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Fractal Dimension of a Pillared Montmorillonite from Nitrogen Adsorption at 77 K

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The Avnir−Jaroniec method has been applied in the evaluation of the fractal dimension of a montmorillonite pillared with alumina and silica−alumina. The nitrogen adsorption data of the solids at 77 K were used in this method and in the relative pressure range 10^{-6} to 0.99. The fractal dimensions depend on the ranges of relative pressures used to apply the Avnir−Jaroniec equation. The interval of relative pressures between 0.08 and 0.2 is proposed to evaluate the fractal dimensions of these solids.

Introduction

Fractal geometry has been used in several theoretical and experimental studies of adsorption on materials to describe the structural heterogeneities.[1−3] The fractal geometry is quantitatively evaluated by the fractal dimension D, which is a measure of the surface and structural irregularities of a given solid. The value of this dimension can vary from 2 to 3.[4] The lower limiting value of 2 corresponds to a perfectly regular smooth surface, whereas the upper limiting value of 3 relates to the maximum allowed complexity of the surface. In addition to the structural heterogeneity, the surface heterogeneity can contribute significantly to the fractal dimension. The surface heterogeneity results from the presence of functional groups and impurities, whereas the structural heterogeneity arises from networking effects related to interconnected pores of various sizes and shapes, and also from the presence of various crystallographic and surface irregularities.[5]

Several simple relationships have been proposed as a means of evaluating the fractal dimension from various types of experiments.[1,2] Recently, Jaroniec[6] briefly revised the main relationships based on adsorption measurements used to determine the fractal dimensions of materials. One of the simplest and most popular relationships is given by the Frenkel−Halsey−Hill (FHH) equation, which in logarithmic form can be expressed as follows:

$$\ln(n) = K - (3 - D)\ln(A) \qquad (1)$$

where n is the amount of adsorbate adsorbed at the relative pressure $p/p°$ and temperature T and A is the adsorption potential, defined as

$$A = RT\ln(p°/p) \qquad (2)$$

Equation 1 was derived by Avnir and Jaroniec[7] by extension of the Dubinin−Radushkevich isotherm equation on structurally heterogeneous solids characterized by the fractal distribution of fine pores. In the general case of microporous solids, the contribution to the geometrical surface heterogeneity from surface irregularities is small in comparison to the one from structural heterogeneities of the micropores. Because of this feature, Jaroniec et al.[8] reported that it is necessary to analyze the adsorption isotherms for small atoms or molecules, as is the case of Ar, He, or N_2, to evaluate the fractal nature of these materials. This methodology, which uses adsorption data from only one adsorbate to calculate the fractal dimension, has also been confirmed and compared to other methods by various authors.[9−11]

Inorganic pillared interlayered clays (in short, PILCs) are prepared by exchanging the charge-compensating cations present in the interlamellar space of the swelling clays with hydroxy-metal polycations. On calcining, the inserted polycations yield rigid, thermally stable oxide species, named *pillars*, which prop apart the clay layers and prevent their collapse. This process results in an interesting two-dimensional porous structure of molecular dimensions characterized by the so-called *interlayer* and *interpillar spacings*.[12] The chemical, surface, and structural properties of these materials determine and limit their potential applications. Many of these properties can be controlled to a great extent by adjusting the different parameters involved in the synthesis process.[13] The most commonly followed procedure to characterize the porous structure generated is to establish the adsorption isotherm of a probe molecule, usually N_2 or, to a lesser extent, Ar or CO_2, at a subcritical temperature and very low relative pressures, and to apply a suitable theoretical pore model in order to interpret the data in terms of pore sizes.[14] As a result, these studies indicate that PILCs have a very complex geometry, which could be described as a slitlike and cylindrical pore geometry. Various studies have also suggested that this complex porous structure can be described in terms of fractal geometry.[15−17]

In this paper, emphasis is put on the exploitation of nitrogen adsorption results at very low relative pressures in order to evaluate the fractal dimensions of two pillared clays. This work claims to enrich the knowledge about the fractal nature of pillared clays.

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Table 1. Textural Properties Derived from the Nitrogen Adsorption at 77 K of the Samples Indicated

				HK slitlike model		
sample	$S_{\mathrm{Lang}}{}^{a}/\mathrm{m^2 \cdot g^{-1}}$	$S_{\mathrm{ext}}{}^{b}/\mathrm{m^2 \cdot g^{-1}}$	$V_{\mathrm{p}}{}^{c}/\mathrm{cm^3 \cdot g^{-1}}$	$V_{\mu\mathrm{p(HK)}}{}^{d}/\mathrm{cm^3 \cdot g^{-1}}$	$d_{\mathrm{p(HK)}}{}^{e}/\mathrm{nm}$	$\sum V_{\mathrm{p}}{}^{f}/\mathrm{cm^3 \cdot g^{-1}}$
sodium montmorillonite	21 ($C^g = 268$)	13	0.062	0.009	0.95	0.042
Al-PILC	451 ($C = 505$)	9	0.184	0.165	0.48; 0.74	0.024
SiAl-PILC	153 ($C = 480$)	18	0.085	0.059	0.48; 0.61	0.042

[a] Specific surface areas from the Langmuir equation ($0.01 \le p/p° \le 0.05$, interval of relative pressure). [b] Specific external surface areas obtained from the α_s-plot method. [c] Specific total pore volumes at $p/p° = 0.95$. [d] Specific micropore volumes derived from the Horvath–Kawazoe (HK) method. [e] Maxima of the Horvath–Kawazoe slitlike micropore size distributions. [f] Cumulative pore volumes from the Barrett–Joyner–Halenda (BJH) method (for pores in the 1.5–50 nm range). [g] Langmuir C values, characteristic of the intensity of the adsorbate–adsorbent interactions.

Table 2. Fractal Dimensions of Clays Calculated Using Eq 1 in the Range of Relative Pressures ($p/p°$) and Pore Sizes (d_p) Considered

	D			
sample	$0 < p/p° < 0.005$ $d_p/\mathrm{nm} < 0.8$	$0.005 < p/p° < 0.08$ $0.8 < d_p/\mathrm{nm} < 1.4$	$0.08 < p/p° < 0.2$ $1.4 < d_p/\mathrm{nm} < 2.0$	$0 < p/p° < 0.2$ $d_p/\mathrm{nm} < 2.0$
sodium montmorillonite		2.60 ($r^a = 0.996$)	2.65 ($r = 0.9992$)	2.58 ($r = 0.96$)
Al-PILC	0.18 ($r = 0.91$)	2.63 ($r = 0.96$)	2.90 ($r = 0.998$)	1.43 ($r = 0.82$)
SiAl-PILC	0.59 ($r = 0.83$)	2.70 ($r = 0.993$)	2.81 ($r = 0.9996$)	1.97 ($r = 0.78$)

[a] Correlation coefficient between experimental data and the fitting curve.

Experimental Section

The starting material used for the alumina and silica–alumina pillared montmorillonite (Al-PILC and SiAl-PILC) preparations was sodium montmorillonite (Kunipia F, Kunimine Co). The preparation of PILCs was carried out as described previously.[18,19] Nitrogen adsorption experiments were performed at 77 K using a static volumetric apparatus (Micromeritics ASAP2000 adsorption analyzer). The samples were previously degassed at 393 K for 24 h. Nitrogen adsorption data were obtained using 0.1 g of sample and successive doses of nitrogen of 5 $\mathrm{cm^3 \cdot g^{-1}}$ measured at STP conditions until $p/p° = 0.01$ was reached. Subsequently, further nitrogen was added and the volume required to achieve a fixed set of $p/p°$ was measured. Only the nitrogen adsorption data up to a relative pressure of 0.2 were considered in the micropore characterization.

Results and Discussion

The nitrogen adsorption of the samples starting from very low pressures is shown in Figure 1. The adsorption isotherm of the sodium montmorillonite is of type II in the Brunauer, Deming, Deming, and Teller (BDDT) classification.[20] The adsorption isotherms of the PILCs were of type I in the same classification, indicating that the amount of nitrogen adsorbed at low pressures ($p/p° < 0.1$) was the most important difference caused by the intercalation process. A summary of the values of the textural properties of the samples is included in Table 1. As expected, the intercalation process caused a notable increase of the specific surface area and both the total and microporous volumes with respect to those of the sodium montmorillonite.

The specific Langmuir surface area (S_{Lang}) was calculated from adsorption data in the relative pressure range 0.01–0.05 using a nitrogen molecule cross-sectional area of 0.160 nm^2.[20] The specific external surface area (S_{ext}) was calculated by means of the α_s-plot method.[20] The standard nitrogen adsorption isotherm at 77 K for sodium montmorillonite treated at 1073 K for 20 h was used as reference.[21] The total pore volume (V_p) was assessed from the amount of nitrogen adsorbed at a relative pressure of 0.95, assuming that the density of the nitrogen condensed in the pores is equal to that of liquid nitrogen at 77 K (0.81 $\mathrm{cm^3 \cdot g^{-1}}$).[20] The microporous volume ($V_{\mu\mathrm{p(HK)}}$) was calculated as the adsorbed volume corresponding to pore sizes up to 2 nm,[22] using the model proposed by Horvath and Kawazoe.[23] The micropore size distributions derived from the Horvath–Kawazoe slitlike model present two maxima for Al-PILC and SiAl-PILC. The cumulative mesopore volume ($\sum V_p$) was determined for pores in the range between 1.5 and 50 nm using the Barrett–Joyner–Halenda (BJH) method.[20]

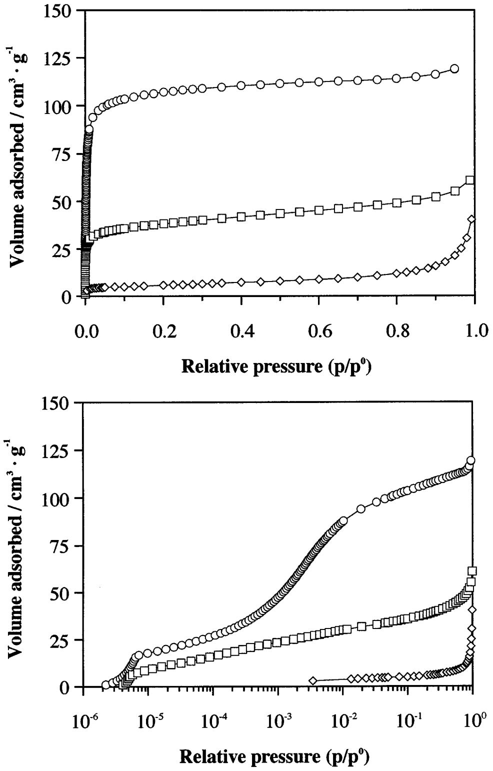

Figure 1. Nitrogen adsorption at 77 K starting from very low pressures: (◇) sodium montmorillonite; (○) Al-PILC; (□) SiAl-PILC.

Considering that eq 1 is based on Dubinin approaches, the fractal dimension D should be estimated from the adsorption data that describe only adsorption on the micropore walls. For that, only the nitrogen adsorption data up to a relative pressure of 0.2 must be considered. In this way, eq 1 has been applied to the nitrogen adsorption data presented in Figure 1, taking into account the stages of micropore filling reported by Kakei et al.,[24] that can be related to various micropore size ranges.[25] The authors indicated that there is an initial process, for $p/p° < 0.005$, taking place in pores having dimensions (<0.8 nm) comparable to that of the nitrogen molecule, called ultramicropores, and a second one occurring at $p/p°$ values between 0.005 and 0.2. In this range of relative pressures, the filling of two types of micropores, known as micropores (0.8−1.4 nm) and supermicropores (1.4−2.0 nm), taking place at relative pressures in the ranges 0.005−0.08 and 0.08−0.2, respectively, may also be considered.

The fractal dimensions of the clay samples calculated by applying eq 1 in various ranges of relative pressures and using the least-squares method to fit experimental data are presented in Table 2. It is interesting to point out that the fractal dimensions vary with respect to the range of relative pressures used in the calculations. This variation was observed to be related to the ability of eq 1 to correlate experimental adsorption data. For sodium montmorillonite, the values do not differ significantly with the pressure ranges. This is due to the relatively low degree of microporosity of this sample, as the results of textural analysis presented in Table 1 indicate. Al- and SiAl-PILC show very low values of the fractal dimension when the low relative pressures ($p/p° < 0.005$) are considered in their calculation. A possible bilayer micropore filling can explain why the same values as those for sodium montmorillonite (2.70−2.60) are obtained when the range of relative pressures between 0.005 and 0.08 is considered. It seems, therefore, that the fractal dimension that characterizes the microporous structure of PILCs can be satisfactorily calculated in the range of relative pressures between 0.08 and 0.2. In this interval, the total micropore filling takes place.

Terminology

A = adsorption potential, $\mathrm{kJ \cdot mol^{-1}}$
BDDT = Brunauer, Deming, Deming, and Teller classification
BJH = Barrett−Joyner−Halenda method
C = characteristic of the intensity of the adsorbate−adsorbent interactions, Langmuir equation
$d_{\mathrm{p(HK)}}$ = pore diameter corresponding to the maximum of the Horvath−Kawazoe micropore size distribution, nm
D = fractal dimension
FHH = Frenkel−Halsey−Hill equation
n = amount of adsorbate adsorbed
p = equilibrium pressure, Pa
$p°$ = saturated vapor pressure of adsorbate, Pa
PILC = pillared interlayered clay
r = correlation coefficient
R = universal gas constant, $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
S = specific surface area, $\mathrm{m^2 \cdot g^{-1}}$
S_{ext} = specific external surface area, $\mathrm{m^2 \cdot g^{-1}}$
S_{Lang} = specific surface area from the Langmuir equation, $\mathrm{m^2 \cdot g^{-1}}$
T = absolute temperature, K
V = specific pore volume, $\mathrm{cm^3 \cdot g^{-1}}$
$V_{\mu\mathrm{p}}$ = specific micropore volume, $\mathrm{cm^3 \cdot g^{-1}}$
$V_{\mu\mathrm{p(HK)}}$ = specific micropore volume derived from the Horvath−Kawazoe model, $\mathrm{cm^3 \cdot g^{-1}}$
V_{p} = specific total pore volume, $\mathrm{cm^3 \cdot g^{-1}}$

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