

The Microporosity of Activated Carbon Fibre KF1500 Assessed by Combined CO₂ Adsorption and Calorimetry Techniques and by Immersion Calorimetry

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ABSTRACT: The microporous structure of the activated carbon fibre KF1500 was investigated by applying a new technique as presented here. This was based on a combination of high-pressure CO₂ adsorption measurements between 253 K and 353 K with direct measurement of the differential heats of adsorption at 298 K at low and medium coverages.

The validity of this approach was tested by using two activated carbons which has been characterized previously by a variety of techniques, including immersion calorimetry. It appears that a combination of high-pressure adsorption and calorimetry with CO₂ alone is a useful tool for the characterization of the whole range of microporosity. This approach confirms earlier observations, according to which the initial stage of adsorption by strongly activated carbons corresponds to adsorption on the walls of large micropores rather than to the primary filling of small micropores.

INTRODUCTION

Unlike zeolites and other well-structured materials, activated carbons have a heterogeneous microporous structure. This is true, in particular, for strongly activated materials of industrial importance such as activated fibres. An accurate characterization of the microporous structure therefore requires a variety of techniques such as vapour adsorption, immersion calorimetry and microscopy (Stoeckli 1990, 1995; Stoeckli *et al.* 1998), but important questions may still remain unanswered. One of these is the problem of primary and secondary micropore filling in the case of highly activated materials. This question has been examined by various authors (Carrott *et al.* 1986, 1991; Kakei *et al.* 1991) and, on the basis of combined adsorption and immersion techniques, Stoeckli *et al.* (1993) came to the conclusion that, for strongly activated carbons, the initial adsorption stage corresponded essentially to secondary filling, i.e. to adsorption on the walls of wide pores followed by their gradual filling. This mechanism also provides information on the true surface area of the micropore walls.

This question is re-examined in the context of CO₂ adsorption, where the determination of adsorption isotherms over a wide range of pressures (0.1–2 MPa) and temperatures (253–353 K) has been combined with adsorption calorimetry from the gas phase. This approach has been made possible by the recent introduction of high-pressure techniques which make CO₂ adsorption more reliable than in the past. In the present paper, we wish to illustrate the potential of this relatively simple

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approach by examining two samples which have been characterized already with other adsorptives. The method is then used for the characterization of a commercially activated fibre, KF1500.

Through the use of a high-pressure volumetric device operating at pressures up to 2 MPa and in the temperature range 253–353 K, Guillot *et al.* (1997) have shown that the complete characterization of the microporosity of KF1500 may be achieved by the analysis of the CO₂ adsorption isotherms, which follow Dubinin's theory (Dubinin 1975, 1989; Stoeckli 1990, 1993, 1995) outlined in the following section. The results are in relatively good agreement with those of Kakei *et al.* (1990) obtained from the nitrogen isotherm and show that the Dubinin–Radushkevich (DR) plot exhibits three linear sections. However, in the present case, they reveal an additional linear section in the low relative pressure range.

THEORY

The characterization of microporous carbons is usually based on Dubinin's theory and its extensions to immersion calorimetry (Stoeckli 1981, 1995) which provide complementary information. The fundamental expression is the Dubinin–Astakhov equation, i.e.

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

where $A = RT \ln(P_s/P)$, N_a is the amount adsorbed (usually given in mol/g) at a relative pressure of P/P_s and temperature T , and N_{a0} is the limiting amount filling the micropores. The quantity E is the characteristic energy of the system which depends on the solid and on the adsorbate. It has been shown that the effect of the adsorbate can be expressed by a factor β called the affinity coefficient, the reference being benzene by convention and therefore $\beta(C_6H_6) = 1$. Under these circumstances, $E = \beta E_0$ and it appears that E_0 is an inverse function of the average micropore width L (Stoeckli *et al.* 1990; Stoeckli 1995), i.e.

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

This expression provides reliable data in the domain $0.4 < L < 1.7\text{--}1.8 \text{ nm}$ or $E_0 > 17\text{--}18 \text{ kJ/mol}$.

For active carbons of low and medium activation (burn-off below 30–40%) the exponent n is equal to 2, which corresponds to the original equation of Dubinin and Radushkevich (DR). On the other hand, in the case of strongly activated carbons, $n < 2$ and E_0 has values between 17 kJ/mol and 14 kJ/mol (Dubinin and Stoeckli 1980).

From the limiting amount adsorbed, N_{a0} , it is possible to estimate the volume filled by the adsorbate by using its molar volume V_m in the condensed state at the corresponding temperature. In the absence of molecular sieve effects, $N_{a0} V_m$ corresponds to the micropore volume, W_{0^*} , of the solid. Molecules of different sizes can therefore be used to assess the micropore distribution between 0.4 nm and 1.5 nm. However, in the case of strongly activated carbons, the structure is equally accessible to most molecular probes, thus indicating the presence of wide micropores (supermicropores) or a flexible structure, as suggested by Kakei *et al.* (1990).

Modifications have also been proposed to allow the adaption of equation (1) to high pressures (where fugacities are used) and to adsorption above the critical temperature (Dubinin 1975). However, until recently, the DA equation has been used mainly in the context of adsorption under moderate pressure (typically 0.1 Pa to 10⁵ Pa).

As shown elsewhere (Stoeckli 1989, 1995), an alternative expression has been suggested for equation (1) on the basis of mathematical modelling, i.e.

$$N_a/N_{a0} = [a/(a + (A/\beta K_0)^3)]^y \quad (3)$$

where a and v are adjustable parameters and K_0 is related to E_0 . This isotherm corresponds to the gamma-type distribution of the micropore widths L , i.e.

$$f(L) = 3L^{(3v-1)}a^v \exp[-aL^3]/\Gamma(v) \quad (4)$$

which is in good agreement with molecular sieve experiments for carbons with low to medium activation (average micropore widths up to approximately 1.5 nm). On the other hand, for strongly activated and therefore heterogeneous carbons, molecular sieve effects are mostly absent and distribution (4) becomes less accurate. It is also likely that the structure becomes flexible and adapts itself to the host molecule as suggested, for example, by Stoeckli *et al.* (1980), Stoeckli (1995) and Kaneko *et al.* (1992). This is a likely behaviour for fibre KF1500 discussed below.

It is well known that, due to restricted diffusion, nitrogen adsorption measurements at 77 K are not suitable for the characterization of narrow micropores which are filled at low relative pressures. Usually, CO_2 adsorption measurements near room temperature provide complementary information. In view of the high values of the saturation pressure of CO_2 in this temperature range and because of the lack of high-pressure measurements, the resulting isotherms correspond to the range of low relative pressure in which the filling of the narrow micropores usually occurs. Except for adsorbents with homogeneous microporosity, the two sets of experiments fail to characterize the full range of microporosity and additional adsorbates are required to complete the characterization.

It has been shown that the enthalpy of immersion of an activated carbon into a liquid whose vapour is adsorbed according to equation (1) is given by:

$$-\Delta h_i(\text{J/g}) = EN_{\text{m}}(1 + \alpha T)\Gamma(1 + 1/n) - h_i S_c \quad (5)$$

or, on introducing the corresponding molar volumes and affinity coefficients, by:

$$-\Delta h_i(\text{J/g}) = \beta E_0 W_0(1 + \alpha T)\Gamma(1 + 1/n)/V_m - h_i S_c \quad (6)$$

where α is the expansion coefficient of the adsorbate in the condensed phase and Γ is the tabulated 'gamma' function. The last term takes into account the wetting ($h_i < 0$) of the external surface area S_c , which can be determined either from equation (1) or from other techniques such as comparison plots (Gregg and Sing 1982).

It is important to point out that the micropore volumes W_0 are determined with an accuracy of 3–5%. In the case of the surface areas S_{mi} and S_c , the accuracy is within 10%.

EXPERIMENTAL

In the present study, activated carbons CAF-B, AGB and fibre KF1500 were examined. The first two had already been characterized by a variety of techniques and the relevant data are found in Table 1 together with the results obtained in the present approach.

For comparative purposes, we have also examined the adsorption and differential heat of adsorption of CO_2 at 298 K on the non-porous carbon black Vulcan 3 which has a BET nitrogen surface area of 71 m^2/g .

The high-pressure adsorption measurements were carried out over the temperature range 253–353 K with a device operating at pressures up to 2 MPa, as described previously (Guillot *et al.* 1997). The differential heats of adsorption of CO_2 were all determined at 298 K and for pressures up to 1.5 MPa with a Tian–Calvet calorimeter (C80 Setaram). Complementary measurements have also been carried out at pressures below 0.1 MPa by coupled thermogravimetry–calorimetry (TG–DSC Setaram).

TABLE 1. Main Characteristics of Carbons Studied

Carbon		W_o (cm ³ /g)	E_o (kJ/mol)	L (nm)	S_{mf}^a (m ² /g)	S_{mf}^b (m ² /g)	S_c (m ² /g)
CAF-B	Stoekli <i>et al.</i> (1993)	0.266	28.3	0.61	870		95
	CO ₂ (DR at 261–353 K)	0.274	28.9	0.62	884		
	Comparison CO ₂ 261 K/Vulcan 3	0.250					72
AGB	Stoekli <i>et al.</i> (1993)	0.455	14.3	>2	310	400	290
	CO ₂ (DA at 298 K)	0.450	16.6	>2	428	413	
	Comparison CO ₂ 258 K/Vulcan 3	0.450					210
KF1500	CO ₂ (DA at 253–298 K)	0.62	18.2	1.6	775	725	
	Comparison CO ₂ 253 K/Vulcan 3	0.60					28
	α_s -Plot for N ₂ 77 K	0.63					22
	Immersion into H ₂ O + caffeine					806	

^aSurface area of micropore walls determined via equation (7). ^bSurface area of micropore walls determined from initial section of DR plot (see Figures 1, 4 and 8).

Prior to measurement, the samples were outgassed at 473 K for 15 h under a residual vacuum better than 1×10^{-4} Pa. For the calorimetry measurement with the C80 calorimeter, the gas was introduced at a constant flow rate of 0.25 cm³ (STP)/min using a mass flow controller (Brooks 5850S). The heats of adsorption have been corrected for the heat due to the expansion of the gas into the calorimeter cell, as suggested by Rouquerol *et al.* (1980).

Characterization of the KF1500 fibre included immersion calorimetry measurements which were carried out in the Chemistry Department of the University of Neuchâtel.

Adsorption measurements at low pressures and immersion calorimetry were carried out as described in detail elsewhere (Stoekli *et al.* 1993).

RESULTS

Carbon CAF-B

As shown by Stoekli *et al.* (1993), this carbon which results from the activation of a vegetable precursor to a weight loss of 37% has a micropore distribution of medium heterogeneity and an average micropore width of 0.61 nm. The characteristics of the solid are listed in Table 1.

The CO₂ adsorption isotherms were determined at 261, 273, 298, 323 and 353 K and at pressures up to 2 MPa. The corresponding DR plot shown in Figure 1 is linear over the entire range of adsorption potentials A. On the basis of the affinity coefficients $\beta(\text{CO}_2) = 0.35$ and $\beta(\text{CH}_2\text{Cl}_2) = 0.66$, one obtains a characteristic energy, E_o , of 28.9 kJ/mol from the CO₂ isotherm, which is close to the value of 28.3 kJ/mol derived earlier from the use of CH₂Cl₂ at 293 K and other vapours.

The differential heat of adsorption of CO₂ at 298 K shown in Figure 2 is almost constant between 0.5 and 4.5 mmol/g, as observed for CH₂Cl₂. It is interesting to note that the ratio of the respective differential heats (28.6 kJ/mol CO₂ and 55 kJ/mol CH₂Cl₂) is very close to the ratio of the corresponding affinity coefficients, β . The pore size distribution derived from the CO₂ isotherm at 298 K on the basis of equations (4) and (5) is shown in Figure 3. It is in relatively good agreement with the distribution obtained with other adsorptives and with the histogram derived from molecular sieve experiments (Stoekli *et al.* 1990, 1993).

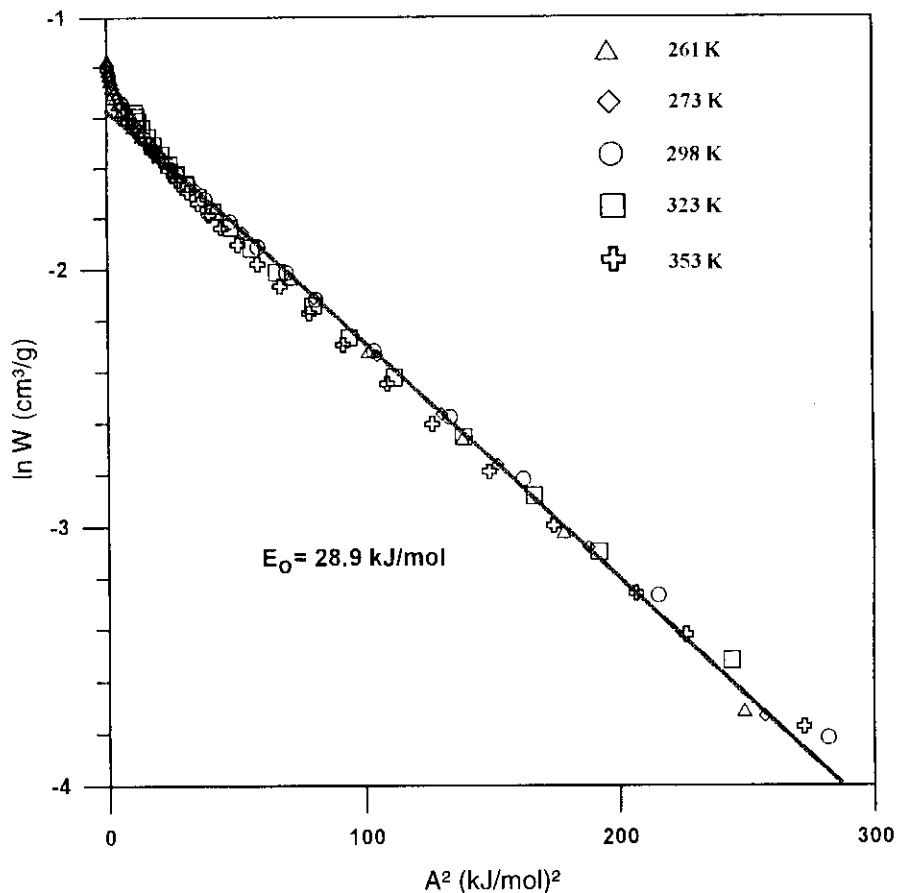


Figure 1. DR plot for the adsorption of CO₂ on carbon CAF-B at 261, 273, 298, 323 and 353 K, respectively.

As listed in Table 1, a comparison of the CO₂ isotherms at 261 K on CAF-B and on Vulcan 3 led to a micropore volume of 0.25 cm³/g and an external surface area of 72 m²/g, in good agreement with earlier determinations.

Carbon AGB

This solid has been characterized previously and its main characteristics are listed in Table 1. These include the determination of the surface area of the micropore walls which was confirmed by the present study.

The DR plot for the adsorption of CO₂ at 258, 273, 298, 323 and 353 K shown in Figure 4 is a smooth curve, as frequently observed for strongly activated carbons. Over the initial linear section ($100 < A^2 < 250$ kJ²/mol²), the data seem to be slightly temperature-dependent as observed earlier by Guillot *et al.* (1997) for the carbon Maxsorb-PX21.

Extrapolation of this section led to a value of 3.50 mmol CO₂/g, which corresponds either to a volume of 0.150 cm³/g using the molar volume of 45.7 cm³/mol at 298 K or to a surface of 413 m²/g assuming a molecular surface area of 19.6×10^{-20} m². The latter was calculated from the density

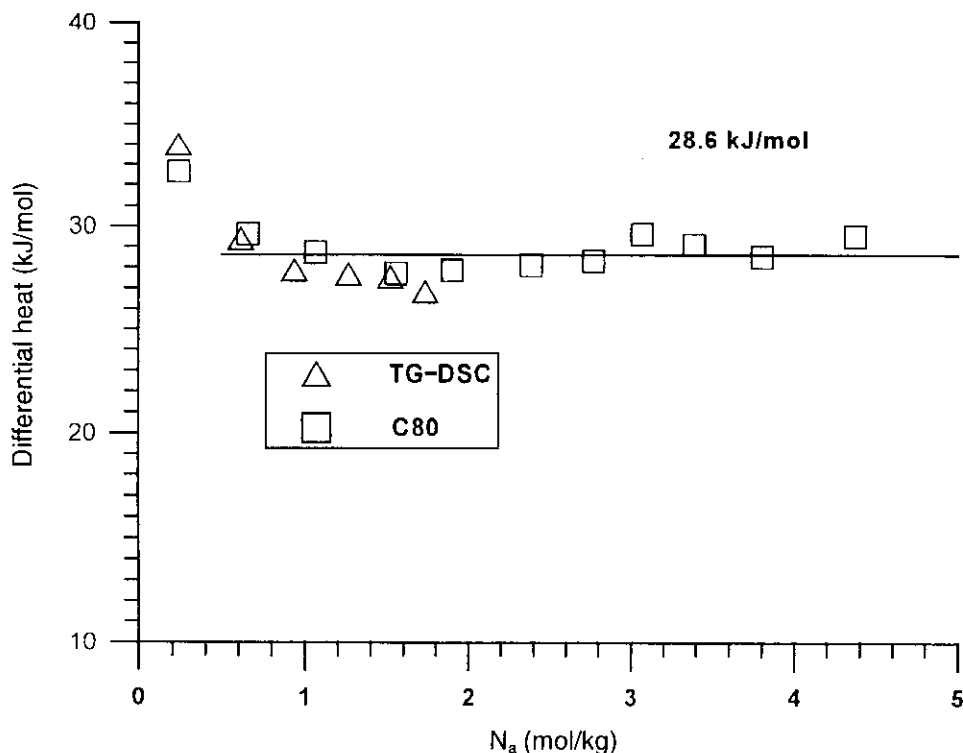


Figure 2. Differential heat of adsorption of CO_2 on carbon CAF-B at 298 K.

(Gregg and Sing 1982) and is in good agreement with the value obtained from CO_2 adsorption at 298 K on Vulcan 3, which has a nitrogen BET surface area of $71 \text{ m}^2/\text{g}$.

The two quantities, $0.150 \text{ cm}^3/\text{g}$ and $413 \text{ m}^2/\text{g}$, correspond either to primary micropore filling or to adsorption on the walls of large micropores. At this stage, however, both mechanisms are plausible and a clear distinction requires further experimental evidence.

In the case of micropore filling and in agreement with equation (2), the characteristic energy of the linear section, $E_0 = 27.2 \text{ kJ/mol}$, would correspond to an average pore width L of 0.7 nm , which is close to the value for carbon CAF-B. However, from the pore size distribution calculated from the overall isotherm and shown in Figure 5, it appears that the volume of the micropores up to 0.9 nm represents only $0.02 \text{ cm}^3/\text{g}$. This is much smaller than suggested by the initial section of the DR plot. Moreover, the differential heat of adsorption of CO_2 at 298 K (Figure 6) is much lower than in the case of CAF-B: it begins at ca. $25\text{--}27 \text{ kJ/mol}$ and rapidly reaches a plateau value at ca. 18 kJ/mol after the adsorption of 1.4 mmol/g or $0.060 \text{ cm}^3/\text{g}$ of CO_2 . As suggested by the heats observed for carbon CAF-B (Figure 2) and the values reported for open graphitic surfaces, the value of 18 kJ/mol excludes any significant filling of small micropores despite the high value of E_0 (27.2 kJ/mol) derived from the slope of the initial section of the DR plot. The latter suggests a priori the presence of narrow micropores, which is not the case in reality.

The present example illustrates the importance of adsorption calorimetry to establish beyond doubt the reduced role of primary micropore filling in carbons such as AGB. The enthalpies of immersion of this carbon into liquids of various molecular dimensions given by Stoeckli *et al.* (1993) also suggest equal accessibility of the micropore volume W_0 , which confirms the general picture.

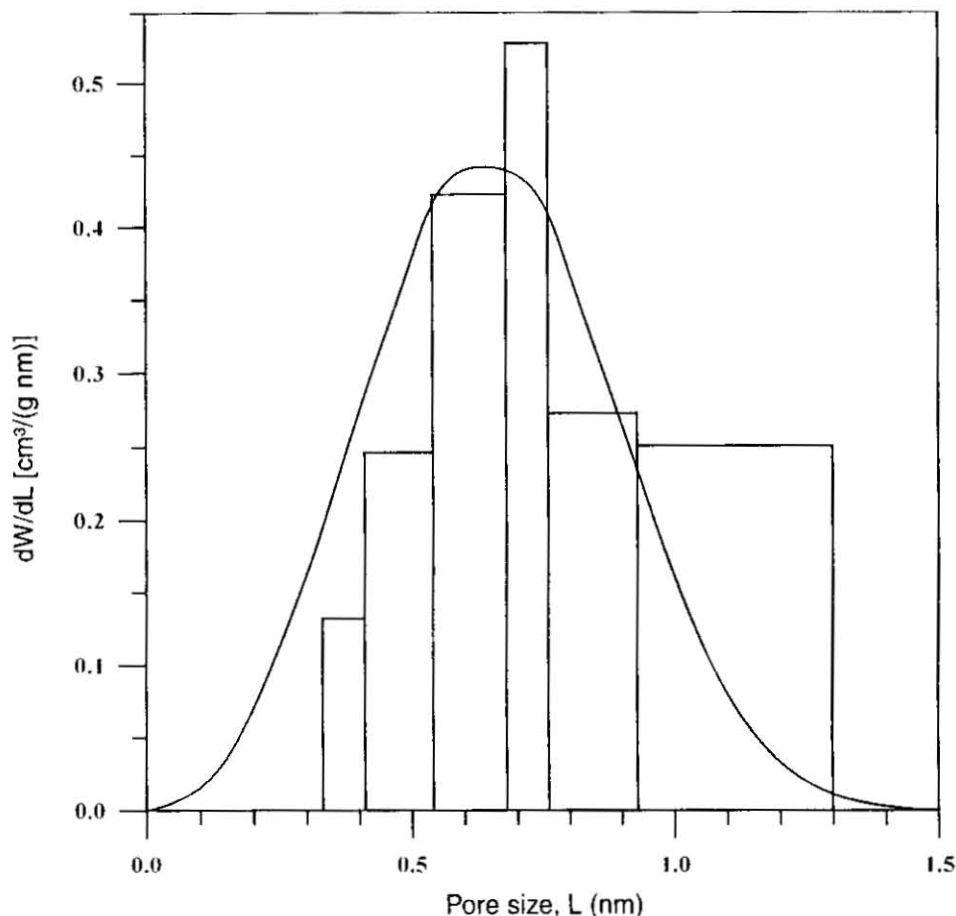


Figure 3. Pore size distribution of carbon CAF-B obtained from molecular sieve experiments (histogram) and from the CO_2 isotherm at 298 K via equations (3) and (4) (curve).

Our observations also confirm the model of Kaneko *et al.* (1992) for strongly activated carbons and it follows that the process reflected by the initial linear section of the DR plot must correspond to the coating of the micropore walls whose area is approximately $413 \text{ m}^2/\text{g}$. After adsorption of 1.4 mmol/g , multilayer adsorption and pore filling sets in. This is followed at a later stage by adsorption on the external surface where the interactions are lowest. According to Bottani *et al.* (1994), the isosteric heat of adsorption on graphitic surfaces varies from 14 kJ/mol to 19 kJ/mol depending on the degree of surface coverage. However, this region was not reached for carbon AGB in our calorimetry experiment at 298 K.

Our combined adsorption and calorimetry experiments with CO_2 confirm therefore the mechanism proposed earlier for adsorption by this solid, for which a micropore surface area of ca. $400 \text{ m}^2/\text{g}$ was obtained. This value is in good agreement with the surface area of $444 \text{ m}^2/\text{g}$ derived from the initial section of the CO_2 isotherm at 298 K.

As reported earlier, carbon AGB has a micropore volume W_0 of $0.455 \text{ cm}^3/\text{g}$ and an external surface area of $290 \text{ m}^2/\text{g}$. It is interesting to point out that comparison of the CO_2 isotherm at 253 K

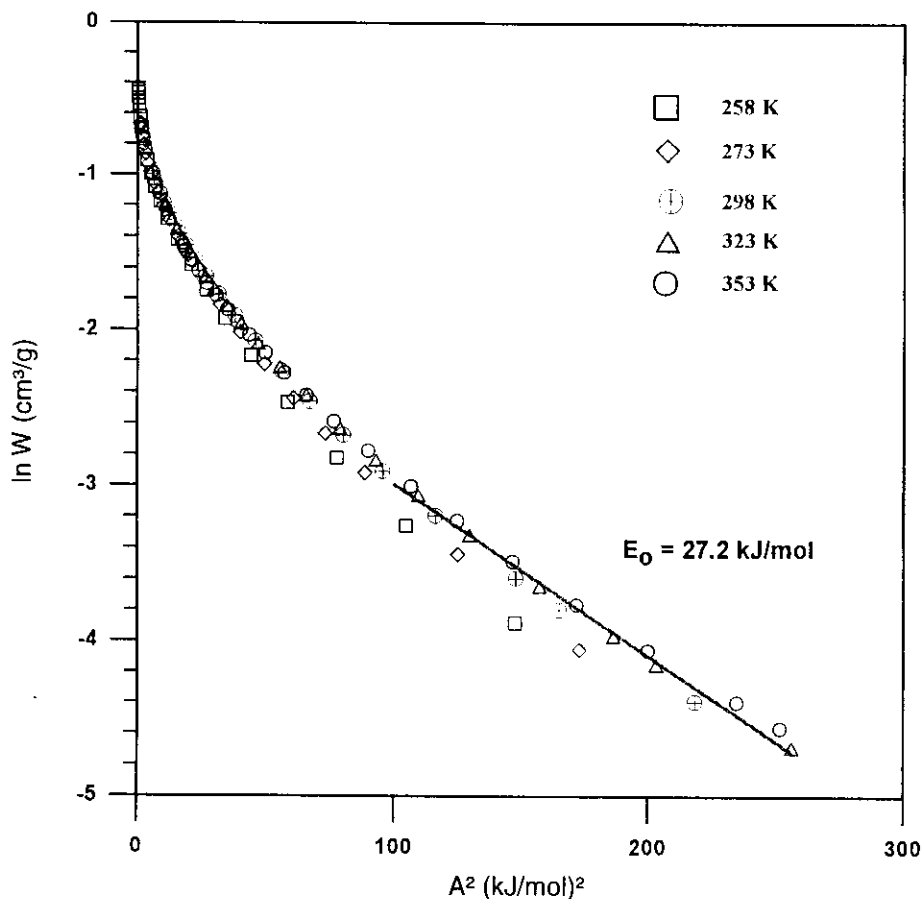


Figure 4. DR plot for the adsorption of CO_2 on carbon AGB at 258, 273, 298, 323 and 353 K, respectively.

with the isotherm obtained on Vulcan 3 at the same temperature led to a micropore volume of $0.45 \text{ cm}^3/\text{g}$ and an external surface area of $210 \text{ m}^2/\text{g}$.

These results show that the present technique, based on CO_2 adsorption and calorimetry and on a reference isotherm for a non-porous sample, can be applied safely in the case of other strongly activated materials such as KF1500 as discussed below.

Activated fibre KF1500

This fibre is microporous as indicated by a first test based on the analysis of the nitrogen isotherm using Sing's α_s -plot (Gregg and Sing 1982) as shown in Figure 7. This suggests a micropore volume of $0.63 \text{ cm}^3/\text{g}$ and an external surface area S_c of $22 \text{ m}^2/\text{g}$, in agreement with other determinations based on equation (1) and on immersion calorimetry. In agreement with the study of Kaneko *et al.* (1992) of carbons with high surface areas, the straight line passing through the origin leads to an apparent surface area of $1660 \text{ m}^2/\text{g}$ as against an S_{BET} value of $1590 \text{ m}^2/\text{g}$.

The various characteristics of KF1500, including the analysis by equation (1), are listed in Table 1. Table 2 gives the enthalpies of immersion of this fibre into liquids of various molecular sizes and into water.

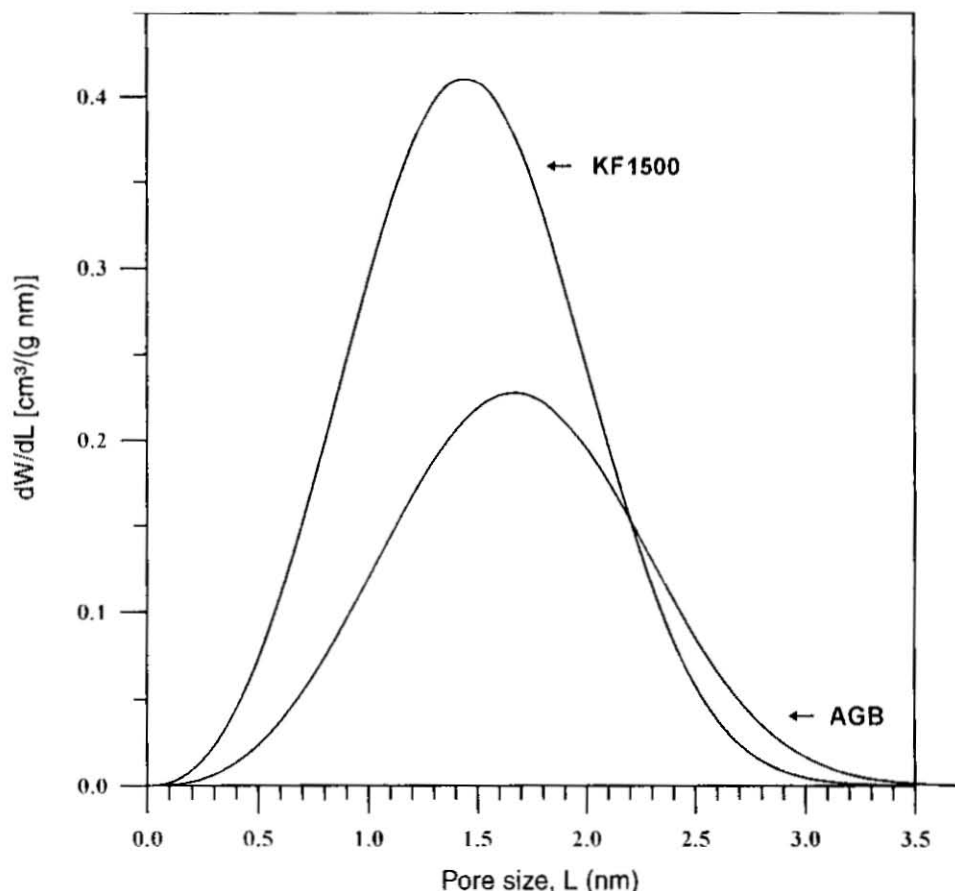


Figure 5. Pore size distributions for carbon AGB and activated fibre KF1500 obtained from the respective CO_2 isotherms at 298 K via equations (3) and (4).

From an analysis of the nitrogen isotherm at 77 K and the CO_2 isotherms between 258 K and 363 K (see Figure 8), it appears that this material was very heterogeneous. The pore size distribution derived from the CO_2 isotherm at 298 K using equations (3) and (4) is shown in Figure 5. The material had an average pore width of 1.63 nm which was less than that found for AGB. The heterogeneity of the micropore system was confirmed by a comparison of the experimental enthalpies of immersion with the values calculated using equation (6) with $W_0 = 0.62 \text{ cm}^3/\text{g}$ and $E_0 = 18.2 \text{ kJ/mol}$. The good agreement between these enthalpies (see Table 2) indicates that the different molecular probes (0.4 nm to 1.5 nm) filled the same micropore volume, W_0 . This suggests the presence of wide micropores and probably some flexibility in the structure.

As pointed out by Kakei *et al.* (1991), the nitrogen DR plot is not linear and three sections were identified. However, Guillot *et al.* (1997) subsequently showed that a fourth linear section exists at lower relative pressures. This corresponds to section I in the CO_2 DR plot shown in Figure 8, with a characteristic energy E_0 of 26.7 kJ/mol. The extrapolation leads to a limiting amount $N_a = 6.15 \text{ mmol/g}$. At 298 K, this corresponds either to a primary filling of $0.28 \text{ cm}^3/\text{g}$ of micropores with an average width of 0.7 nm, or to the coating of micropore walls with a total area of $725 \text{ m}^2/\text{g}$. The latter value may be compared with the total surface area of $828 \text{ m}^2/\text{g}$ derived from the enthalpy

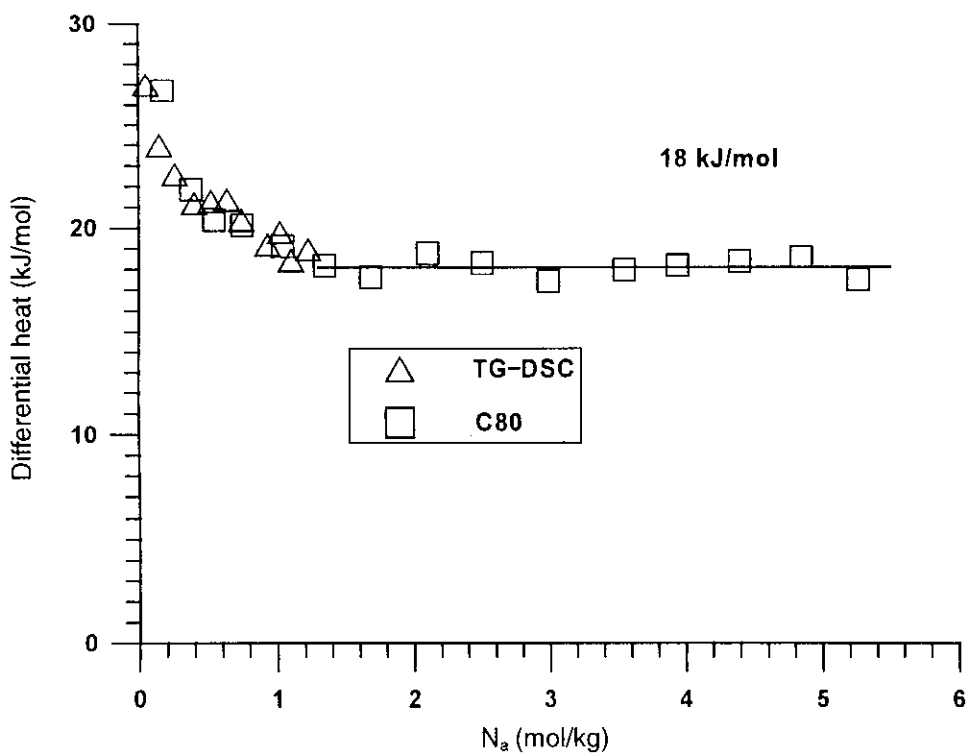


Figure 6. Differential heat of adsorption of CO_2 on carbon AGB at 298 K.

TABLE 2. Enthalpies of Immersion of Fibre KF1500 into Various Liquids of Critical Molecular Dimensions L_c at 293 K^a

Liquid	L_c (nm)	$-\Delta h_{i, \text{exp}}$ (J/g)	$-\Delta h_{i, \text{calc}}$ (J/g)
C_6H_6	0.41	149 \pm 5	151
CCl_4	0.63	149 \pm 5	143
Tetrabutylurea	0.93	161 \pm 7	148
Tri(2,4-xylyl)phosphate	1.50	118 \pm 4	123
H_2O	0.35	73.4 \pm 5	–

^aCalculated enthalpies obtained from equation (6).

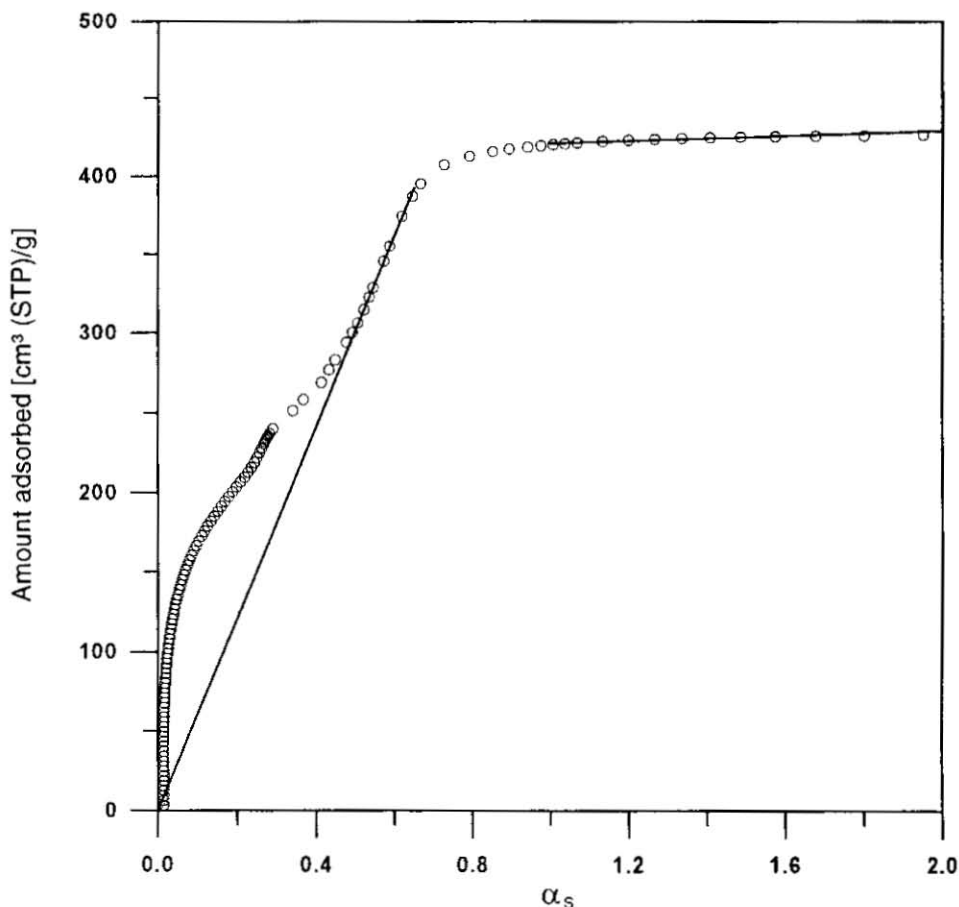


Figure 7. α_s -Plot for the adsorption of N_2 (77 K) by activated fibre KF1500.

of immersion into an aqueous solution of caffeine. This technique, which has been described in detail elsewhere (Stoekli 1995), provides a reasonable estimate of the true surface area of carbonaceous materials, caffeine being adsorbed from the solution as a monolayer with a specific enthalpy of -0.113 J/m^2 (the uncertainty being ca. 10%). Since the external surface area of KF1500 was $22 \text{ m}^2/\text{g}$, it follows that the surface area of the micropore walls was ca. $806 \text{ m}^2/\text{g}$. For locally slit-shaped micropores (Innes *et al.* 1989; Stoekli 1990; Kaneko *et al.* 1992), the surface area of the walls can also be estimated on the basis of the volume W_o and the average width L given by equation (2), i.e.

$$S_m (\text{m}^2/\text{g}) = 2000W_o/L(\text{nm}) \quad (7)$$

The data given in Table 1 lead to $775 \text{ m}^2/\text{g}$ and the three different estimates of the surface area of the micropores walls (725 , 806 and $775 \text{ m}^2/\text{g}$) are therefore in good agreement.

As in the case of carbon AGB, the differential heat of adsorption of CO_2 at 298 K (Figure 9) provided further and independent information on the mechanism associated with the early stage of adsorption. It appears that no significant adsorption occurred above the first plateau of 24 kJ/mol , which ends at 2.2 mmol/g ($0.100 \text{ cm}^3/\text{g}$). Comparison with carbon CAF-B (Figure 2) suggests that

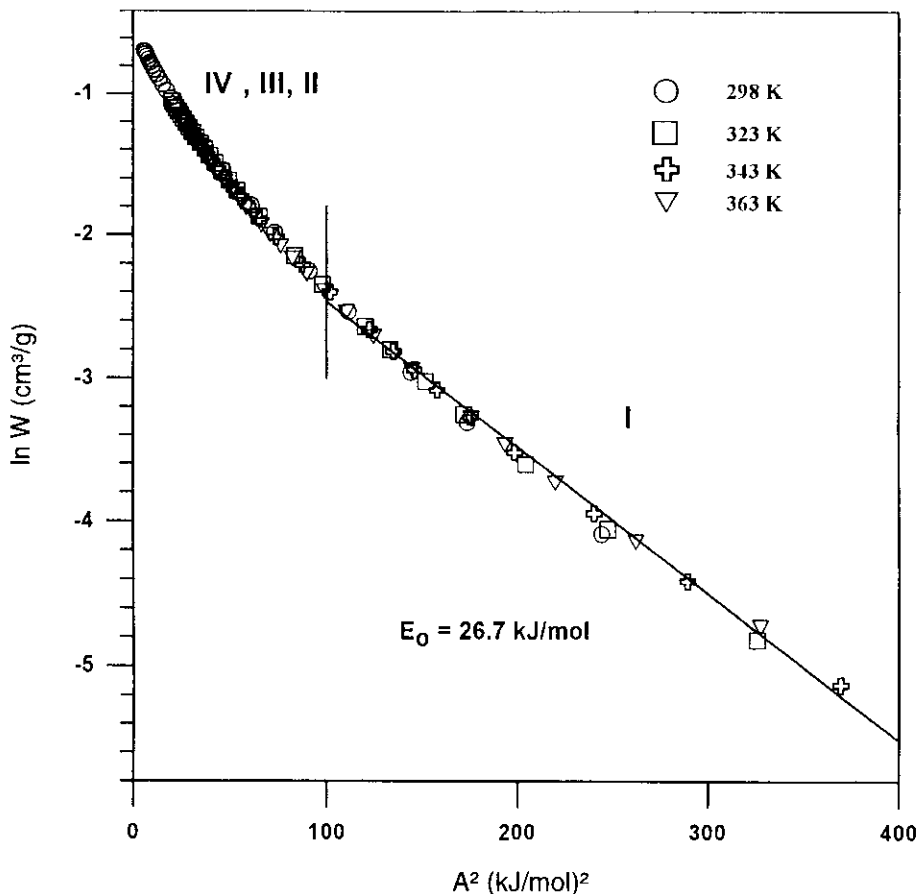


Figure 8. DR plot for the adsorption of CO₂ on activated fibre KF1500 at 298, 323, 343 and 363 K, respectively. (For the sake of clarity, the data for 258 K are omitted.) The upper part of the curve contains sections II–V as discussed by Kakei *et al.* (1990).

primary filling of small micropores was virtually absent and the mechanism corresponded to the coating of the walls of larger micropores. The drop in the differential heat of adsorption near 2.2 mmol/g, leading to an average heat of 22 kJ/mol, probably reflects the filling of the large micropores since the adsorption energy of the intermediate layers is lower than on the walls. In agreement with the approximate pore size distribution shown in Figure 5, the differential heats of adsorption of KF1500 and AGB (22 kJ/mol and 18 kJ/mol, respectively) indicate the presence of somewhat smaller micropores in fibre KF1500.

It is also interesting to point out that comparison of the CO₂ isotherms at 258 K on KF1500 and on Vulcan 3 suggests a micropore volume of 0.60 cm³/g and an external surface area $S_c = 28$ m²/g. These independent estimates are in good agreement with the values derived from the α_s -plot quoted above.

CONCLUSIONS

Our results confirm those obtained earlier by the combination of adsorption and immersion

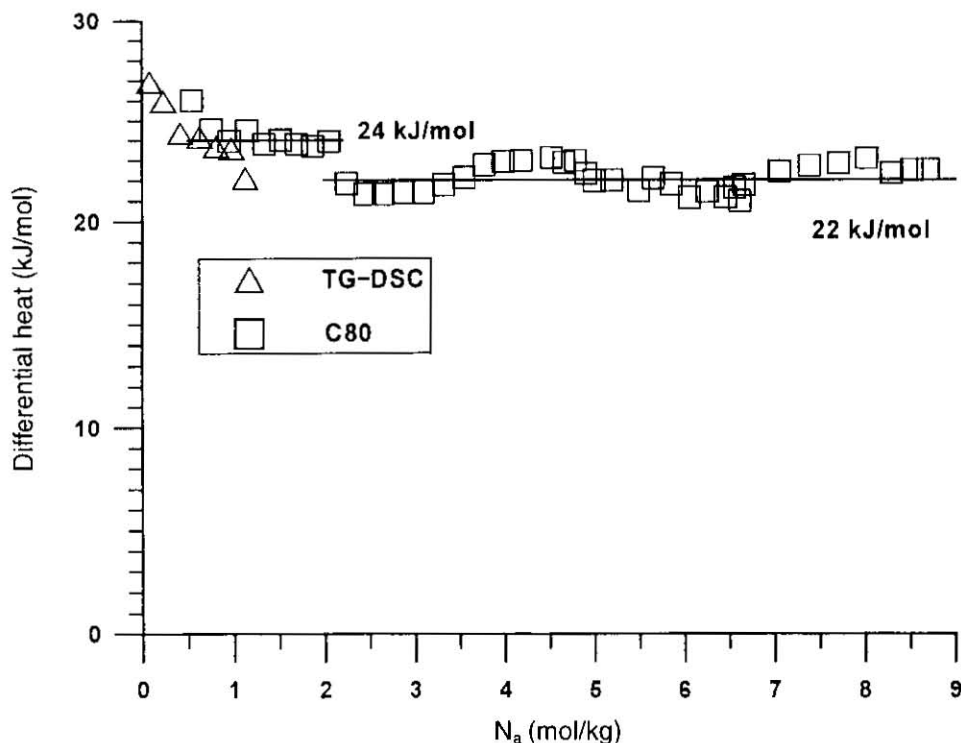


Figure 9. Differential heat of adsorption of CO_2 at 298 K on activated fibre KF1500.

techniques, using standard adsorbates and working at pressures below atmospheric. The present study also illustrates the usefulness of the technique based on CO_2 adsorption at high pressures combined with the determination of the corresponding differential heats of adsorption near 298 K. In the present case, the mechanism of secondary micropore filling (adsorption on the walls of large micropores rather than filling of narrow micropores) has been confirmed unambiguously by adsorption calorimetry. It was therefore possible to describe in detail the porous structure of active fibre KF1500 which had been examined by different authors.

It appears that the present approach, using a single adsorbate but combining adsorption and calorimetry techniques, is suitable for the characterization of homogeneous and heterogeneous carbons over the whole range of microporosity. By means of a reference isotherm for CO_2 adsorption on a non-porous carbon black (for example at 253 K), it is also possible to cross-check the data and to determine the external surface area of the carbon. This point will be discussed in detail later.

REFERENCES

- Bottani, E.J., Bakaev, V. and Steele, W. (1994) *Chem. Eng. Sci.* **49**, 2931.
 Carrott, P.J.M. and Sing, K.S.W. (1986) *Characterization of Porous Materials*, Unger, K., Ed, Elsevier, Amsterdam.
 Carrott, P.J.M., Ribeiro, M.L. and Roberts, R.A. (1991) *Colloids Surf.* **58**, 385.
 Dubinin, M.M. (1975) *Progress in Surface and Membrane Science*, Cadenhead, D.A., Ed, Academic Press, New York.

- Dubinin, M.M. (1989) *Carbon* **27**, 457.
- Dubinin, M.M. and Stoeckli, F. (1980) *J. Colloid Interface Sci.* **75**, 34.
- Gregg, S.J. and Sing, K.S.W. (1982) *Adsorption, Surface Area and Porosity*, Academic Press, London.
- Guillot, A., Follin, S. and Poujardieu, L. (1997) *Characterization of Porous Solids*, McEnaney, B., Ed, Royal Society of Chemistry, Cambridge.
- Innes, R.W., Fryer, J. and Stoeckli, F. (1989) *Carbon* **27**, 71.
- Takei, K., Ozeki, S., Suzuki, T. and Kaneko, K. (1990) *J. Chem. Soc., Faraday Trans.* **86**, 371.
- Takei, K., Ozeki, S., Suzuki, T. and Kaneko, K. (1991) *Characterization of Porous Solids*, Reinoso, F., Ed, Elsevier, Amsterdam.
- Kaneko, K., Ishii, C., Ruike, M. and Kunabara, H. (1992) *Carbon* **30**, 1075.
- Rouquerol, F., Rouquerol, J. and Everett, D.H. (1980) *Thermochim. Acta* **41**, 311.
- Stoeckli, F. (1981) *Izv. Akad. Nauk SSSR, Ser. Khim.* 63.
- Stoeckli, F. (1989) *Carbon* **27**, 962.
- Stoeckli, F. (1990) *Carbon* **28**, 1.
- Stoeckli, F. (1993) *Adsorp. Sci. Technol.* **10**, 3.
- Stoeckli, F. (1995) *Porosity in Carbons*, Patrick, J., Ed, Edward Arnold, London.
- Stoeckli, F., Hugi-Cleary, D. and Centeno, T.A. (1998) *J. Eur. Ceram. Soc.* **18**, 117.
- Stoeckli, F., Huguenin, D. and Greppi, A. (1993) *J. Chem. Soc., Faraday Trans.* **89**, 205.
- Stoeckli, F., Perret, A. and Mena, Ph. (1980) *Carbon* **18**, 443.
- Stoeckli, F., Rebstein, P. and Ballerini, L. (1990) *Carbon* **28**, 907.