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The characterization of microporosity in carbons with molecular sieve effects

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Abstract

The apparent and the real micropore size distributions (PSDs) of molecular sieve carbons can be assessed by combining the adsorption of CO_2 at 273 K with immersion calorimetry into liquids of increasing molecular dimensions. On the basis of model isotherms resulting from computer simulations, the adsorption of carbon dioxide, a relatively small probe, leads to the overall PSD of the carbon (essentially the internal micropore system). Immersion calorimetry, on the other hand, reveals the distribution of the pores accessible directly from the liquid phase, that is without constrictions. Liquid CS_2 probes the same volume as CO_2 and can be used as a reference. The paper describes the case of an industrial molecular sieve carbon obtained by blocking partly the entrance to a relatively broad micropore system, thus limiting its accessibility to molecules with diameters below 0.5–0.6 nm. It is shown how activation by steam at 900 °C removes the constrictions and leads to a gradual overlap of the two PSDs. The distribution of the pore widths on the surface, observed directly by scanning tunnelling microscopy, is also given.

Keywords: Molecular sieve carbons; Pore size distribution; Adsorption; Calorimetry; Modelling

1. Introduction

Unlike zeolites and other well-crystallized materials, microporous carbons are disorganized and possess variable pore size distributions (PSDs), depending on their origin and their preparation [1] (carbonisation and activation). The common feature is the presence of locally slit-shaped micropores, at least in the region of width up to 1–1.5 nm.

Various techniques have been described to characterize these distributions, for example the determination and the analysis of adsorption isotherms [2], the use of liquid probes with variable molecular sizes combined with immersion calorimetry [1,3] and direct observation of the surface by high-resolution electron microscopy or by scanning tunnelling microscopy (STM) [4–6]. More recently, computer modelling combined with the determination of adsorption isotherms has been used successfully to characterize microporous

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carbons, and the present authors have suggested the use of CO_2 at 273 K [7,8].

These techniques have led to a good correlation in carbons where the micropores are freely accessible to the molecules of the corresponding sizes. Under these circumstances, the PSDs obtained with the different techniques show a high degree of correlation. This may include the direct probing of the surface by STM, although the frequency of the pore width L observed on the surface, $\Delta N/\Delta L$, does not necessarily coincide with the volume distribution of the micropores in the matrix, $\Delta W/\Delta L$.

For a number of carbons the accessibility of the micropore system may be limited by gate effects. This is often the case in carbons with low degree of burn-off during activation. Constrictions can also be created specifically to add selectivity to a carbon with relatively wide pores. A popular technique is the coating of the carbon with a polymer, followed by carbonisation and possibly limited activation [1]. As a result, the original micropore volume is accessible through constrictions acting selectively (gate effect).

The presence of gate effects may lead to the wrong conclusions, since small probes such as N_2 at 77 K or CO_2 and CH_2Cl_2 near room temperature are not affected by the constrictions and will provide information on the internal porosity. A clear distinction must therefore be made between the internal microporosity, with its own size distribution, and the apparent porosity found between the constrictions and the vapor phase. In the present paper, we illustrate an approach combining the adsorption of CO_2 at 273 K with immersion calorimetry, using liquids of variable molecular dimensions. As described recently [7], the CO_2 isotherm can be analyzed in terms of model isotherms obtained from computer simulations, which leads to the PSD of the internal micropore system, probed by this molecule.

The present study deals with an industrial carbon, where the molecular sieve properties correspond to a gate effect rather than to a narrow size distribution of the internal micropore system. The latter is gradually exposed by activation of the solid with steam at 900 °C up to 35% weight loss. As a consequence, the accessibility to larger molecules, revealed by immersion calorimetry, gradually increases and the apparent and the internal micropore distributions become similar.

2. Theory

As discussed in detail elsewhere, microporous carbons can be characterized within the framework of Dubinin's theory [1,3,9,10] and its extension to immersion calorimetry [1,3]. The basic relation is the Dubinin–Astakhov equation

$$N_a = N_{a0} \exp[-(A/\beta E_0)^n] \quad (1)$$

where N_a (mmol g^{-1}) represents the amount adsorbed at relative pressure p/p_s, N_{a0} is the limiting amount filling the micropores and $A = RT \ln(p_s/p)$. Exponent $n = 2$ corresponds to the classical Dubinin–Radushkevich (DR) equation [9,10], valid for most activated carbons. The parameters β (affinity coefficient) and E_0 (characteristic energy, given in kJ mol^{-1}) depend, respectively, on the adsorptive and on the solid. The experimental affinity coefficients are given in the literature [1,3, 11], the reference vapor being benzene [9,10]. In the present study we used $\beta(CO_2) = 0.35$ [12], as confirmed by recent studies [7,8]. It has been shown [3] that in the case where the DR equation applies, the average micropore width L_0 is related to E_0 by

$$L_0\ (\text{nm}) = 10.8\ (\text{nm kJ mol}^{-1})/(E_0 - 11.4\ \text{kJ mol}^{-1}) \quad (2)$$

E_0 and W_0 are usually obtained from the adsorption of small molecular probe molecules (typically CO_2, CH_2Cl_2, C_6H_6) with critical dimensions around 0.33–0.40 nm, and unhindered by constrictions in the structure. Eq. (2) reflects therefore the average pore size of the actual micropore distribution.

The limiting micropore volume $W_0 = N_{a0}V_m$, where V_m is the molar volume in the adsorbed state. To a first and often good approximation [1,3,9,10], it is assumed to be that of the corresponding liquid or solid, but differences may exist. For example [7], in the case of CO_2 at 273 K, the molar volume in the adsorbed state appears to be 42.90 $cm^3\,mol^{-1}$, against 48.23 $cm^3\,mol^{-1}$ for the

free liquid at this temperature. The difference may be due to some degree of order in the micropores.

As shown elsewhere [1,3], Eq. (1) leads to an expression for the enthalpy of immersion into the corresponding liquid,

$$\Delta_i H\ (\mathrm{J\,g^{-1}}) = -\beta E_0 (W_0/V_\mathrm{m}) \times (1+\alpha T)\Gamma(1+1/n) + h_i S_\mathrm{e} \qquad (3)$$

where α is the expansion coefficient of the liquid; Γ, the *Gamma* function and $h_i S_\mathrm{e}$ represents the wetting of the external (non-microporous) surface area of the solid, S_e. The specific enthalpy of wetting h_i is typically around $-0.1\ \mathrm{J\,m^{-2}}$. With the help of Eq. (3) it is possible to calculate the micropore volume $W_0(L_\mathrm{c})$ actually filled by a molecular probe with a critical dimension L_c, which leads to the volume micropore distribution $\Delta W/\Delta L = f(L)$. This is true as long as entry into wider pores is not limited by constrictions smaller than their actual size. If such constrictions are present, a pore may not be filled by a liquid probe with a diameter L_c larger than the constriction and one obtains an apparent PSD.

It has also been shown [1,3] that in the absence of such constrictions (carbons with a sufficiently high degree of activation), a reasonable micropore distribution can be derived from a modified Dubinin equation proposed by Stoeckli [3] and discussed by Carrott and Carrott-Ribeiro [13],

$$\theta(A) = N_\mathrm{a}/N_\mathrm{a0} = [a/(a+(A/\beta K_0)^3)]^v \qquad (4)$$

a and v are adjustable parameters and K_0 is related to the average micropore width L_0 by $K_0 = E_0 L_0$. The corresponding distribution $\mathrm{d}W/\mathrm{d}L = f(L)$ is

$$f(L) = 3W_0 L^{(3v-1)} a^v \exp[-aL^3]/\Gamma(v) \qquad (5)$$

Computer modelling of adsorption and the determination of PSDs based on standard isotherms has become increasingly popular in the field of carbons [14]. We have shown recently that the use of CO_2 adsorption at 273 K, up to 3.2 MPa, provides good correlations with other techniques [8]. The standard isotherms were determined for slit-shaped micropores with effective widths of 0.4–2.5 nm, by adapting a commercially available program for "Monte-Carlo" type calculations (Cerius-2, Molecular Simulations Ltd.).

3. Experimental

We used a commercially available molecular sieve carbon T-0, known to adsorb molecules smaller than approximately 0.6 nm.

The original sample, T-0, was activated by steam at 900 °C, to weight losses (burn-off) of 18%, 21% and 35%, which led to samples T-18, T-21 and T-35. We used batches of 3 g and steam provided by a bath at 70 °C, carried by a stream of nitrogen ($300\ \mathrm{cm^3\,min^{-1}}$). Under these conditions, the rate of burn-off was approximately $0.16\%\,\mathrm{min^{-1}}$, in good agreement with other carbons.

The samples were subjected to CO_2 adsorption at 273 K, using a high-pressure device described by Guillot and coworkers [12,15,16]. The isotherms were subsequently analyzed with the help of the DR equation and of the model isotherms [7,8]. This leads to the effective PSDs based on CO_2, a molecular probe of less than 0.4 nm.

The apparent PSDs, reflecting the volume of the pores without any gate effect, were determined by immersion calorimetry, using Eq. (3). Back calculations based on the experimental enthalpies of immersion lead to the volumes $W(L_\mathrm{c})$ actually filled by the molecular probe of critical dimension L_c.

The characteristic energy E_0 and the external surface area S_e are known from the DR equation and from the comparison of the CO_2 isotherm with the reference isotherm on the non-porous carbon black *Vulcan3-G* up to 3.2 MPa [16].

STM observations were carried out on sample T-21 with a Digital Instruments Nanoscope-E instrument, as described previously for other microporous carbons.

4. Results and discussion

The DR plots and the comparison plots of the CO_2 isotherms at 273 K (reference Vulcan3-G [16]) are shown in Figs. 1 and 2. These plots lead to the structural characteristics given in Table 1. In the case of the micropore volumes W_0, we used the value of $42.90\ \mathrm{cm^3\,mol^{-1}}$ for the molar volume of CO_2 in the adsorbed state, as suggested by different authors. One observes a good correlation

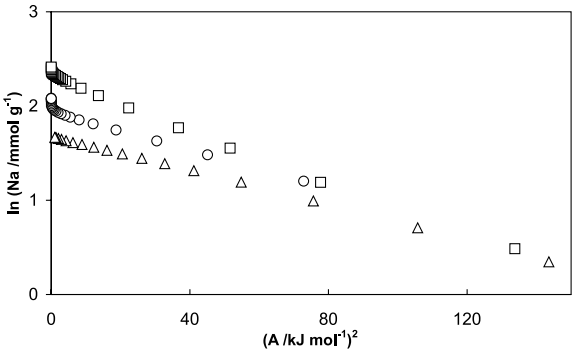

Fig. 1. DR plots for the adsorption of CO_2 at 273 K on carbons T-0 (△), T-21 (○) and T-35 (□).

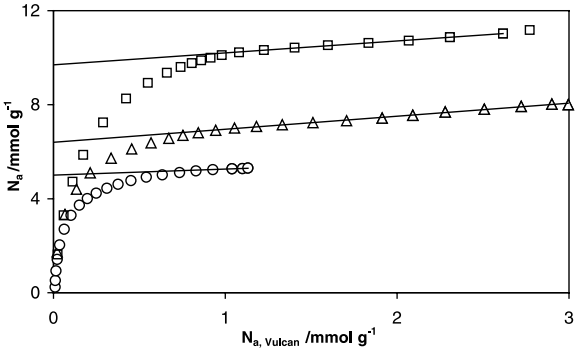

Fig. 2. Comparison of CO_2 adsorption at 273 K on carbons T-0 (△), T-21 (○) and T-35 (□) and on carbon black Vulcan3-G.

between the micropore volumes W_0 obtained from the DR and the comparison plots.

The data for E_0, W_0 and S_e has been cross-checked by comparing the experimental enthalpies of immersion into CS_2 at 293 K, with those calculated by Eq. (3). This liquid was chosen in view of its structural similarity with CO_2, which means that both molecules probe the same micropore volume. The calculated and the experimental values of $-\Delta_i H(CS_2)$ in J g^{-1} are respectively 102/117 (T-0), 123/121 (T-18), 127/123 (T-21) and 158/149 (T-35), the experimental uncertainty being around 2–3%. The good agreement indicates self-consistency between the adsorption and immersion data.

Following Eq. (2), the internal micropore systems probed by CO_2 and by liquid CS_2 have therefore average widths L_0 of 0.6 nm (T-0), 0.67 nm (T-21) and 0.92 nm (T-35). This is due to the simultaneous reaction of steam with the constrictions and, to some extent, with the overall (mainly internal) micropore system.

The analysis of the CO_2 isotherms in terms of a weighted contribution of the standard isotherms derived from modelling [8] leads to the PSDs shown in Figs. 3–5. These distributions are also in agreement with the predictions based on the analysis of the adsorption data by Eqs. (4) and (5). They correspond to the actual PSD in the solid.

On the basis of Eq. (3), the enthalpies of immersion of the samples into a series of liquids, given in Table 2, lead to the PSDs also shown in Figs. 3–5.

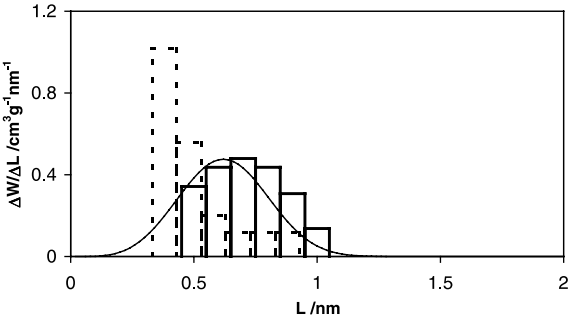

Fig. 3. PSD in carbon T-0 obtained from modelling (—) and from liquid probes (- - -). The continuous curve corresponds to Eq. (5).

Table 1
Structural characteristics of samples T-0 to T-35 based on the CO_2 (273 K) isotherms

Sample	DR analysis			Comparison/Vulcan3-G		Eqs. (4) and (5)			Modelling
	E_0/kJ mol^{-1}	W$_0$/cm^3 g^{-1}	L_0/nm	W_0/cm^3 g^{-1}	S_e/m^2 g^{-1}	a/nm^{-3}	v	K_0/kJ nm mol^{-1}	L_0/nm
T-0	29.31	0.23	0.60	0.21	18	5.46	1.51	17.67	0.71
T-21	27.62	0.31	0.67	0.31	20	1.84	0.76	18.33	0.76
T-35	23.10	0.45	0.92	0.42	36	0.72	0.92	21.32	0.93

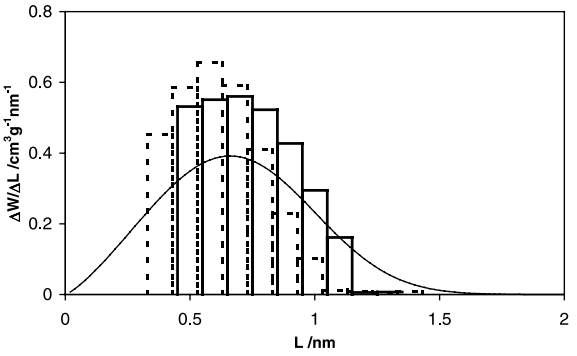

Fig. 4. PSDs in carbon T-21 obtained from modelling (—) and from liquid probes (- - -). The continuous curve corresponds to Eq. (5).

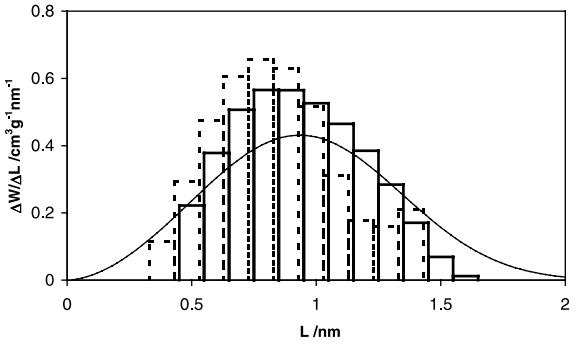

Fig. 5. PSDs in carbon T-35 obtained from modelling (—) and from liquid probes (- - -). The continuous curve corresponds to Eq. (5).

Table 2
Enthalpies of immersion $-\Delta_i H$ (J g^{-1}) at 293 K into liquids of critical dimensions L_c

Sample	Liquid (L_c/nm)				
	CS_2 (0.33)	C_6H_6 (0.41)	c-C_5H_{10} (0.44)	CCl_4 (0.63)	Trixy[a] (1.5)
T-0	117.1	76.6	49.0	18.0	
T-18	121.3	100.5	68.1	46.4	4.4
T-21	123.0	109.3	87.4	83.8	7.0
T-35	149.0	131.9	122.5	118.0	19.2

[a] Tri-2,4-xylyl phosphate.

It appears that, up to a burn-off of approximately 20%, these distributions are not as wide as the real distribution probed by CO_2 or benzene. It is a direct consequence of the 'gate' effect at the entrance to certain pores, which reduces their accessibility to molecules normally compatible with their size. As a result, one obtains apparent PSDs, also characterized by a total volume smaller than that obtained with CO_2 or benzene.

Figs. 3–5 show the effect of progressive activation by steam on both the constrictions and the internal system. (Activation to 18% burn-off, an intermediate between 0% and 20%, is not shown here). Up to 21% burn-off, the changes affect preferentially the constrictions, and one observes an increase in the accessibility of the pores system for larger molecules. As a consequence, the apparent distribution shifts gradually towards the real distribution. With respect to sample T-0, the latter also changes, due to the effect of activation (see Table 1).

STM observations carried out on sample T-21 lead to the frequency distribution $\Delta N/\Delta L$ of the pores found on the surface of the solid, as shown in Fig. 6. The study is based on a total of 50 pores observed on five different regions considered to be representative of the surface. The distribution has been adjusted to the apparent PSD obtained by immersion calorimetry, $\Delta W/\Delta L$ (see Fig. 4), shown for comparison purposes. It appears that the pores located on the surface are relatively wide, which suggests a funnel-type structure. It probably results from the activation process. The constrictions, which are gradually eliminated during activation, are obviously placed between the surface and the bulk of the micropores.

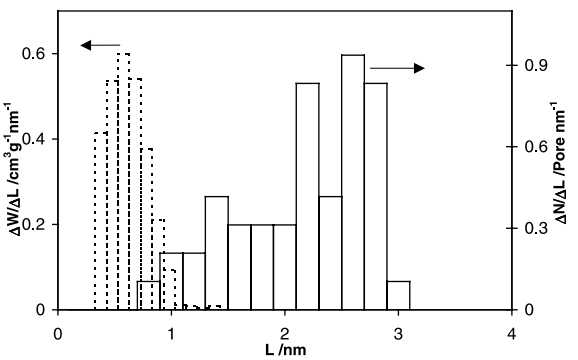

Fig. 6. Frequency distribution $\Delta N/\Delta L$ of the pore widths observed by STM on the surface of sample T-21. For comparison purposes, the apparent PSD $\Delta W/\Delta L$ obtained by immersion calorimetry (see Fig. 4) is also shown.

In conclusion, the present study shows how gate effects in microporous carbons and their evolution can be assessed by the combination of CO_2 adsorption at 273 K with immersion calorimetry at 293 K. With the help of model isotherms, the former technique leads to the effective PSD. It is given by CO_2, a small molecular probe, which can by-pass constrictions wider than 0.4 nm. On the other hand, immersion calorimetry reveals the apparent distribution, which corresponds to pores without constrictions, filled by the various liquid probes (0.33–1.5 nm). The gradual opening of the internal micropore system by activation with steam can also be followed by these techniques.

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