Adsorption 7: 265–269, 2001

Comparative Studies of the Micropore Size Distributions of an Alumina Pillared Montmorillonite and a Molecular Sieve Carbon

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Received February 26, 2001; Revised June 18, 2001; Accepted June 18, 2001

Abstract. The aim of this work is to applicate and to compare various analysis methods for the characterization of the microporous structure from nitrogen adsorption at 77 K of an alumina pillared montmorillonite and a molecular sieve carbon. The adsorption potential distribution (X(A)), the Horvath-Kawazoe (HK) method, the Jaroniec-Gadkare-Choma (JGC) one and a numerical algorithm for the reconstruction of the micropore size distribution (MPSD) from the adsorption equilibrium isotherm have been applied. Comparison of all distributions revealed that the molecular sieve carbon shows smaller micropores and smaller structural hetereogeneity than the alumina pillared montmorillonite.

Keywords: micropore size distribution, molecular sieve carbon, alumina pillared montmorillonite

The information about the pore size distribution (PSD) of materials continues to attract attention of workers interested in mixture fuel storage, heterogeneous catalysis, removal of trace impurities and separation processes. It is well established that gas adsorption proved to be a fast and convenient characterization technique. These measurements depend on the internal physical and chemical structure of the material and on the nature of the adsorbate molecule. Thus, the results of these measurements contain information about structural and energetical properties of the surface materials (Jaroniec, 1995). Therefore, obtaining the information related to the true structure of a solid is an extraordinarily difficult problem.

Techniques or methods for characterization of pore size of mesoporous and macroporous materials are well established (Gregg and Sing, 1991). Therefore, the extension of the above methods to microporous materials does not yield satisfactory results. Due to the considerable effort that it has been made in the last years in the synthesis of new microporous materials (Karge and Weitkamp, 1998; Gil et al., 2000a), several approaches have emerged with respect to the estimation of micropore size distribution (MPSD) (Lastoskie et al., 1993; Jaroniec et al., 1996; Rege and Yang, 2000).

It has been proposed methods for the determination of the MPSD taking into account the description of the energetic heterogeneity of solid surfaces (Jaroniec et al., 1989; Jagiello and Schwarz, 1993). The Dubinin-Radushkecich (DR) and Dubinin-Astakhov (DA) equations have been applied to the description of the adsorption on structurally heterogeneous solids (Gil and Grange, 1996; Gil, 1998). The isotherm expression can be represented as:

$$\theta = \sum_{i=1}^{m} f_i \exp[-(A/E_i)^n] \qquad (1)$$

The energetic heterogeneity associated with micropores of microporous materials can be characterized by means of the adsorption potential distribution, and the distributions ($X(A)$), related to the Dubinin equations:

$$X(A) = -\frac{d\theta(A)}{dA} = nA^{n-1}\sum_{i=1}^{m} f_i \frac{1}{E_i^n}\exp[-(A/E_i)^n] \tag{2}$$

A simple method for evaluating MPSD is based on the Horvath-Kawazoe (HK) procedure (Horvath and Kawazoe, 1983) and its modifications. By assuming micropore-filling and equating the free-energy adsorbing molecules (Everett and Powl, 1976), the "step" in the isotherm data is translated into a MPSD. The HK method has been widely applied to characterize various microporous solids as activated carbons and pillared interlayered clays. The HK equation considering that the adsorption isotherm follows Henry's law and for a slitlike geometry:

$$-A = N_{Av}\frac{N_a A_a + N_A A_A}{\sigma^4(x-2d_0)} \times \left[\frac{\sigma^4}{3(x-d_0)^3} - \frac{\sigma^{10}}{9(x-d_0)^9} - \frac{\sigma^4}{3d_0^3} + \frac{\sigma^{10}}{9d_0^9}\right] \tag{3}$$

Recently, Jaroniec et al. (1996) proposed a simple thermodynamic approach to characterize microporous solids (JGC model). The MPSD, $J(x)$, is related to the adsorption potential distribution through the following equation:

$$J(x) = -X(A)\left(\frac{dA}{dx}\right) \tag{4}$$

dA/dx depends on the pore range and pore geometry. In the case of slitlike micropores, the derivative of the adsorption potential A with respect to the pore width x can be write as:

$$\frac{dA}{dx} = \frac{C_1}{(x-d_A)}\left[\frac{3C_2}{(x+d_0)^4} - \frac{9C_3}{(x+d_0)^{10}}\right] - \frac{C_1}{(x-d_A)^2}\left[\frac{C_3}{(x+d_0)^9} - \frac{C_2}{(x+d_0)^3} + C_4\right] \tag{5}$$

The most promising methods for evaluating MPSD are based on advanced computational techniques. In these methods, the experimental adsorption isotherm measured on a porous solid is considered as the aggregate of the isotherms for the individual pores that make up the pore structure of the solid. In mathematical terms, the experimental isotherm is the integral of the single-pore isotherm multiplied by the pore size distribution, and can be simply written as:

$$W(p) = \int_{x_{min}}^{x_{max}} f(x)\varphi(p,x)dx \tag{6}$$

It is possible to obtain the PSD inverting the integral equation for the total amount adsorbed with respect to $f(x)$. Several methods based on statistical mechanisms (Nicholson, 1994; Do and Do, 1995; Suzuki et al., 1996) and classical thermodynamic concepts (Adamson, 1976) of molecular adsorption have been used to predict the individual pore isotherms. Considering that the physical adsorption in micropores is better described on the basis of the classical theory of volume filling of micropores (TVFMP) (Dubinin, 1989), many researchers have used approaches based on DR and DA equations (Dubinin, 1975). These equations were used to represent the individual pore isotherms in the integral equation for the total amount adsorbed.

$$\varphi(p,E) = \exp\left\{-\left[\frac{RT\ln(p^0/p)}{E}\right]^n\right\} \tag{7}$$

Taking into account the relationships $A = RT\ln(p^0/p)$, $E = \beta E_0$ (Dubinin, 1975) and $E_0 = k/x$ (Dubinin, 1985), the integral equation transforms as:

$$W(A) = \int_{x_{min}}^{x_{max}} f(x)\exp\left[-\left(\frac{Ax}{k\beta}\right)^n\right]dx \tag{8}$$

In the work (Cherkashinin et al., 2000) it was proposed a simple numerical algorithm for solving the TVFMP inverse problem, obtaining $f(x)$, based on Tikhonov's regularization method.

In this work, the MPSD of an alumina pillared clay (Al-PILC) and a molecular sieve carbon have been obtaining using the Eq. (8) and compared with the adsorption potential, the HK and the JGC slitlike model distributions. The preparation of Al-PILC was carried out as described previously (Gil and Grange, 1997). A commercial molecular sieve carbon (Merck, 18-35 mesh ASTM) was also used. 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 obtaining

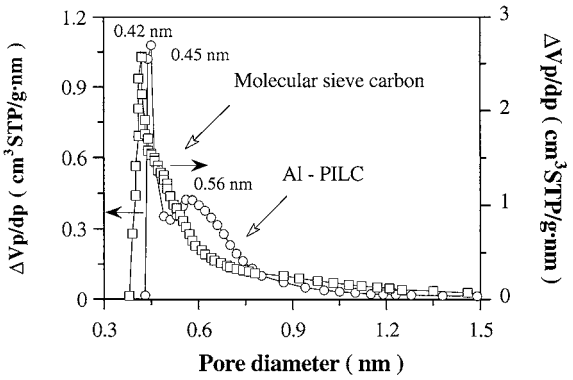

Figure 1. Micropore size distributions derived from the Horvath-Kawazoe slitlike model. (○) alumina pillared montmorillonite and (□) molecular sieve carbon.

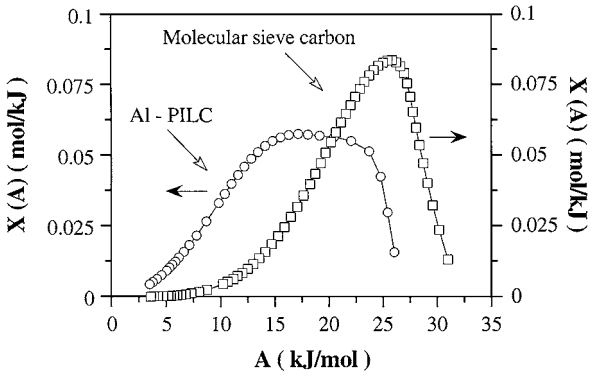

Figure 2. Adsorption potential distributions. (○) alumina pillared montmorillonite and (□) molecular sieve carbon.

using 0.1 g of sample and successive doses of nitrogen of 5 cm^3 STP/g until $p/p^0 = 0.01$ was reached. Subsequently, further nitrogen was added and the volume required to achieve a fixed set of p/p^0 was measured.

The MPSD derived from the HK slitlike model (Fig. 1) shows two maxima (0.45 and 0.56 nm) for Al-PILC and only one (0.42 nm) for the molecular sieve carbon. The comparison of both distributions indicated that the molecular sieve carbon shows smaller micropores than A1-PILC. The physicochemical properties of the adsorbate-adsorbent system required for this model have been stimated from the procedure proposed by Gil and Grange (1997).

The microporous structure of Al-PILC is characterized by the distance between the clay layers (interlayer spacing) and the distance between the intercalated solids (interpillar spacing). The interlayer spacing depends on the chemical nature and the height of the intercalating species. The interpillar distance is mainly related to the density of pillars, also depends on the distribution of the charge density of the clay layers and on the size of the pillars (Gil et al., 2000b; Hutson et al., 1999). It has been proposed that the interpillar rather than the interlayer distance can control the micropore size distribution of pillared clays (Yang and Baksh, 1991). An asymmetrical micropore size distribution centered about 0.5–1.0 nm is presented in Fig. 1 for Al-PILC. Integrating the areas under the micropore size distribution, that represent the micropore volume, a 60% of the micropore volume in the 0.5–1.0 nm micropore range is obtained, that can be considered as representative of the interpillar distance.

The DA equation has been applied to estimate V_0 and E, which are necessary to obtain the adsorption potential distribution (see Eq. (2)). In order to obtain E values that characterize all the micropore size range, the p/p^0 range between 10^{-6} and 0.2 have been considered. The adsorption potential distributions (Fig. 2) show a large distribution for Al-PILC, that it has been related to a poorly resolved double-peaked distribution, and a single-peaked distribution for the molecular sieve carbon. The distributions indicate that the molecular sieve carbon presents a size micropore smaller than Al-PILC, in accordance with the MPSD obtained from the HK slitlike model (see Fig. 1).

Maxima pore diameters at 0.43 and 0.46 nm have been obtained for molecular sieve carbon and Al-PILC, respectively, when the JGC model is considered (Fig. 3). The uniformity of the results comparing HK and JGC models, must be considering that the way which the MPSD are obtained. The two methods from mathematical viewpoint are identical (Jaroniec et al., 1996) and the final results can be very close, mainly

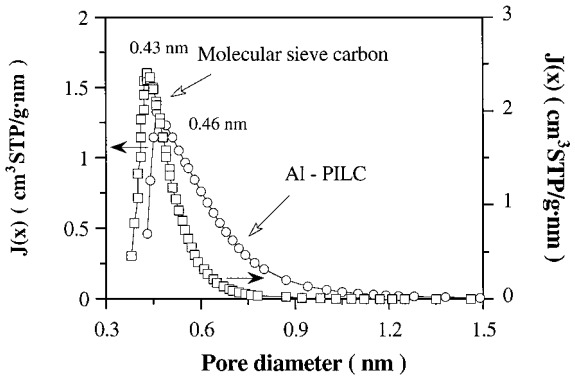

Figure 3. Micropore size distributions calculated from the Jaroniec-Gadkare-Choma model. (○) alumina pillared montmorillonite and (□) molecular sieve carbon.

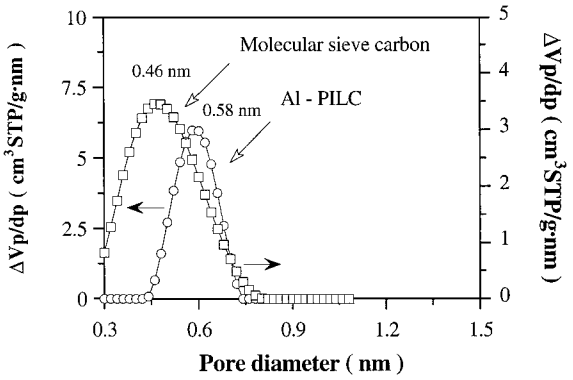

Figure 4. Micropore size distributions derived from the inversion of the integral Eq. (8). (○) alumina pillared montmorillonite and (□) molecular sieve carbon.

due that the same pore geometry is used and the same relation between pressure and pore width.

The MPSD obtained from the inversion of the integral Eq. (8) with respect to the distribution function in terms of the pore volume (Cherkashinin et al., 2000) are presented in Fig. 4. The characteristics of the samples obtained by other methods, HK distribution and DA equation, have been used in this new model (19.53 and 20.97 kJ/mol, as characteristic energy; 0.56 and 0.45 nm, as pore width; 3.1 and 2.7 as exponent of the DA equation; and 0.31 and 0.33, as affinity coefficient). As in the previous models, the comparison of the two distributions show that the molecular sieve carbon have smaller micropores than Al-PILC.

Various methods (adsorption potential distributions and, HK and JGC models) have been applied to the nitrogen adsorption data obtained at 77 K in order to analyze the microporous structure of an alumina pillared montmorillonite and a molecular sieve carbon. All methods describe satisfactorily the experimental results and qualitatively reproduce the MPSD. Comparison of all distributions revealed that the molecular sieve carbon shows smaller micropores and smaller structural heterogeneity than the alumina pillared montmorillonite. Our studies also show that the MPSD reconstruction obtained from Eq. (8) showed a good agreement with the known results.

Nomenclature

A	Adsorption potential, kJ/mol
A_a	Dispersion constant in Eq. (3)
A_A	Dispersion constant in Eq. (3)
C_1	Constant in Eq. (5), kJ/mol
C_2	Constant in Eq. (5), nm^4
C_3	Constant in Eq. (5), nm^{10}
C_4	Constant in Eq. (5), nm
d_a	Diameter of the adsorbent atom, nm
d_A	Diameter of the adsorbate molecule, nm
d_0	Arithmetic mean diameter of the adsorbent atom (d_a) and the adsorbate molecule (d_A), nm
E	Characteristic energy in the Dubinin-Astakhov equation, kJ/mol
E_0	Characteristic energy with respect to a reference adsorbate, kJ/mol
$f(x)$	Pore size distribution, cm^3/(g·nm)
f_i	Fraction of adsorption ($f_i = V_0/V_0$)
HK	Horvath-Kawazoe model
k	Adsorbent characteristic constant, kJ·nm/mol
JGC	Jaroniec-Gadkare-Choma model
$J(x)$	Differential distribution of pore volume (V) with respect to the pore width (x), cm^3/(g·nm)
n	Exponent of the Dubinin-Astakhov equation
N_a	Number of oxide ions per unit area of surface, Eq. (3)
N_A	Number of molecules of adsorbate per unit surface area of adsorbate, Eq. (3)
N_{Av}	Avogadro's number
$N_aA_a + N_AA_A$	Interaction parameter, cal·nm^4/mol
p	Pressure, Pa
p^0	Saturated vapor pressure of adsorbate, Pa
R	Universal gas constant, J/(mol·K)
T	Temperature, K
V	Specific pore volume, cm^3/g
V_0	Maximum micropore adsorption capacity from the Dubinin-Astakhov equation, cm^3/g
x	Pore width, nm
x_{max}	Largest pore width, nm
x_{min}	Smallest pore width, nm
$X(A)$	Adsorption potential distribution, mol/kJ
$W(p)$	Experimental isotherm, cm^3/g

Greek Letters

β	Adsorbate affinity coefficient
σ	Constant in Eq. (3), nm

$\varphi(p, x)$ Individual pore isotherm, cm^3/g
θ Relative adsorption

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