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Structural heterogeneity of microporous materials from nitrogen adsorption at 77 K

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The structural heterogeneity of four microporous materials, namely an alumina pillared clay; an activated carbon and two zeolites, Y-82 and ZSM-5, and of their physical binary mixtures (50-50 wt%) has been studied by nitrogen adsorption at 77 K. The Dubinin-Radushkevich (DR) and Dubinin-Astakhov (DA) equations have been applied to characterize the microporous properties and to obtain the adsorption potential distributions.

Key words: structural heterogeneity, micropore structure, adsorption potential distributions.

Heterogeneidad estructural de materiales microporosos a partir de la adsorción de nitrógeno a la temperatura de 77 K.

La heterogeneidad estructural de cuatro materiales microporosos (una arcilla intercalada con una disolución hidrolizada de aluminio; un carbón activado y dos zeolitas comerciales, Y-82 y ZSM-5), así como sus respectivas mezclas físicas binarias (50-50 % en peso) se analizaron a partir de la adsorción de nitrógeno a la temperatura de 77 K. Las ecuaciones de Dubinin-Radushkevich (DR) y de Dubinin-Astakhov (DA) se emplearon para caracterizar las propiedades microporosas de estos materiales, así como para obtener las distribuciones de potencial de adsorción.

Palabras clave: heterogeneidad estructural, estructura microporosa, distribuciones de potencial de adsorción.

1. INTRODUCTION

Microporous materials are widely used as adsorbents, catalysts and catalytic supports. Their chemical, surface and structural properties are important factors that determine and limit their applications. A quantitative evaluation of these properties is necessary for the design and the optimization of several sorption-based separation, purification, and catalytic processes. However, this quantification is complicated by the fact that microporous solids are usually heterogeneous materials. Their heterogeneity has been described by Jaroniec (1) as: *chemical heterogeneity*, which results from various functional groups and impurities present on the solid surface; *structural heterogeneity*, which arises from interconnected pores of different sizes and shapes, and *surface heterogeneity*, which is due to the presence of various crystallographic and geometrical irregularities on the surface.

Gas adsorption measurements have been widely used to obtain basic information on the structural properties of the solids. The adsorption equilibrium isotherm can be used to obtain the pore volume distribution function, which provides information about the structural heterogeneity, and the adsorption energy distribution, which provides quantitative information about the energetic heterogeneity of a given adsorbate-adsorbent system.

Dubinin (2) proposed a simple functional relationship between the volume of gas adsorbed in micropores and the adsorption potential, describing the physical adsorption of gases on microporous solids. This relationship, together with Langmuir and BET equations, is one of the most popular isotherm equations in adsorption theory; it has been extensively studied and used to describe the experimental data of adsorption of gases and vapors. An important conclusion from many of these studies was that the DR equation applies particularly on homogeneous microporous solids, i.e. solids with a uniform microporous structure (3-5). Several generalized equations have been proposed (2-4, 6-10), among which the well-known Dubinin-Astakhov (DA) equation (2), for obtaining a quantitative evaluation of the microstructure of heterogeneous microporous materials, i.e. materials with micropores of various sizes and shapes. Most of these generalized equations were of semi-empirical derivation and differentiate from each other mainly on the type of pore size distribution function assumed. Other studies were focused on the development of the theoretical background of the adsorption of gases on microporous solids, aiming to provide a physical interpretation of the estimated model parameters (11). Another useful tool for the better and more precise characterization of the heterogeneous microporous solids is the adsorption potential distributions (6, 11, 12). These distributions take into account the structural and the energetic heterogeneity of microporous solids, the latter being possible even for pores of similar size.

2. THEORETICAL BASIS. THE DUBININ FORMALISM

Dubinin and co-workers (2, 13-15) formulated the so-called micropore volume filling theory (MVFT), associated with the Polanyi concept of a characteristic curve (16). Assuming a Gaussian distribution of the pore sizes (12), they proposed a semi-empirical expression, the Dubinin-Radushkevich (DR) equation, giving the characteristic micropore volume of microporous adsorbents

$$V = V_0 \exp\left[-\left(\frac{A}{E}\right)^2\right] \quad [1]$$

where V is the volume adsorbed in micropores, V_0 represents the maximum volume adsorbed in micropores, E is the characteristic energy for a given adsorbate-adsorbent system, related also to the pore size, and A is the adsorption potential of the Polanyi theory, corresponding to the change of molar free energy related to the change of vapor pressure

$$A = -\Delta G = RT\ln\left(p^o/p\right) \quad [2]$$

where ΔG is the change of the Gibbs' free energy of adsorption, T is the absolute temperature, p is the pressure in the gas phase, and p^o is the saturation vapor pressure of the adsorbate.

From the combination of Eqs. [1] and [2], it can be seen that the plot of $\log V$ versus $\log^2(p^o/p)$, corresponds to a straight line having an intercept equal to $\log V_0$. If the density of the adsorbate is known, then the micropore volume of the solid can be calculated. The characteristic energy E of the system can be obtained from the slope of the straight line.

In some cases, the DR approach can give rise to curved plots which do not permit the easy determination of the micropore volume. In order to cover these cases, a more generalized expression was developed also by Dubinin and co-workers [2], based on the assumption of a Weibull distribution for pore sizes (17), and containing an additional variable parameter n

$$V = V_0 \exp\left[-\left(\frac{A}{E}\right)^n\right] \quad [3]$$

Equation (3), known as the Dubinin - Astakhov (DA) equation, describes the adsorption on structurally heterogeneous solids (18). In fact, the exponent n was linked to the degree of heterogeneity of the microporous system, with the original DR equation being the particular case of DA equation for n=2.

An even more generalized form of the DA expression [3] was proposed for gas adsorption on solids that possess a very broad range of pore dimensions, like some types of highly activated carbons (18). The overall isotherm is considered as the sum of several isotherms, each one corresponding to a particular pore group, having its own characteristic energy, E_i, and volume adsorbed in micropores, $V_{0,i}$,

$$V = V_0 \sum_{i=1}^{m} f_i \exp\left[-\left(\frac{A}{E_i}\right)^n\right] \quad [4]$$

where f_i ($f_i = V_{0,i}/V_0$) is the fraction of adsorption sites located in the micropore group with a characteristic energy of adsorption E_i.

Finally, the adsorption potential distribution, $X(A)$, related to the DA isotherm equation, may be evaluated by means of the condensation approximation method [19], as

$$X(A) = -\frac{d\left(V/V_0\right)}{dA} = nA^{n-1}\sum_{i=1}^{m} f_i \frac{1}{E_i^n}\exp\left[-\left(\frac{A}{E_i}\right)^n\right] \quad [5]$$

This expression can be used as a first approximation, to investigate the relationship which exists between the parameters of DA equation and the distribution of the micropore widths [20-22].

In the present work, the micropore structures of various microporous materials, as well as their physical binary mixtures (50-50 wt%), as derived from the nitrogen adsorption isotherms, have been characterized and compared to each other. The DR and DA equations have been used to describe the volume filling of micropores and the structural heterogeneity of the solids.

3. EXPERIMENTAL PROCEDURE

Two zeolites (Y-82, Union Carbide; ZSM-5, VALFOR CBV-5020), a commercial granular, microporous, gas-activated carbon (AC) derived from coconut shell (Merck-9631), and a laboratory prepared alumina pillared clay (Al-PILC) were used in this work. The starting material used in the alumina pillared clay preparation was Na-montmorillonite (Kunipia F, Kunimine Co.). The clay was dispersed in water and aged for a least two months. It was then washed by dialysis until the conductivity of the surrounding water was less than 1.5 μS. The solid content of the dialyzed clay dispersion was 7-10 g L^{-1}. Aluminum polycations were prepared by slow addition of a 0.2 M $AlCl_3$ solution with a 0.2 M NaOH one under vigorous stirring, using a OH/Al mole ratio equal to 2, and aged at 363 K for 4 h (pH = 3.9). Intercalated clay was obtained by dropwise addition of the aqueous montmorillonite suspension into the polycation solution under vigorous stirring, to obtain a Al_2O_3/montmorillonite ratio of 30 mmol Al (g of clay)$^{-1}$. The solid was kept in contact with the solution at room temperature for 24 h, then centrifuged and dried at 393 K for 16 h.

Nitrogen adsorption experiments of the four microporous samples and the respective binary mixtures (50-50 wt%) were performed at 77 K using a static volumetric apparatus (Micromeritics Adsorption Analyzer, Model ASAP 2000). The sample weight in each experiment was 0.1 g. Prior to nitrogen adsorption, the samples were degassed at 10^{-4} Torr and 393 K for 24 h. The procedure for nitrogen adsorption measurements was as following: first, successive fixed doses of nitrogen , 5 ml STP g^{-1} each, were fed to the sample until a value of p/p^o equal to 0.01 was reached. Then, the adsorption isotherm was completed by further addition of nitrogen so that measurements were achieved at a fixed set of p/p^o values, up to a value of 0.95.

4. RESULTS AND DISCUSSION

The nitrogen adsorption isotherms of the pure samples and the corresponding binary mixtures are of the type I in the Brunauer, Deming, Deming and Teller (BDDT) classification (17), indicating exactly that they are microporous solids. Representative isotherms are shown in Figures 1 and 2. The main differences among the various samples are observed at low relative pressures (p/p^o<0.2). In this region, micropore filling takes place, with the interaction of nitrogen with the micropore surface being stronger than that with the adsorption sites on the solid surface. Various stages of micropore filling occur, related to the different micropore structures. The low-pressure region of the nitrogen adsorption isotherms in general corresponds to two stages of micropore filling (23): an initial process, at $p/p^o < 0.005$, that takes place in pores having

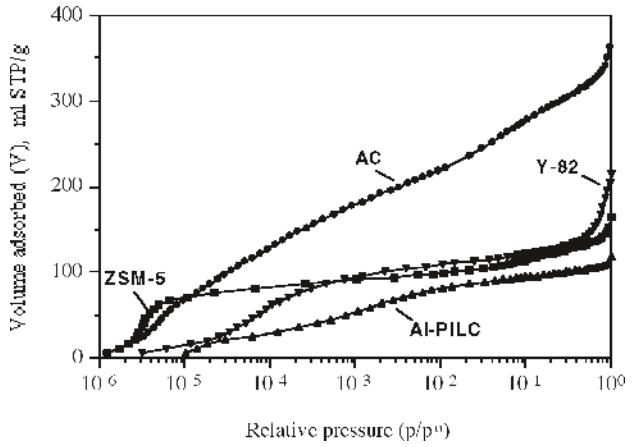

Figure 1. Nitrogen adsorption isotherms of the pure samples.

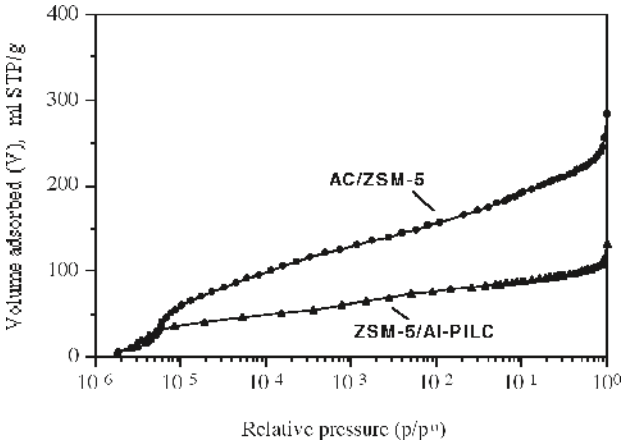

Figure 2. Nitrogen adsorption isotherms of representative binary mixtures.

dimensions comparable to nitrogen molecule, called ultramicropores, and a molecule interaction process that occurs at p/p^o higher than 0.005 (0.005-0.2). In this latter relative pressure range, it is also possible to consider the filling of two micropore ranges, referred as micropores and supermicropores (24), which occurs at the relative pressure ranges of 0.005-0.08 and 0.08-0.2, respectively. Initially, monolayer adsorption takes place on each micropore wall, and in this way single or double layers can be formed between two walls. The procedure proceeds by the filling of the residual space between the opposite monolayers on micropore walls (25).

The microporous properties of the samples were evaluated using the DR and DA formalisms (2); the DR and DA equations have been applied to obtain the micropore volume, V, and the characteristic energy, E, from the plot of $\log^n(p^o/p)$ versus $\log V$. The n exponents of the Dubinin-Astakhov equation were calculated by linear regression, in the range of relative pressures of $2\cdot10^{-6} \le p/p^o \le 0.2$.

The DR and DA plots of the Al-PILC sample show two sections with respect to the application of the DR and DA equations, that suggest the existence of two sizes of micropores (7). The presence of two types of surfaces of adsorption in the micropores, namely pillar and montmorillonite surfaces, can also be considered in order to explain the presence of these two sections (21,26). It is possible to apply the DR and DA equations to each section independently, and evaluate a micropore volume and a characteristic energy for each one of these sections. The results are shown in Table I, along with the values of the n exponents. The variables V_1 and E_1 (see Table I) are the ones corresponding to low relative pressures, V_2 and E_2 correspond to high relative pressures, while V_0 represents the total specific micropore volume ($V_0 = V_1+V_2$).

On the other hand, the DR and DA plots of the activated carbon and the two zeolites show only one section with respect to the application of the DR and DA equations. This suggests that there is only one kind of micropores in these solids. The variables V_2 and E_2 of Table I, are, for these samples, the ones corresponding to the whole relative pressure range con-

TABLE I. MICROPOROUS SAMPLE PROPERTIES FROM THE NITROGEN ADSORPTION AT 77 K.

	Dubinin - Radushkevich					Dubinin - Astakhov					
	Specific micropore volume $ml\cdot g^{-1}$			Characteristic energy $kJ\cdot mol^{-1}$			Specific micropore volume $ml\cdot g^{-1}$			Characteristic energy $kJ\cdot mol^{-1}$	
	V_1	V_2[a]	V_0	E_1	E_2	n[b]	V_1	V_2[a]	V_0	E_1	E_2
Pure samples											
Al-PILC	0.058	0.096	0.154	18.9	22.8	3.1	0.056	0.094	0.150	23.0	16.7
AC	-	0.400	0.400	-	25.8	5.4	-	0.339	0.339	-	20.8
Y-82	-	0.200	0.200	-	27.3	4.5	-	0.168	0.168	-	24.2
ZSM-5	-	0.161	0.161	-	43.1	10.0	-	0.149	0.149	-	23.4
Binary Mixtures											
AC/ Al-PILC	-	0.278	0.278	-	23.3	4.1	-	0.238	0.238	-	20.9
Y-82/Al-PILC	-	0.190	0.190	-	24.6	4.2	-	0.183	0.183	-	15.3
ZSM-5/Al-PILC	0.084	0.056	0.140	30.9	26.2	9.8	0.079	0.050	0.129	28.6	13.0
AC/ZSM-5	-	0.278	0.278	-	27.1	7.8	-	0.236	0.236	-	19.2
AC/Y-82	0.084	0.208	0.292	21.6	26.9	3.5	0.088	0.176	0.264	28.0	23.3
ZSM-5/Y-82	0.133	0.031	0.164	22.6	34.7	5.0	0.075	0.077	0.152	29.1	22.7

[a] $V_2=V_0-V_1$
[b] Exponent of the Dubinin - Astakhov equation

sidered. Therefore, values of V_1 and E_1 are not given for these samples, and V_0 is equal to V_2.

The DR and DA equations have also been applied to the DR and DA plots of the binary mixtures. The total specific micropore volumes calculated theoretically from the results obtained for the initial samples are generally in accordance with the values obtained for the binary mixtures by application of the DR and DA equations to the experimental data. Weighting errors in the mixture preparation could explain the possible differences. The DR and DA plots of the mixtures ZSM-5/Al-PILC, AC/Y-82 and ZSM-5/Y-82, show two sections with respect to the application of the DR and DA equations. This can be explained by the fact that the nitrogen adsorption is carried out in different intervals of nitrogen relative pressures for the two components of each one of these samples. For example, ZSM-5 adsorbs a significant quantity of nitrogen at lower relative pressures, much more than Al-PILC. The same explanation can be considered to interpret the presence of two sections in the mixtures AC/Y-82 and ZSM-5/Y-82, although the corresponding initial materials present only one section. The DR and DA plots of the rest of the mixtures, namely AC/Al-PILC, Y-82/Al-PILC and AC/ZSM-5, show only one section with respect to the application of the DR and DA equations. The nitrogen adsorption is carried out in the same intervals of relative pressures of nitrogen for the mixture components, explaining the observation, as it happens for example in the case of the samples ZSM-5 and AC.

As it can be seen from the results presented in Table I, DR and DA formalisms give similar values of the total specific micropore volumes (V_0) in the case of the pure samples. When the characteristic energies are compared, it can be seen that the values obtained with the two formalisms are different, with the DA formalism for the micropores and supermicropores giving lower energy (E_2) values than the DR formalism. The same observation can be made in the case of the mixtures, where significant differences can be observed only in the values of characteristic energies calculated by the two methods. The differences are more evident for the mixtures that contain ZSM-5 and when the values of E_2 are considered.

These differences can be attributed to the high heterogeneity of the samples. As mentioned previously, the DA equation takes into consideration the degree of heterogeneity in the microporous structure of each solid. Therefore, when the parameters estimated by means of this formalism, especially the ones related to the pore size and nature, are compared to the values estimated by another formalism that does not take that strongly into account the solid heterogeneity, as is the DR equation, differences can be observed. These differences are more pronounced in the case of solids that possess a large amount of very fine pores. This is the case with zeolite ZSM-5, which, as mentioned previously, shows a relatively high adsorption of nitrogen at low pressures, indicative of the existence of pores having very small dimensions. It is with this zeolite and its mixtures, where the greater differences of the E_2 values, as estimated by the two formalisms, are observed.

The adsorption potential distributions for the various samples have been evaluated in terms of the condensation approximation method (19). Representative distributions are shown in Figure 3, and are the ones obtained for the samples ZSM-5, Y-82 and the corresponding mixture. The physical interpretation of the adsorption potential distributions of microporous solids is often difficult, since the energetic heterogeneity can be either due to a non-uniform microporous structure or to surface heterogeneity. In this case, it was considered

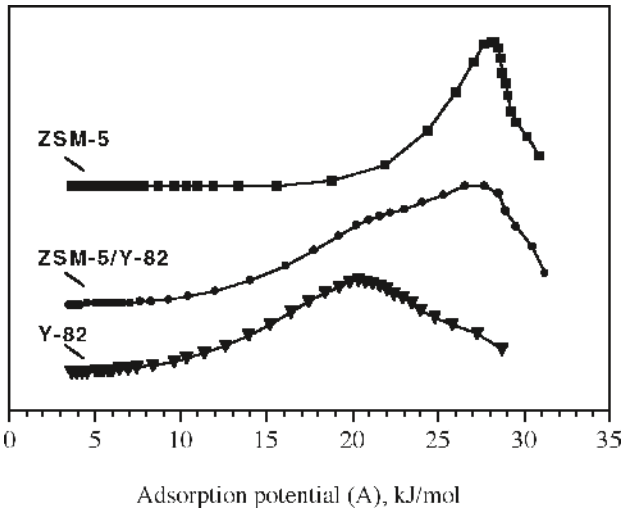

Figure 3. Adsorption potential distributions of ZSM-5, Y-82 and their mixture.

that the observed heterogeneity is due to the structural microporosity, and that the external surface area is negligible compared to the specific microporous surface area (21). The position of the distribution maxima of the pure samples can be used for the comparison of the microporosity of the samples, with smallest pores corresponding to higher adsorption potential. Therefore, the decrease of the micropore size of the various samples follows the order: Al-PILC > Y-82 > AC > ZSM-5. As it can be seen in Figure 3, the mixture ZSM-5/Y-82 present double-peaked distribution in the adsorption potential region from zero up to 35 kJ/mol. This distribution can be considered as the sum of the distributions of the samples which compose the mixture. As these distributions show maxima at different values of adsorption potential, the addition of these distributions results to double-peaked distributions.

5. CONCLUSIONS

The main difference in the studied materials is the adsorption of nitrogen at low pressures. Two micropore sizes and/or two types of surfaces of adsorption exist in the microporous structure of Al-PILC, and of only one kind of micropore in the activated carbon and the two zeolites. In the case of the binary mixtures obtained by physical mixing of the original samples, two micropore sizes are present when the samples which compose the physical mixture have micropores of different size.

The structural heterogeneity from the adsorption potential distributions indicates that the micropore sizes follow the order Al-PILC > Y-82 > AC > ZSM-5.

REFERENCES

1. M. Jaroniec, "Characterization of Nanoporous Materials", p. 259 in Access in Nanoporous Materials, Ed. T.J. Pinnavaia and M.F. Thorpe. Plenum Press, New York, 1995.
2. M.M. Dubinin, "Physical Adsorption of Gases and Vapors in Micropores", pp. 1-70 in Progress in Surface and Membrane Science, Ed. J.F. Danielli, M.D. Rosenberg and D.A. Cadenhead. Academic Press, New York, 1975.
3. M.M. Dubinin and H.F. Stoeckli, "Homogeneous and Heterogeneous Micropore Structures in Carbonaceous Adsorbents", J. Colloid Interface Sci. **75**, 34-42 (1980).
4. M. Jaroniec, R. Madey, X. Lu and J. Choma, "Characterization of Energetic

and Structural Heterogeneities of Activated Carbons", Langmuir **4**, 911-917 (1988).
5. M. Jaroniec and J. Piotrowska, "Isotherm Equations for Adsorption on Heterogeneous Microporous Solids", Monah. Chem. **117**, 7-19 (1986).
6. M. Jaroniec and J. Choma, "On the Characterization of Structural Heterogeneity of Microporous Solids by Discrete and Continuous Micropore Distribution Functions", Mater. Chem. Phys. **19**, 267-289 (1988).
7. A. Gil and M. Montes, "Analysis of the Microporosity in Pillared Clays", Langmuir **10**, 291-297 (1994).
8. M.M. Dubinin, "Inhomogeneous Microporous Structures of Carbonaceous Adsorbents", Carbon **19**, 321-324 (1981).
9. M. Jaroniec, R.K. Gilpin, K. Kaneko and J. Choma, "Evaluation of Energetic Heterogeneity and Microporosity of Activated Carbon Fibers on the Basis of Gas Adsorption Isotherms", Langmuir **7**, 2719-2722 (1991).
10. M. Rozwadowski and R. Wojsz, "An Attempt at Determination of the Structural Heterogeneity of Microporous Adsorbents", Carbon **22**, 363-367 (1984).
11. M. Jaroniec and P. Bräuer, "Recent Progress in Determination of Energetic Heterogeneity of Solids from Adsorption Data", Surf. Sci. Rep. **6**, 65-117 (1986).
12. H.F. Stoeckli, "A Generalization of the Dubinin-Radushkevich Equation for the Filling of Heterogeneous Micropore Systems", J. Colloid Interface Sci. **59**, 184-185 (1977).
13. M.M. Dubinin, "The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Nonuniform Surfaces", Chem. Rev. **60**, 235-241 (1960).
14. M.M. Dubinin, "Porous Structure and Adsorption Properties of Active Carbons", Chem. Phys. Carbon **2**, 51-120 (1966).
15. M.M. Dubinin, "Fundamentals of the Theory of Adsorption in Micropores of Carbon Adsorbents - Characteristics of Their Adsorption Properties and Microporous Structures", Carbon **27**, 457-467 (1989).
16. A. Eucken and M. Polanyi, "Adsorption at the Solids/Gas Interface", pp. 26-108 in Adsorption. Ed. J. Oscik. John Wiley, 1982.
17. S.J. Gregg and K.S.W. Sing, in Adsorption, Surface Area and Porosity. Academic Press, London, 1991.
18. F. Stoeckli, T. Jakubov and A. Lavanchy, "Water Adsorption in Active Carbons Described by the Dubinin-Astakhov Equation", J. Chem. Soc. Faraday Trans. **90**, 783-786 (1994).
19. G.F. Cerofolini, "Adsorption and Surface Heterogeneity", Surf. Sci. **24**, 391-403 (1971).
20. H.F. Stoeckli, A. Lavanchy and F. Kraehenbuehl, "Recent Developments in the Context of the Dubinin-Astakhov Equation", pp. 201-209 in Adsorption at the Gas-Solid and Liquid-Solid Interface. Ed. J. Rouquerol and K.S.W. Sing. Elsevier, Amsterdam, 1982.
21. A. Gil and P. Grange, "Application of the Dubinin-Radushkevich and Dubinin-Astakhov Equations in the Characterization of Microporous Solids", Colloids and Surfaces A: Physicochemical and Engineering Aspects **113**, 39-50 (1996).
22. A. Gil and P. Grange, "Comparison of the Microporous Properties of an Alumina Pillared Montmorillonite and an Activated Carbon from Nitrogen Adsorption at 77 K", Langmuir **13**, 4483-4486 (1997).
23. K.S.W. Sing, "The Use of Physisorption for the Characterization of Microporous Carbons", Carbon **27**, 5-11 (1989).
24. K. Kakei, S. Ozeki, T. Suzuki and K. Kaneko, "Multi-Stage Micropore Filling Mechanism of Nitrogen on Microporous and Micrographitic Carbons", J. Chem. Soc., Faraday Trans. **86**, 371-376 (1990).
25. K. Kaneko, "Micropore Filling Mechanism in Inorganic Sorbents", pp. 573-598 in Adsorption on New and Modified Inorganic Sorbents. Ed. A. Dabrowski and V.A. Tertykh. Elsevier, Amsterdam, 1996.
26. M. Brotas de Carvalho, J. Pires and A. P. Carvalho, "Characterisation of Clays and Aluminium Pillared Clays by Adsorption of Probe Molecules", Micropor. Mater. **6**, 65-77 (1996).