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Analysis of the Micropore Structure of Various Microporous Materials from Nitrogen Adsorption at 77 K

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Abstract. The micropore structure of four microporous materials (two zeolites, ZSM-5 and Y-82; an activated carbon and an alumina pillared clay) and their binary physical mixtures (50-50 wt%) have been examined by nitrogen adsorption at 77 K. Various micropore sizes have been considered from the stages on the micropore filling mechanism in the microporous materials. The application of the Dubinin-Astakhov (DA) equation to characterize and obtain the adsorption potential distributions of the microporous materials is presented.

Keywords: adsorption isotherms, adsorption potential distributions, micropore structure, structural heterogeneity

1. Introduction

Microporous materials are widely used as adsorbents, catalytic supports and catalysts. The knowledge of their basic sorption and structural characteristics is an important factor that determines and limits their applications. In this way, various modern techniques (i.e., electron microscopy, small angle X-ray scattering, NMR, etc.) and classical measurements (i.e., calorimetric measurements, adsorption-desorption of vapors and liquids, etc.) have been applied. Classical adsorption measurements are very popular because they can be used to obtain basic structural properties and provide direct insight of material microestructure. Various authors (Parent and Moffat, 1995; Russell and Levan, 1994) have used several methods to analyze and compare the porous structure of the microporous materials. The most popular methods used for the assessment of the microporosity (t- and α_s-methods (Gregg and Sing, 1991; Lippens and de Boer, 1965)) are based on the comparison of the shape of a given isotherm with that of a standard isotherm of a nonporous reference solid. These methods allow the measurement of the micropore volume and external surface area. The classical method to obtain the mean pore size of molecular sieves is from probe molecule sorption data (Baksh et al., 1992; Rouquerol et al., 1994). When only a molecule is used to characterize the micropore structure, the continuous distribution of micropore sizes can be obtained. In the last years, several methods have proposed for the determination of the micropores size distribution using only a molecule as adsorbate (Baksh and Yang, 1991; Dollimore and Heal, 1964; Horvath and Kawazoe, 1983; Mehandjiev et al., 1994; Mikhail et al., 1968; Patrykiejew et al., 1988; Russell and Levan, 1994; Saito and Foley, 1991; Zhu et al., 1994).

An important problem in the characterization of microporous solids is the evaluation of the parameters that characterize the microporous structure as well as the adsorbate-adsorbent interactions (Jaroniec and Madey, 1988). Dubinin (1975) proposed an equation for describing the physical adsorption of gases on microporous solids. This equation is one of the most popular isotherm equations in adsorption theory, and it has been widely used to describe the experimental data of adsorption of gases and vapors on microporous carbons. Other equations have also been proposed (Dubinin and Stoeckli, 1980; Jaroniec et al., 1988) and one of them is the well-known Dubinin-Astakhov (DA) equation (Dubinin, 1975). These equations have been used with the aim of to obtain a quantitative evaluation of the microestructure of porous materials. In this way, significant progress in the theoretical description of gas adsorption on heterogeneous solids has provided the foundation for utilizing low-pressure adsorption measurements to evaluate adsorption potential distributions (Jaroniec and Bräuer, 1986; Jaroniec and Choma, 1988; Stoeckli, 1977). These distributions characterize the energetic heterogeneity of microporous solids and they can be related with the microporous structure.

In the following, the Dubinin's formalism is briefly presented. Dubinin (1975) developed the micropore volume filling theory (MVFT), based on the Polanyi concept of a characteristic curve (Eucken and Polanyi, 1982). These authors proposed an empirical expression for the characteristic curves of microporous adsorbents considering a Gaussian distribution function (Stoeckli, 1977)

$$\theta = \exp\left[-\left(\frac{A}{E}\right)^2\right] \tag{1}$$

where θ is the relative adsorption, which is defined as the ratio of the amount adsorbed in the micropores (V) to the maximum micropore adsorption capacity (V_0), A is the adsorption potential corresponding to the change of molar free energy related with the change of vapor pressure and E is the characteristic energy for a given adsorbate-adsorbent system.

A more general expression was developed by Dubinin (1975). To obtain this expression, a Weibull distribution function is assumed for θ (Gregg and Sing, 1991)

$$\theta = \exp\left[-\left(\frac{A}{E}\right)^n\right]. \tag{2}$$

The exponent n was linked to the degree of heterogeneity of the microporous system (Carrasco-Marín et al., 1993; Chen and Yang, 1994; Rozwadowski et al., 1981; Stoeckli et al., 1994). Obviously, the Dubinin-Radushkevich equation is the particular case for $n = 2$.

Various workers (Dubinin and Stoeckli, 1980; Jaroniec and Piotrowska, 1986; Jaroniec et al., 1988) proposed that Eq. (1) or (2) describes the adsorption on structurally homogeneous solids. Others (Dubinin, 1981; Gil and Montes, 1994; Jaroniec and Choma, 1988; Jaroniec et al., 1991; Rozwadowski and Wojsz, 1984), suggested a modification of this equation when a microporous solid shows micropores of the same shape but of different sizes. In the same way, the DA expression (Eq. (2)) can be applied to the description of the adsorption on structurally heterogeneous solids (Stoeckli et al., 1994). The isotherm expression can be represented as

$$\theta = \sum_{i=1}^{m} f_i \exp\left[-\left(\frac{A}{E_i}\right)^n\right] \tag{3}$$

where f_i ($f_i = V_{0i}/V_0$) gives the fraction of adsorption sites located in the micropores with an adsorption characteristic energy E_i.

In previous works (Gil and Montes, 1994; Gil and Grange, 1996; Jaroniec et al., 1996) it was found that the adsorption potential distribution characterizes the energetic heterogeneity associated with micropores, structural heterogeneity, of highly microporous solids. The adsorption potential distribution $X(A)$, related to the DA isotherm equation, may be evaluated by means of the condensation approximation method (Cerofolini, 1971)

$$\begin{aligned} X(A) &= -\frac{d\theta(A)}{dA} \\ &= nA^{n-1}\sum_{i=1}^{m} f_i \frac{1}{E_i^n} \exp\left[-\left(\frac{A}{E_i}\right)^n\right]. \end{aligned} \tag{4}$$

Stoeckli et al. (1982) proposed that this expression can be used, as a first approximation, to investigate formally the relationship which exists between the parameters of the DA equation and the distribution of the micropore widths.

In this work, the micropore structure derived from the nitrogen adsorption isotherms of various microporous materials has been characterized and compared. The nitrogen isotherms of the binary physical mixtures (50-50 wt%) of these materials have also been compared in order to check if the microporous structure of both microporous materials can be resolved. Throughout this work the Dubinin formalism has been applied.

2. Experimental

Two zeolites (Y-82, Union Carbide; ZSM-5, VALFOR CBV-5020), a commercial granular microporous gas activated carbon based on coconut shell (Merck-9631) and an alumina pillared clay (Al-PILC) were used in this work. The preparation of the alumina pillared clay was carried out as described previously (Gil and Montes, 1994). Nitrogen adsorption experiments of these four microporous samples and the respective binary mixtures (50-50 wt%) were performed at 77 K using a static volumetric apparatus (Micromeritics

ASAP 2000 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 ml STP/g until $p/p^o = 0.01$ was reached. Subsequently, further nitrogen was added and the volumes required to achieve a fixed set of p/p^o were measured.

3. Results and Discussion

3.1. Nitrogen Adsorption Isotherms

The nitrogen adsorption isotherms over the whole relative pressure range of the zeolites, activated carbon and pillared clay are shown in Fig. 1. The adsorption isotherms are of type I in the Brunauer, Deming, Deming and Teller (BDDT) classification (Gregg and Sing, 1991) indicating, as expected, that they are microporous solids. In order to have a detailed observation of the micropore region, the nitrogen isotherms presented in Fig. 1 are displayed as semilog plots. These isotherms indicate that the main difference between the samples is the adsorption ability at low relative pressures.

The main characteristic of solids that show type I nitrogen adsorption isotherms (Gregg and Sing, 1991) is that the predominant monolayer adsorption occurs at the low relative pressure region compared with the monolayer adsorption on the flat surface. The interaction of nitrogen with the micropores surface is greater than on the flat surface. In this region, various stages of the micropore filling have been considered which could be related with different micropore structures. In this way, the region at low pressures in the nitrogen adsorption isotherms has been described considering two stages of micropore filling (Sing, 1989): an initial process, at $p/p^o < 0.005$, that takes place in pores of nitrogen molecular dimensions, named ultramicropores and a cooperative process that occurs at higher p/p^o than 0.005 (0.005–0.2). In this last relative pressure range it is also possible to consider the presence of two micropore ranges, named micropores and supermicropores (Kakei et al., 1990), at the relative pressure ranges of 0.005–0.08 and 0.08–0.2, respectively. This initial process has been related with the monolayer adsorption on each micropore wall, therefore a single layer or double layers can be formed between two walls. The secondary process has been related with the filling in the residual space between the opposite monolayers on micropore walls (Kaneko, 1996).

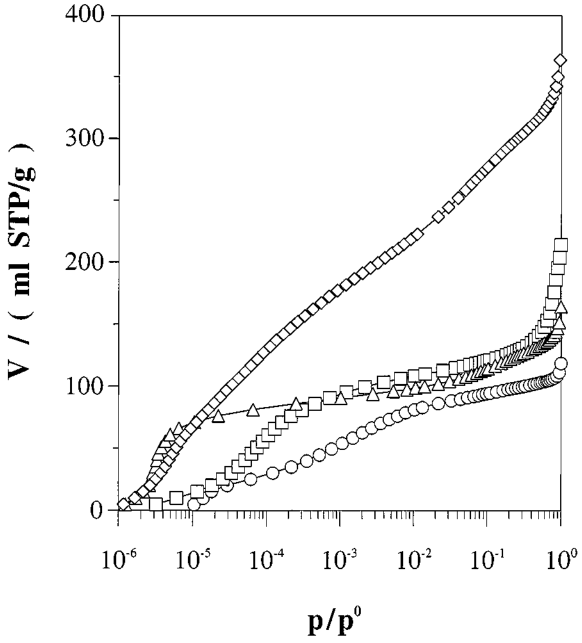

Figure 1. Nitrogen adsorption isotherms at very low pressures. (○) alumina pillared clay, (□) Y-82, (△) ZSM-5 and (◇) activated carbon.

The nitrogen adsorption isotherms from ZSM-5 and Y-82 display a transition in the micropore adsorption region at relative pressures of 3.0×10^{-6} and 7.5×10^{-5}, respectively. Almost the same volume of liquid nitrogen is adsorbed in both cases (0.145–0.170 ml/g). The nitrogen adsorption isotherm of Al-PILC shows two transitions at relative pressures of 2.0×10^{-5} and 5.0×10^{-4}. Finally, the nitrogen adsorption isotherm of the activated carbon shows a continuous increase of the volume adsorbed with the relative pressure and it is difficult to show a relative pressure of transition. Nevertheless, a relative pressure of 10^{-4} can be considered. The results obtained from the nitrogen adsorption isotherms for the two zeolites are in agreement with their regular pore structure. ZSM-5 is a medium-pore zeolite (Breck, 1974) having ellipsoidal tubular pores with a maximum aperture of 0.56 nm. Zeolite Y is a large-pore zeolite which presents main channels having a maximum pore opening of 0.74 nm. Taking into account these geometrical considerations, the comparison of the nitrogen adsorption isotherms suggests that ZSM-5 shows pores of nitrogen molecular dimensions where a single layer of nitrogen adsorbed could be formed between two walls. Al-PILC also shows pores of nitrogen molecular dimensions, as ZSM-5 does, and pores where a double

Table 1. Textural properties from the nitrogen adsorption at 77 K of the samples indicated.

					Dubinin-Astakhov					
Sample	S_{Lang} ($\text{m}^2\,\text{g}^{-1}$)[a]	S_{ext} ($\text{m}^2\,\text{g}^{-1}$)[b]	V_{pT} (ml g^{-1})[c]	$V_{\mu\text{pt}}$ (ml g^{-1})[b]	n	V_1 (ml g^{-1})	V_2 (ml g^{-1})[d]	V_0 (ml g^{-1})	E_1 (kJ mol^{-1})	E_2 (kJ mol^{-1})
Al-PILC	407 (622)[e]	13	0.184	0.152	3.1[f]	0.056	0.094	0.150	23.04	16.74
Y-82	520 (769)	96	0.331	0.148	4.5	—	0.168	0.168	—	24.17
Activated carbon	1181 (352)	72	0.598	0.449	5.4	—	0.339	0.339	—	20.84
ZSM-5	485 (542)	34	0.255	0.185	10	—	0.149	0.149	—	23.41
Activated carbon/ Al-PILC	728 (624)	44	0.385	0.295	4.1	—	0.238	0.238	—	20.87
Y-82/Al-PILC	504 (776)	44	0.288	0.206	4.2	—	0.183	0.183	—	15.32
ZSM-5/Al-PILC	380 (601)	24	0.205	0.140	9.8	0.078	0.050	0.129	28.59	12.98
Activated carbon/ ZSM-5	831 (397)	56	0.439	0.307	7.8	—	0.236	0.236	—	19.21
ZSM-5/Y-82	463 (846)	83	0.286	0.142	5.0	0.075	0.077	0.152	29.10	22.67

[a] Specific surface area from Langmuir method ($0.01 \le p/p^o \le 0.05$, interval of p/p^o).

[b] Specific external surface area and micropore volume, respectively, from t-method.

[c] Specific total pore volume at $p/p^o = 0.99$.

[d] ($V_2 = V_0 - V_1$).

[e] Langmuir C-value, characteristic of the intensity of the adsorbate-adsorbent interactions.

[f] Exponent of the Dubinin-Astakhov equation.

layer of nitrogen adsorbed could be formed between two walls. Y-82 also shows this last type of pores. All these pores can be considered as ultramicropores.

The specific surface areas (S) and the specific pore volumes (V) are presented in Table 1. The specific external surface areas (S_{ext}) and the specific micropore volumes ($V_{\mu\text{p}}$) of the samples were obtained from the t-method (Lippens and de Boer, 1965). Almost all the specific surface area (93–97%) and the specific pore volume (70–85%) are a result of pores in the micropore size range for ZSM-5, the activated carbon and Al-PILC. Y-82 presents an 18% of specific external surface area and a 45% of specific micropore volume indicating that there is an important contribution of the mesopores.

The nitrogen adsorption isotherms over the whole relative pressure range of the microporous samples and the respectives binary physical mixtures are shown in Fig. 2. The isotherm of activated carbon/Al-PILC mixture shows a similar behavior that the observed for the isotherm of the activated carbon, a continuous increase of the volume adsorbed in all range of relative pressure. In both isotherms of Al-PILC and the activated carbon, the presence of transitions are observed, as it was been considered previously. The isotherm of the mixture of both samples does not allow to show any transition. The isotherm of the Y-82/Al-PILC mixture is nearly identical to that of Y-82 and a clear transition at a relative pressure of 8.5×10^{-5} is observed. The presence of Al-PILC, a sample with slightly higher micropore sizes that Y-82, in this mixture makes broader the interval of relative pressures of this transition. The isotherm of ZSM-5/Al-PILC mixture shows two clear transitions, the first transition at a relative pressure of 3.5×10^{-6} and the second transition at 5.0×10^{-3}. The first transition can be related with the transition observed in the isotherm of ZSM-5 and the second transition with the second transition observed in the isotherm of Al-PILC. The presence of both ZSM-5 and activated carbon gives a first transition at a relative pressure of 5.5×10^{-6} in the nitrogen isotherm of this mixture. This transition is related with thepresence of ZSM-5 in the mixture. As the relative pressure increases, the adsorption behavior must be related with the presence of the activated carbon, thus a continuous increase of the volume adsorbed takes place. The isotherm of Y-82/ZSM-5 mixture shows clearly two transitions related with the two transitions that can be observed in the nitrogen isotherm of Y-82 and ZSM-5, respectively. The first transition occurs at a relative pressure of 3.0×10^{-6} and the second at 7.5×10^{-5}.

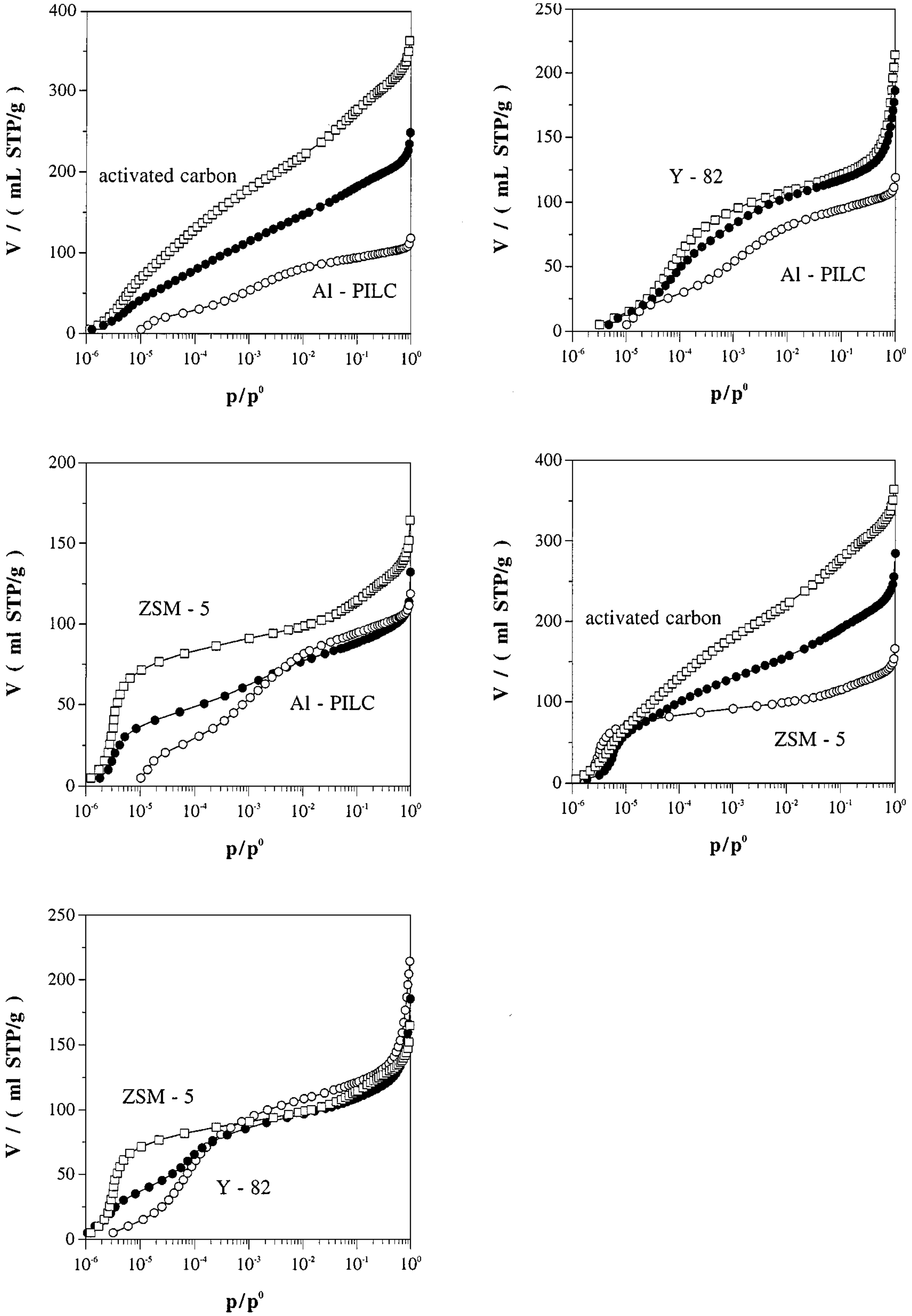

Figure 2. Comparison of the nitrogen adsorption isotherms of the microporous materials and (●) the binary physical mixtures.

The specific surface areas and the specific pore volumes of the mixtures are presented in Table 1. The values calculated theoretically from the results obtained for the initial samples indicated a good agreement with the results obtained from the nitrogen adsorption isotherms and only discrepancies between 1% and 18% have been obtained.

3.2. Dubinin Analysis

The microporous properties and the adsorption potential distributions were calculated from the DA formalism (Dubinin, 1975) and the DA equation has been applied to obtain V and E. These properties, micropore volume (V) and characteristic energy (E), as well as the value of the n exponent of the samples studied are presented in Table 1. The n exponents were calculated by linear regression and selected as the value of n which gives the smallest standard error of the y-intercept (log V_0). The DA formalism was applied in the range of relative pressures of $2 \times 10^{-6} \leq p/p^o \leq 0.2$.

The DA plot for Al-PILC shows two sections with respect to the application of the DA equation, that suggest the existence of two sizes of micropores (Gil and Montes, 1994). The presence of two types of surfaces of adsorption in the micropores (pillar and montmorillonite surfaces) was also considered previously to explain the presence of these two sections (Brotas de Carvalho et al., 1996; Gil and Grange, 1996). Therefore, it is possible to apply the DA equation to each section and describe the adsorption on the micropore structure by a two-term DA equation (Dubinin, 1981; Jaroniec et al., 1991; Rozwadowski and Wojsz, 1984). The values of V and E which characterize these micropores were obtained by extrapolation and from the slope, respectively, of the sections of the DA plot. The variable V_0 (see Table 1) represents the specific total micropore volume ($V_0 = V_1 + V_2$), V_1 and V_2 are related to the specific micropore volume for each micropore size, V_1 and E_1 were obtained from low relative pressures, and V_0 and E_2 from high relative pressures. The first and second transitions respectively described from the nitrogen isotherm. If the micropore volumes (V_1 and V_2) of Al-PILC are compared, 37% of the specific total micropore volume is given by the volume of pores of nitrogen molecular dimensions. The DA plots the two zeolites and the activated carbon only show a section with respect to the application of the DA equation. This suggests that there is only one size of micropores in these solids. With respect to the n exponents obtained from the DA equation, they are different for all the samples. Several exponent values have been proposed (Stoeckli, 1981) indicating that they depend on both the adsorbate and the adsorbent. Stoeckli et al. (1982) indicated that this value can be related with the micropore structure of activated carbons. As the samples do not present comparable values of the characteristic energy (E_2), it is not possible to compare the structure of the samples on the basis of the n exponent (Stoeckli et al., 1994).

The adsorption potential distributions obtained for the samples are shown in Fig. 3. These distributions have been evaluated in terms of the condensation approximation method (Cerofolini, 1971). It should be noted that the physical interpretation of the adsorption potential distributions of microporous solids is often difficult because energetic heterogeneity can be either due to a nonuniform microporous structure or surface heterogeneity. In this case, it was considered that for all samples $S_{\mu p} \gg S_{ext}$ (with $S_{\mu p} = S_{Lang} - S_{ext}$, the specific microporous surface area) and that the observed heterogeneity is due to the structural microporosity. Al-PILC shows a large distribution that could be related with a double-peaked distribution (Gil and Montes, 1994). The two zeolites and the activated

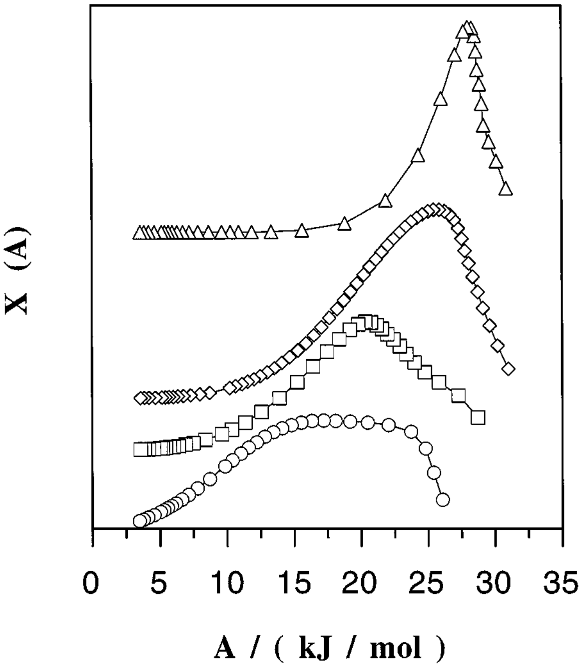

Figure 3. Adsorption potential distributions. (○) alumina pillared clay, (□) Y-82, (△) ZSM-5 and (◇) activated carbon.

carbon present a single-peaked distribution. As all samples show a high microporosity, the maxima of the distributions can be used to compare them and, in this aspect, the decrease of the micropore sizes follows the order Al-PILC > Y-82 > activated carbon > ZSM-5.

The DA equation has also been applied to the DA plots of the mixtures and they are presented in Table 1. As for the specific surface areas and the specific pore volumes of the samples, the micropore volumes calculated theoretically from the results obtained for the initial samples are in good agreement with the results obtained from the application of the DA equation. These results gave discrepancies only between 3% and 18%. The DA plots of the mixtures activated carbon/Al-PILC, Y-82/Al-PILC and activated carbon/ZSM-5 show a section with respect to the application of the DA equation. When the DA plot of Al-PILC is analyzed, two sections with respect to the application of the DA equation have been considered previously. Nevertheless, the presence of the activated carbon and Y-82 produce that only a section will be observed. This observation can be explained by the fact that the nitrogen adsorption on Al-PILC is carried out in the same interval of relative pressures of nitrogen of these two samples. The nitrogen adsorption isotherm of the activated carbon shows a high volume of nitrogen adsorbed in the same interval and the isotherm of Y-82 a broad interval of relative pressures of nitrogen adsorption. The same interval includes two sections of adsorption for Al-PILC. The DA plots of the mixtures ZSM-5/Al-PILC and ZSM-5/Y-82 show two sections with respect to the application of the DA equation. The isotherm of ZSM-5 shows an important nitrogen adsorption at lower relative pressures than the isotherm of Al-PILC, which shows two sections. The same explanation can be considered to interpret the presence of two sections in the mixture ZSM-5/ Y-82.

The adsorption potential distributions obtained for the mixtures are shown in Fig. 4. The mixtures activated carbon/Al-PILC, Y-82/Al-PILC, ZSM-5/Al-PILC and activated carbon/ZSM-5 present single-peaked distributions in the A region from zero up to 35 kJ/mol. These distributions are similar to the distributions of the activated carbon, Y-82 and ZSM-5, respectively. Only slight modifications can be observed. The distribution of activated carbon/Al-PILC shows an asymmetrical broad distribution centered with the maximum of the distribution of the activated carbon. The distribution of activated carbon/ZSM-5 shows differences with respect to the distribution of ZSM-5 that affect both the maximum and the width of the adsorption potential distribution. These modifications are in agreement with the presence of activated carbon in the sample mixture. The mixture ZSM-5/Y-82 present double-peaked distributions in the A region from zero up to 35 kJ/mol. This distribution could be considered as addition of the distributions of the samples which compose the mixture. As these distributions show maxima at various values of adsorption potential, the addition of these distributions produces double-peaked distributions.

4. Conclusions

In order to analyze the microporosity of materials with different microporous properties, the nitrogen adsorption isotherms of two zeolites (ZSM-5 and Y-82), an activated carbon and an alumina pillared clay have been considered. The isotherms have indicated that the main difference between these materials is the adsorption at low pressures.

Taking into account the stages on the micropore filling mechanism from the nitrogen adsorption isotherms and geometrical considerations, it has been obtained that ZSM-5 shows pores of nitrogen molecular dimensions where a single layer of nitrogen adsorbed could be formed between two walls. The alumina pillared clay also shows pores of nitrogen molecular dimensions, and pores where a double layer of nitrogen adsorbed could be formed between two walls. Y-82 also shows this last type of pores. The activated carbon presents micropores of various dimensions.

The structural heterogeneity from the adsorption potential distributions indicated that the decrease of micropore sizes follows the order Al-PILC > Y-82 > activated carbon > ZSM-5.

The nitrogen adsorption study of the physical mixtures obtained from binary samples indicated that when the samples which compose the physical mixture show micropores of different size, the physical mixture also shows two micropore sizes. From the adsorption potential distributions, these mixtures show a double-peaked distribution or a broad single-peaked distribution, as it can be concluded from the results obtained with the mixture ZSM-5/Y-82.

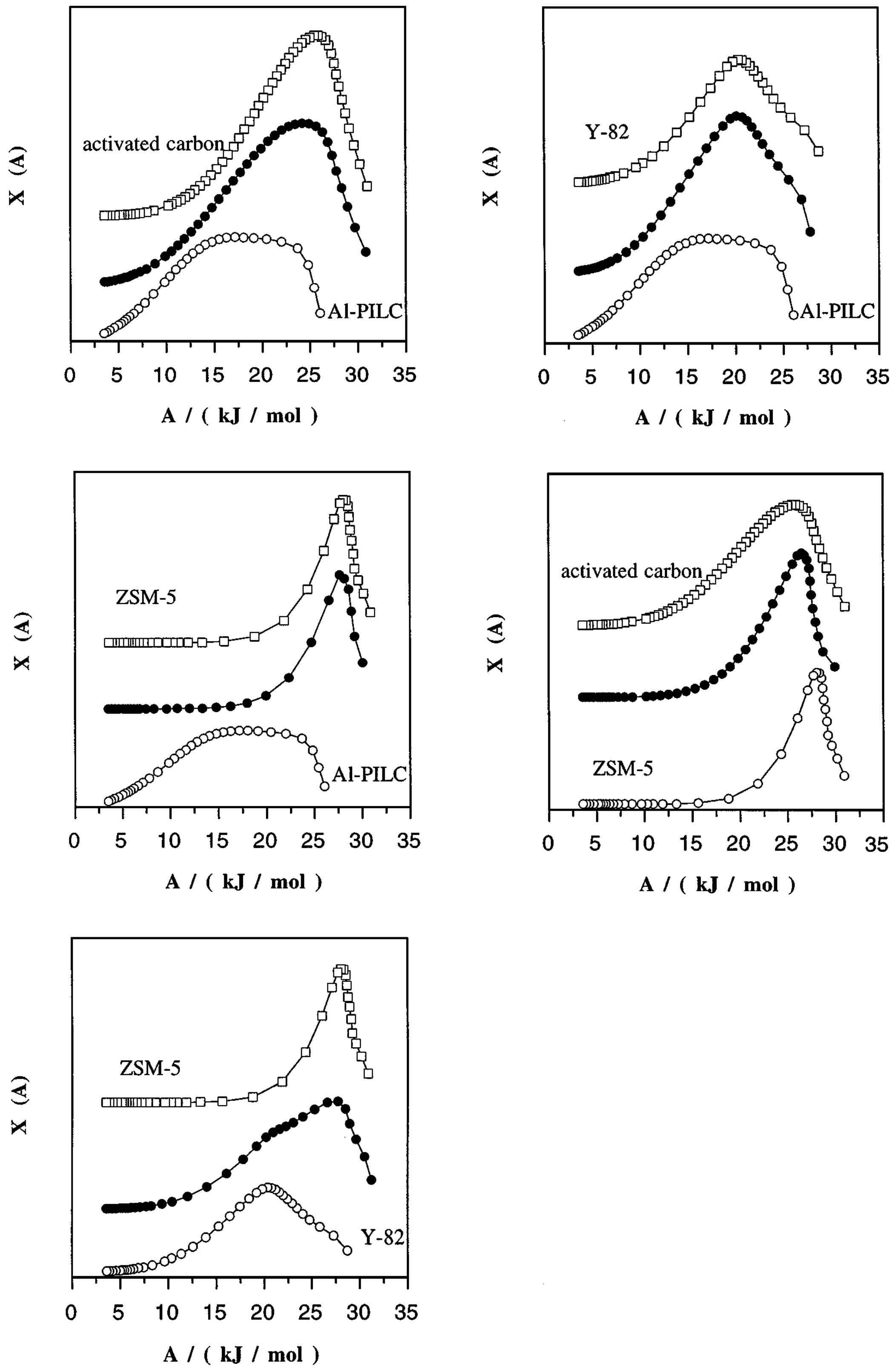

Figure 4. Comparison of the adsorption potential distributions of the microporous materials and (●) the binary physical mixtures.

Nomenclature

A	Adsorption potential	kJ/mol
E	Characteristic energy for a given adsorbate-adsorbent system	kJ/mol
f_i	Fraction of adsorption sites in the micropores	—
n	Exponent of the Dubinin-Astakhov equation	—
p	Pressure	—
p^o	Saturated vapor pressure of adsorbate	—
S	Specific surface area	m^2/g
S_{ext}	Specific external surface area	m^2/g
S_{Lang}	Specific surface area from Langmuir method	m^2/g
$S_{\mu \mathrm{p}}$	Specific micropore surface area	m^2/g
V	Specific pore volume	ml/g
$V_{\mu \mathrm{p}}$	Specific micropore volume	ml/g
V_0	Maximum micropore adsorption capacity from the Dubinin-Astakhov equation	ml/g
$X(A)$	Adsorption potential distribution	mol/kJ

Greek Letter

θ	Relative adsorption	—

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