(x_{\min}, x_{\max})=(0.15; 1.0 \text{ nm}), (0.3; 1.0 \text{ nm})$ and $(0.3; 1.5 \text{ nm})$. In Fig. 1 we present adsorption curves $\Theta(A)$ calculated according to Eq. (6) for $D=2.2$ and 2.9 . It follows from this figure that a decrease in the x_{\min} -value causes an increase in the adsorption Θ , whereas an increase in the x_{\max} -value causes a decrease in Θ . For a selected region (x_{\min}, x_{\max}) , an increase in the D -value causes an increase in the adsorption Θ ; more generally, when a solid possesses a significant portion of small micropores (x_{\min} and x_{\max} are relatively small and/or D approaches three), we observe a significant increase in the adsorption Θ .

The theoretical isotherms $\Theta(A)$ calculated for different values of D and (x_{\min}, x_{\max}) were described by the JC Eq. (8). The numerical studies showed that the JC

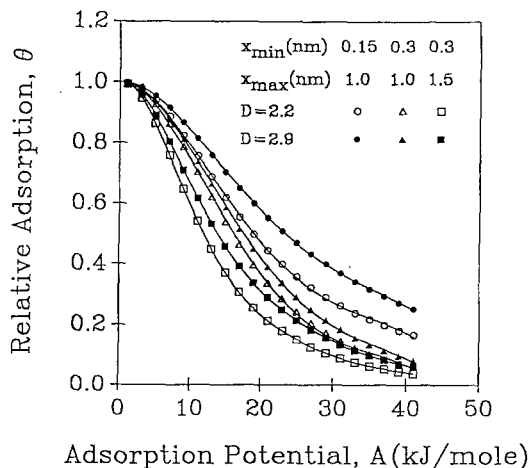


Fig. 1. Adsorption curves $\Theta(A)$ generated for fractal surfaces of microporous solids according to Eq. (6)

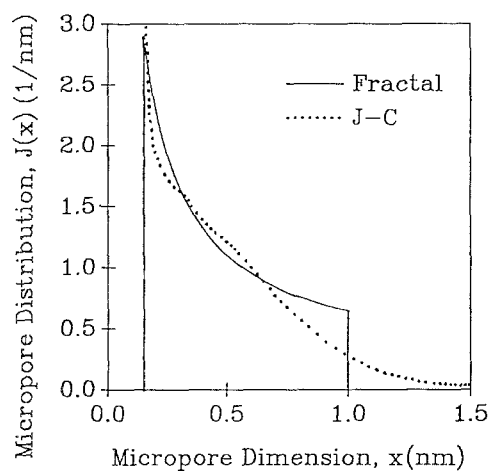


Fig. 2. Comparison of the fractal and JC micropore-size distributions. Parameters used in calculations were: $D=2.8$, $\nu=-0.35$ and $q=323$ (kJ/mol)²

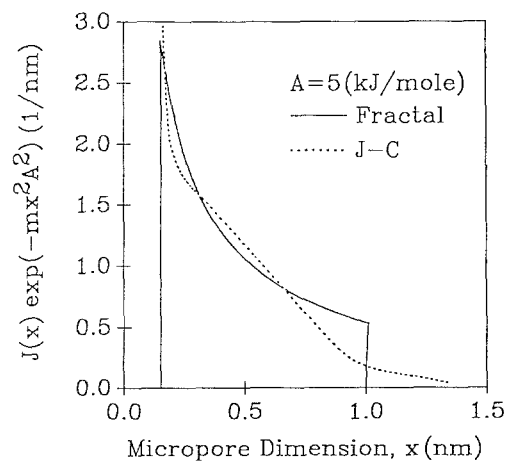


Fig. 3. Comparison of the integrand of Eq. (1) for the micropore-size distributions given by Eqs. (4) and (7). The adsorption potential $A=5$ kJ/mol; other parameters are the same as in Fig. 2

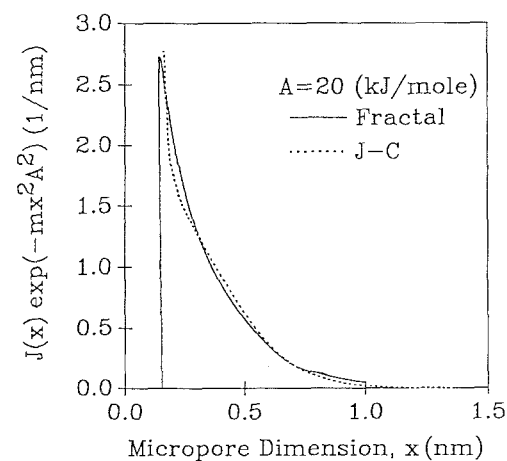


Fig. 4. Same as Fig. 3 except that $A=20$ kJ/mol

Eq. (8) gives a good representation of the adsorption curves calculated for various values of the fractal dimension D . In Fig. 2 we present a comparison of the fractal micropore distribution $J(x)$ calculated according to Eq. (7) for the best-fit parameters $q = 323 \text{ (kJ/mol)}^2$ and $v = -0.353$. Presented in Figs. 3 and 4 is a comparison of the integrand function $\exp(-mx^2A^2) J(x)$ for the fractal and gamma micropore distributions; these functions were calculated for the same parameters as those in Fig. 2 and for the adsorption potential $A = 5 \text{ kJ/mol}$ (Fig. 3) and 20 kJ/mol (Fig. 4). As seen in Fig. 4, the integrands associated with fractal and gamma micropore distributions differ only slightly for high values of A . For high values of A (small values of the equilibrium pressure p), this result shows that the gamma micropore distribution provides essentially the same information as the fractal distribution gives by Eq. (4).

Table 1 contains parameters of the JC Eq. (8) calculated for the model isotherms generated for various values of the fractal dimension D . As shown in Table 1 for selected intervals of x , the value of q is nearly insensitive to a change in the fractal

Table 1. Parameters \tilde{x} and q calculated by fitting the JC Eq. (8) to the adsorption isotherms generated for fractal surfaces of a microporous solid

Isotherm generated for a fractal solid			Parameters of the JC equation (8)	
$x_{\min}(\text{nm})$	$x_{\max}(\text{nm})$	D	$-v$	$q \text{ (kJ/mol)}^2$
0.15	1.0	2.2	0.17	301
		2.3	0.20	302
		2.4	0.24	304
		2.5	0.27	308
		2.6	0.30	312
		2.7	0.33	317
		2.8	0.35	323
		2.9	0.38	330
0.3	1.0	2.2	-0.05	371
		2.3	-0.01	365
		2.4	0.01	367
		2.5	0.03	370
		2.6	0.06	374
		2.7	0.08	378
		2.8	0.10	383
		2.9	0.11	388
0.3	1.5	2.2	0.14	128
		2.3	0.16	131
		2.4	0.18	135
		2.5	0.21	138
		2.6	0.22	142
		2.7	0.24	144
		2.8	0.26	152
		2.9	0.28	158

dimension D , whereas the parameter ν is sensitive to a change in the fractal dimension D . Another feature of the results presented in Table 1 is connected with the value of the parameter ν . Analysis of the adsorption isotherms on fractal surfaces of microporous solids by means of the JC Eq. (8) gives mostly negative values of ν , which are between zero and unity. Experimental verification of Eq. (8) [22] showed that the JC equation gives negative values of ν for adsorption of small gaseous molecules such as nitrogen or carbon dioxide on microporous activated carbons. For benzene adsorption, the evaluated values of ν are positive. This result appears to be connected with the accessibility of the micropores to the adsorbate molecules. Because benzene molecules are larger than nitrogen molecules, very small micropores are not accessible to benzene; therefore, the micropore-size distribution does not include these small micropores. Because nitrogen molecules penetrate very small micropores, the micropore-size distribution becomes analogous to a decreasing exponential function. It is noteworthy that the calculation of the micropore-size distribution can be improved by establishing an accurate empirical relationship between x and E_0 . The above discussion indicates that the fractal pore distribution (Eq. 4) characterizes many microporous solids, but it is necessary to analyze the adsorption isotherms for small molecules to evaluate the fractal pore distribution. Application of the adsorption isotherms for larger molecules like benzene provides only limited information about the fractal nature of microporous solids. Further study is required to prove the above hypothesis.

Finally, we calculated and plotted the root-mean-square value \tilde{x} for fractal surfaces of microporous solids against the fractal dimension D (cf. Fig. 5). The parameter \tilde{x} associated with the fractal pore distribution $J(x)$ given by Eq. (4) was calculated according to the following expression

$$\tilde{x} = x_{\min} \left(\frac{3-D}{5-D} \right)^{1/2} \left(\frac{r^{5-D} - 1}{r^{3-D} - 1} \right)^{1/2}, \quad (11)$$

where

$$r = x_{\max}/x_{\min}. \quad (12)$$

As shown in Fig. 5, Eq. (11) yields an almost linear dependence of \tilde{x} on the fractal dimension D in the physical region of D between two and three [12]. When \tilde{x} is

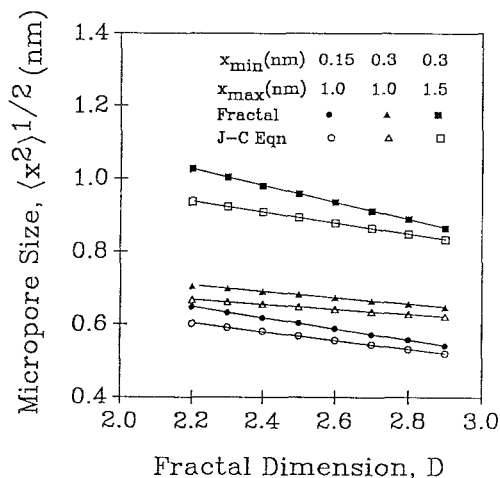


Fig. 5. Dependence of the root-mean-square micropore size \tilde{x} obtained in terms of the fractal approach and the JC Eq. (8)

calculated according to JC Eq. (9), we observed a linear relationship between \bar{x} and D , as shown in Fig. 5 also. The linear plots obtained on the basis of the fractal approach and the JC isotherm equation are analogous. This result indicates that the JC Eq. (8) may be used for describing gas adsorption on fractal surfaces of microporous solids.

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References

- [1] Jaroniec M., Madey R. (1988) *Physical Adsorption on Heterogeneous Solids*. Elsevier, Amsterdam
- [2] Jaroniec M., Bräuer P. (1986) *Surf. Sci. Rep.* **6**: 65
- [3] Young D. M., Crowell A. D. (1962) *Physical Adsorption of Gases*. Butterworths, London
- [4] Ross S., Olivier J. P. (1964) *On Physical Adsorption*. Wiley, New York
- [5] Jaroniec M. (1983) *Advan. Coll. Interf. Sci.* **18**: 149
- [6] Jaroniec M., Choma J. (1987) *Chem. & Phys. of Carbon* **22**: 197
- [7] Dubinin M. M. (1985) *Carbon* **23**: 373
- [8] Gregg S. J., Sing K. S. W. (1982) *Adsorption, Surface Area and Porosity*, 2nd Ed. Academic Press, London
- [9] Jaroniec M., Choma J. (1986) *Mater. Chem. Phys.* **15**: 521; Jaroniec M. (1987) *Langmuir* **3**: 795; Jaroniec M., Lu X., Madey R. (1988) *Chem. Scripta* **28**: 369
- [10] Kraehenbuehl F., Stoekli H. F., Addoun A., Ehrburger P., Donnet J. B. (1986) *Carbon* **24**: 483
- [11] Carrott P. J. M., Roberts R. A., Sing K. S. W. (1987) In: Unger K. K., Rouquerol J., Sing K. S. W., Karl H. (eds) *Characterization of Porous Solids*. Elsevier, Amsterdam, pp. 89–110
- [12] Pfeifer P., Avnir D. (1983) *J. Chem. Phys.* **79**: 3558; (1984) *J. Chem. Phys.* **80**: 4573
- [13] Avnir D., Pfeifer P. (1983) *Nouv. J. Chim.* **7**: 71
- [14] Avnir D., Farin D., Pfeifer P. (1984) *Nature* **308**: 261
- [15] Farin D., Avnir D. (1987) *J. Chromatogr.* **406**: 317
- [16] Farin D., Avnir D. (1987) *J. Phys. Chem.* **91**: 5517
- [17] Avnir D. (ed.) (1989) *The Fractal Approach to Heterogeneous Chemistry*. Wiley, Chichester
- [18] Avnir D., Jaroniec M. (1989) *Langmuir* **5**: 1431
- [19] Dubinin M. M. (1975) *Prog. Surf. Membr. Sci.* **9**: 1
- [20] Jaroniec M., Madey R., Lu X., Choma J. (1988) *Langmuir* **4**: 911; Jaroniec M., Choma J., Swiatkowski A., Radeke K. H. (1988) *Chem. Eng. Sci.* **43**: 3151; Jaroniec M., Choma J. (1988) *Carbon* **26**: 747
- [21] Jaroniec M., Madey R. (1988) *J. Chem. Soc. Faraday II* **84**: 1139
- [22] Choma J., Jaroniec M. (1988) *Mater. Chem. Phys.* **20**: 179

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