Supplementary Information

Capacitance in carbon pores of 0.7 to 15 nm: a regular pattern

Teresa A. Centeno [*], Olha Sereda, Fritz Stoeckli [*]

E-mail: fritz.stoeckli@unine.ch, teresa@incar.csic.es

Materials and Methods

The study is based on 28 porous carbons of different origins. They are listed in Tables S1-S3 with their main structural, electrochemical and calorimetric properties and further details regarding the experimental procedures can be found elsewhere.[1-4] For comparison purposes, 6 mesoporous carbons[5] characterized by the same structural and electrochemical protocols were also used (Table S4). These carbons have low oxygen contents, as confirmed by TPD and/or the comparison of the enthalpies of immersion into water and benzene.[6] Consequently, as indicated in the main text, pseudocapacitance effects may be neglected and the capacitance in the aprotic $TEABF_4$/ACN electrolyte depends essentially on the surface area.

The structural characterizations were performed by gas adsorption, using nitrogen at 77 K (*Micromeritics ASAP 2010*) for routine measurements. The standard software package provided the surface areas S_{NLDFT} and S_{BET}, but the data was also analyzed by applying Kaneko's comparison plot technique and Dubinin's theory. The total surface area was also determined by immersion calorimetry into 0.4 M solutions of phenol in water, using the factor of -0.105 J m^{-2}. This technique,[1] like the comparison plot, is model-free and does not depend on the shape of the pores. Carbon tetrachloride (CCl_4) and 2,5-norbornadiene (NBD) isotherms were determined separately at 293 K in a gravimetric apparatus of the MacBaine type. For certain samples, earlier results for N_2 (77 K), CH_2Cl_2 (293 K), C_6H_6 (293-298 K), CO_2 (273 K) and CCl_4 (293-298 K) isotherms and comparison plots were also used, in order to increase the available data. The different techniques (a)-(i) and the molecular probes used for each sample are listed in Table S1.

Immersion calorimetry was also used as a complementary technique to determine the enthalpies of immersion of the carbons into benzene, carbon tetrachloride and norbornadiene at 293 K. The Tian-Calvet calorimeters and the experimental procedures are described in detail elsewhere.[7]

The electrochemical performances were tested in a sandwich-type capacitor, set up with two carbon pellets and 1M $(C_2H_5)_4NBF_4$ in acetonitrile as electrolyte. The capacitance was determined by galvanostatic charge-discharge cycles from 0 to 2 V at 1 mA cm^{-2} and cyclic voltammetry at 1 mV s^{-1}. Tests with a three-electrode cell for a selection of carbons provided comparable results for the 2M H_2SO_4 electrolyte.[2]

Outline of Dubinin's theory and its extension to immersion calorimetry

This theory describes the volume filling of micropores by vapours over a wide range of relative pressures and temperature. The fundamental expression is the Dubinin-Astakhov equation (1970)[7-9]

$$W = W_o \exp[-(RT\ln(p_s/p)/E)^n] \qquad (n = 2 \text{ to } 3) \qquad (S1)$$

where

- W_o is the limiting volume of the micropores and W the volume filled at $(T; p/p_s)$. The experimental information is the amount adsorbed n_a, usually in mmol g^{-1} and $W = n_a V^a_m$. It is assumed that V^a_m, the molar volume in the adsorbed state, is close to the molar volume of the free liquid at the same temperature and pressure.

- E is the so-called characteristic energy of adsorption, which depends on both the solid and the adsorbate. It has been shown that for adsorptives without specific interactions with the carbon, there exists a scaling factor, called the affinity coefficient β, relative to benzene taken as a reference. For a given vapour (i), $E_i = \beta_i E_o$, where $E_o = E(C_6H_6)$. For the adsorbates used in this study, carbon tetrachloride and 2,5-norbornadiene, $\beta(CCl_4) = 1.05$, and $\beta(NBD) = 1.12$. These coefficients have been listed by Wood[10] and empirical relations exist for their calculation.

- n is related to the width of the adsorption energy distribution and the most frequent case, where exponent n = 2, is known as the Dubinin-Radushkevich (DR) equation. On the other hand, for adsorption in relatively narrow pores a better fit is frequently obtained with n between 2 and 3. This is the case for CCl_4 and NBD in pores of less than 1 nm.

It has been shown that E_o itself is related to the average width L_o (nm) of locally slit-shaped micropores by [4,11,12]

$$L_o(DR) \text{ (nm)} = 10.8/(E_o - 11.4 \text{ kJ mol}^{-1}) \qquad (S2)$$

As shown in Table S1, the values of $L_o(DR)$ and $L_o(NLDFT)$, also based on the model of slit-shaped pores, show some scatter, but statistically their overall correlation is close to unity. The surface area of the micropore walls is therefore

$$S_{mi}(m^2 \text{ g}^{-1}) = 2000 W_o(cm^3 \text{ g}^{-1})/ L_o(nm) \qquad (S3)$$

It follows that the total surface area accessible to the probe is

$$S_{tot} = S_{mi} + S_e \qquad (S4)$$

where S_e is the area found in larger pores and on the outside of the sample.

Equations (S2) and (S3) are valid for pores up to approximately 1.5 nm. Beyond these dimensions, their morphology may change, but S_{tot} can still be determined by other techniques. They include Kaneko's comparison plot technique,[1] which leads to both S_{mi} and S_e, and the selective adsorption of sparingly soluble molecules from aqueous solutions (*e.g.* phenol) limited to a single monolayer on the carbon. The latter approach is based either on the liquid-solid isotherm, or the specific enthalpy of transfer from the solution onto the carbon (for phenol -0.105 ± 0.05 J m^{-2}).[3]

Dubinin's theory has the property that its parameters E and n are temperature invariant and a theoretical development of (S1) leads to the enthalpy of immersion into the corresponding liquid adsorbate [4,7]

$$- \Delta_i H (J\ g^{-1}) = E_o \beta W_o (1 + \alpha T) \sqrt{\pi}/2V_m\ -\ h_i S_e \qquad (S5)$$

α is the thermal expansion coefficient of the liquid of molar volume V_m and $-h_i S_e$ represents the wetting of the external surface, usually a small fraction of the total enthalpy. Typical values are $h_i(C_6H_6) = -0.114$ J m^{-2}, $h_i(CCl_4) = -0.115$ J m^{-2} and $h_i(NBD) = -0.110$ J m^{-2} (for the latter, a recent determination).

Since $W_o = n_{ao}(mmol\ g^{-1})V_m(cm^3\ g^{-1})$, Eqn (S5) can also be written in the form

$$- \Delta_i H (J\ g^{-1}) = E_o \beta n_{ao} (1 + \alpha T) \sqrt{\pi}/2\ -\ h_i S_e \qquad (S6)$$

which does not contain explicitly the micropore volume W_o, but only the gravimetric amount n_{ao} adsorbed at saturation.

The experimental determination of $\Delta_i H$ provides an important test for self-consistency for the adsorption data of a given vapour, for example C_6H_6, CCl_4 and NBD used in the present study (see Table S3). This is illustrated, for example, by the agreement between the experimental enthalpies of immersion $\Delta_i H(C_6H_6)$ and the values calculated using the parameters of the N_2 (77 K) isotherm, two small molecules probing the same micropore volume for our carbons.

Moreover, as confirmed experimentally, in the case of equal accessibility of a micropore system by CCl_4 and C_6H_6 where $W_o(CCl_4)/ W_o(C_6H_6) = 1$, Equation (S5) leads to $\Delta_i H(CCl_4)/\Delta_i H(C_6H_6) = 0.97$. The comparison of the two enthalpies of immersion provides a quick test for the accessibility of the pore system by CCl_4 and, consequently, the $(C_2H_5)_4N^+$ ion examined in the present study.

If the ratio of the enthalpies is close to 0.97, the total $S_{tot} = S_{mi} + S_e$ determined by small probes such as nitrogen, argon and benzene, is also accessible to CCl_4. On the other hand, smaller values (samples 6-11/Table S3) indicate a reduced accessibility to S_{mi} and the area $S_{mi}(CCl_4)$ must be determined separately. This requires the determination of the CCl_4 adsorption isotherm (typically at 293 K or 298 K) and its analysis with the help of equations (S1)-(S3). The characteristic energy $E(CCl_4)$ leads to $E_o = E(CCl_4)/\beta(CCl_4)$ which corresponds to the part of micropore system filled by CCl_4. If it were probed by C_6H_6, one would obtain this value of E_o.

The average pore width $L_o(CCl_4)$ is given by (S2) and (S4) leads to the total surface area accessible to CCl_4, $S_{tot}(CCl_4)$. This area can be compared with the value obtained from the comparison of the CCl_4 isotherm with a reference CCl_4 isotherm on a non porous carbon of known surface area (in our case *Vulcan 3G*; 71 m^2 g^{-1}). Moreover, the quality of the adsorption data for CCl_4 can be cross-checked by comparing the experimental enthalpy of immersion $\Delta_i H(CCl_4)$ with the value calculated from equation (S4) by using $W_o(CCl_4)$, $E(CCl_4)$ and S_e. The same approach applies to norbornadiene and the corresponding results obtained for carbons with narrow pores are shown in Tables S2-S3 (samples 7 to 11).

Table S1. Structural properties of the microporous carbons obtained by different techniques, where SM refers to small molecules. For carbons 12-22, only N_2 (77 K) isotherms were determined and it is assumed that $W_o(N_2)$ and $W_o(CCl_4)$ are identical, as suggested by the enthalpies of immersion into carbon tetrachloride (CCl_4), norbornadiene (NBD) and benzene (C_6H_6) (seeTable S3).

No	Carbon (origin)	Average micropore size (nm)		Total surface area S_{tot} ($m^2\,g^{-1}$)		Specific surface area ($m^2\,g^{-1}$)		S_e ($m^2\,g^{-1}$)	W_o ($cm^3\,g^{-1}$)		Techniques used (see list below)
		$L_o(DR)$	$L_o(NLDFT)$			$S_{BET}(N_2)$	$S_{NLDFT}(N_2)$		N_2	CCl_4	
1	N-125-08 (Peat)	1.60 1.60	1.18	SM 791 ± 40 (5) CCl₄ 846 ± 40 (1)		1317	958	157	0.51	0.64	(a)(b)(d)(e)(i)
2	F-02 (Coconut)	1.48 1.50	1.12	SM 849 ± 70 (4) CCl₄ 840 ± 30 (2)		1223	953	45	0.50	0.63	(a)(b)(c)(d)(i)
3	DCG-5 (Coal)	1.15 1.34	1.02	SM 956± 85 (5) CCl₄ 827 ± 15 (1)		1121	923	25	0.49	0.53	(a)(b)(c)(d)(g)(h)(i)
4	A056 (Coal)	1.22 1.32	1.52	SM 457 ± 28 (4) CCl₄ 488 ± 23 (2)		678	215	20	0.26	0.29	(a)(b)(d)(e)
5	TiC/SiC (Carbide)	0.94 0.90	1.16	SM 1241 ± 48 (3) CCl₄ 1357 ± 55 (1)		1237	634	18	0.60	0.59	(a)(b)(d)(i)
6	CEP-2008 (Wood)	0.95 0.92	0.95	SM 1040 ± 90 (2) CCl₄ 1061 ± 25 (1)		1266	983	7	0.50	0.48	(a)
7	AC-507-17 (Fibre)	0.87 0.90 0.89	0.85	SM 1258 ± 93 (3) CCl₄ 1082 ± 35 (1) NBD 1035 ± 25 (1)		1176	1098	1	0.58	0.49	(a) (i)
8	CMS-H2- 2007 (Coal)	0.81 0.94 0.96	0.81	SM 686 ± 33 (7) CCl₄ 500 ± 20 (2) NBD 515 ± 25 (1)		567	570	25	0.27	0.23	(a)(b)(c)(d)(e)(f)(h)(i)
9	PAU-1 (Saran)	0.73 0.74 0.68	0.81	SM 1266 ± 60 (3) CCl₄ 930 ± 36 (1) NBD 913 ± 30(1)		1001	975	4	0.48	0.33	(a)(b)(d)(f)(i)
10	PAU-1-950 (Saran)	0.75 0.71 0.78	0.83	SM 1197 ± 120 (4) CCl₄ 977 ± 35 (1) NBD 817 ± 25(1)		1063	848	4	0.50	0.35	(a)(d)(f)(i)
11	HK-650-8 (PET)	0.66 0.72	0.80	SM 1000 ± 170(3) CCl₄ 374 ± 15 (2)		661	573	65	0.30	0.12	(a)(d)(i)
12	U03 (Coal)	1.56	1.09	SM 690 ± 30(4)		1172	914	25	0.50	-	(a)(b)(c)(i)
13	M30 (Pitch)	1.45	1.43	SM 1145 ± 41(3)		2298	1286	10	0.79	-	(a)(i)
14	M1R-950 (Coconut)	1.41	1.06	SM 966 ± 117(3)		1417	1137	5	0.64	-	(a)(i)

Table S1.   Continued

No	Carbon (origin)	Average micropore size (nm)		Total surface area S_{tot} (m^2 g^{-1})		Specific surface area (m^2 g^{-1})		S_e (m^2 g^{-1})	W_o (cm^3 g^{-1})		Techniques used (see list below)
		L_o(DR)	L_o(NLDFT)			$S_{BET}(N_2)$	$S_{NLDFT}(N_2)$		N_2	CCl_4	
15	KF-1500/08 (Fibre)	1.38	1.12	SM	987 ± 66(6)	1568	1198	21	0.60	-	(a)(b)(c)(h)(i)
16	Super DLC-30 (Coconut)	1.24	1.10	SM	961 ± 20(3)	1618	1147	9	0.60	-	(a)(i)
17	M1R (Coconut)	1.23	1.38	SM	1072 ± 20(9)	1555	1053	7	0.67	-	(a)(i)
18	BCK-A (Coconut)	1.14	1.08	SM	1007 ± 94(3)	1405	1138	6	0.60	-	(a)(i)
19	SiC-800 (Carbide)	0.90	0.85	SM	1261 ± 40(3)	1200	1064	17	0.56	-	(a)(i)
20	SiC-900 (Carbide)	0.92	0.84	SM	1320 ± 120(3)	1350	1254	35	0.60	-	(a)(i)
21	SiC-1000 (Carbide)	0.90	0.95	SM	1376 ± 61(3)	1234	1024	50	0.58	-	(a)(i)
22	TiC-600 (Carbide)	0.88	0.86	SM	1290 ± 127 (3)	1373	1178	2	0.60	-	(a)(i)

List of techniques used for the structural characterization
(a) N_2 (77 K) isotherm with comparison plot, DR, BET and NLDFT analysis
(b) C_6H_6 and/or CH_2Cl_2 isotherm (293 K)
(c) C_6H_6 and/or CH_2Cl_2 comparison plot (293 K) (ref. *Hoechst*, *N234-G*)
(d) CCl_4 isotherm (293 K, in some cases also 298 K and 303 K)
(e) CCl_4 (293 K) comparison plot (ref. *Vulcan-3G* and/or *Hoechst*)
(f) NBD isotherm (293 K)
(g) CO_2 (273 K) isotherm
(h) CO_2 (273 K) comparison plot (ref. *Vulcan-3G*)
(i) Phenol adsorption from aqueous solution (mainly calorimetry; some liquid-solid isotherms)

Table S2. Calorimetric properties of the carbons. Experimental and calculated enthalpies of immersion.
For carbons 1 to 12, the enthalpies of immersion $\Delta_iH(CCl_4)$ and $\Delta_iH(NBD)$ were calculated from the corresponding isotherms.
For carbons 12-22, where no CCl_4 and NBD isotherms are available, the enthalpies of immersion are calculated on the basis of data from N_2 (77 K) adsorption. For these carbons, the agreement between the experimental and calculated values of $\Delta_iH(C_6H_6)$, $\Delta_iH(CCl_4)$, $\Delta_iH(NBD)$ and their ratios confirm the accessibility of the entire pore system to the $(C_2H_5)_4N^+$ ion.

No	Carbon (origin)	$-\Delta_iH(C_6H_6)$ (J g^{-1})		$-\Delta_iH(CCl_4)$ (J g^{-1})		$-\Delta_iH(NBD)$ (J g^{-1})		$\Delta_iH(CCl_4)/\Delta_iH(C_6H_6)$	
		exp	calc	exp	calc	exp	calc	exp	calc
1	N-125-08 (Peat)	156	153	162	160	147	149	1.04	1.05
2	F-02 (Coconut)	168	168	168	165	156	163	1.00	0.98
3	DCG-5 (Coal)	151	141	143	139	156	140	0.95	0.99
4	A056 (Coal)	92	78	89	84	106	86	0.97	1.08
5	TiC/SiC (Carbide)	201	189	205	182	191	184	1.02	0.96
6	CEP-2008 (Wood)	156	156	138	148	143	151	0.89	0.95
7	ACC-507-17 (Fibre)	177	156	162	154	154	142	0.92	0.99
8	CMS-H2-2007 (Coal)	92	92	65	70	77	70	0.70	0.76
9	PAU-1 (Saran)	175	171	133	118	119	111	0.76	0.69
10	PAU-1-950 (Saran)	172	176	133	121	114	105	0.77	0.69
11	HK-650-8 (PET)	120	103	56	47	-	-	0.47	0.46
12	UO3 (Coal)	130	127	126	123	117	124	0.97	0.97
13	M30 (Pitch)	219	204	207	195	218	198	0.95	0.96
14	M1R-950 (Coconut)	166	160	160	160	175	161	0.96	1.00
15	KF-1500/08 (Fibre)	149	151	149	143	152	146	1.00	0.95

Table S2. Continued

No	Carbon (origin)	$-\Delta_iH(C_6H_6)$ (J g^{-1})		$-\Delta_iH(CCl_4)$ (J g^{-1})		$-\Delta_iH(NBD)$ (J g^{-1})		$\Delta_iH(CCl_4)/\Delta_iH(C_6H_6)$	
		exp	calc	exp	calc	exp	calc	exp	calc
16	Super DLC-30 (Coconut)	155	165	148	158	189	160	0.96	0.96
17	M1R (Coconut)	175	185	163	177	175	179	0.93	0.96
18	BCK-A (Coconut)	179	171	162	156	162	166	0.91	0.91
19	SiC-800 (Carbide)	192	180	164	174	189	176	0.85	0.97
20	SiC-900 (Carbide)	204	193	198	186	200	188	0.97	0.96
21	SiC-1000 (Carbide)	183	190	178	184	190	182	0.97	0.97
22	TiC-600 (Carbide)	208	194	187	187	196	188	0.90	0.96

Table S3. Electrochemical properties of the carbons.

No	Carbon (origin)	C ($F\ g^{-1}$)	C/S(SM) ($F\ m^{-2}$)	C/S(CCl$_4$) [C/S(NBD)] ($F\ m^{-2}$)	C/S$_{NLDFT}$ ($F\ m^{-2}$)	C/S$_{BET}$ ($F\ m^{-2}$)
1	N-125-08 (Peat)	83	0.105 ± 0.011	0.098 ± 0.010	0.087	0.063
2	F-02 (Coconut)	89	0.105 ± 0.014	0.106 ± 0.010	0.093	0.073
3	DCG-5 (Coal)	83	0.087 ± 0.012	0.100 ± 0.007	0.090	0.074
4	A056 (Coal)	52	0.114 ± 0.012	0.107 ± 0.011	0.242	0.078
5	TiC/SiC (Carbide)	130	0.105 ± 0.009	0.096 ± 0.009	0.205	0.105
6	CEP-2008 (Wood)	90	0.086 ± 0.007	0.085 ± 0.006	0.091	0.071
7	ACC-507-17 (Fibre)	95	0.076 ± 0.009	0.088 ± 0.009 [0.092 ± 0.007]	0.086	0.081
8	CMS-H2-2007 (Coal)	55	0.080 ± 0.008	0.110 ± 0.010 [0.107 ± 0.010]	0.096	0.097
9	PAU-1 (Saran)	75	0.060 ± 0.006	0.081 ± 0.008 [0.082 ± 0.007]	0.077	0.075
10	PAU-1-950 (Saran)	93	0.078 ± 0.012	0.095 ± 0.009 [0.114 ± 0.009]	0.110	0.087
11	HK-650-8 (PET)	40	0.040 ± 0.009	0.107 ± 0.010	0.068	0.061
12	UO3 (Coal)	66	0.096 ± 0.009	0.096 ± 0.009	0.073	0.057
13	M30 (Pitch)	121	0.109 ± 0.008	0.109 ± 0.008	0.094	0.053
14	M1R-950 (Coconut)	90	0.093 ± 0.016	0.093 ± 0.016	0.079	0.063
15	KF-1500/08 (Fibre)	107	0.108 ± 0.013	0.108 ± 0.013	0.089	0.068
16	Super DLC-30 (Coconut)	95	0.099 ± 0.007	0.099 ± 0.007	0.083	0.059
17	M1R (Coconut)	91	0.085 ± 0.006	0.085 ± 0.006	0.086	0.058
18	BCK-A (Coconut)	92	0.091 ± 0.013	0.091 ± 0.013	0.081	0.065

Table S3. Continued

No	Carbon (origin)	C (F g^{-1})	C/S(SM) (F m^{-2})	C/S(CCl$_4$) [C/S(NBD)] (F m^{-2})	C/S$_{NLDFT}$ (F m^{-2})	C/S$_{BET}$ (F m^{-2})
19	SiC-800 (Carbide)	93	0.074 ± 0.006	0.074 ± 0.006	0.087	0.077
20	SiC-900 (Carbide)	120	0.091 ± 0.013	0.091 ± 0.013	0.096	0.089
21	SiC-1000 (Carbide)	129	0.094 ± 0.009	0.094 ± 0.009	0.126	0.105
22	TiC-600 (Carbide)	119	0.092 ± 0.014	0.092 ± 0.014	0.101	0.087

Table S4. Structural and electrochemical properties of predominantly mesoporous carbons. D_p is the NLDFT-based pore diameter.

No	Carbon (origin)	D_p (nm)	Pore volume ($cm^3\ g^{-1}$)	Total surface area S_{tot} ($m^2\ g^{-1}$)	Specific surface area ($m^2\ g^{-1}$)		C ($F\ g^{-1}$)	C/S(SM) ($F\ m^{-2}$)	Remarks
					$S_{BET}(N_2)$	$S_{NLDFT}(N_2)$			
23	Picactif (Coconut)	3.4	1.35 (N_2)	SM 1230 ± 57 (2)	2260	1181	107	0.087 ± 0.009	Micropore volume 0.79 $cm^3\ g^{-1}$ $\Delta_i H(CCl_4)/\ \Delta_i H(C_6H_6)_{exp} = 1$
24	MP00-2 *(PVA/MgO)	5.1	2.11 (N_2) 1.74 (CCl_4)	SM 1285 ± 85 (4) CCl_4 1247 ± 53 (1)	1810	1000	100	$0.078 \pm\ 0.009$	Micropore volume 0.65 $cm^3\ g^{-1}$ $\Delta_i H(CCl_4)/\ \Delta_i H(C_6H_6)_{exp} = 1$
25	MP64-2 *(PVA/MgO)	5.4	2.02 (N_2)	SM $1286 \pm\ 65$(3)	1736	978	112	0.087 ± 0.006	Micropore volume 0.66 $cm^3\ g^{-1}$
26	MP55-2 *(PVA/MgO)	5.8	2.20 (N_2)	SM $1138 \pm\ 46$(3)	1727	980	100	0.088 ± 0.006	Micropore volume 0.65 $cm^3\ g^{-1}$
27	MP37-2 *(PVA/MgO)	10.5	2.02 (N_2)	SM $930 \pm\ 39$ (3)	1197	697	84	0.090 ± 0.008	Micropore volume 0.46 $cm^3\ g^{-1}$
28	MP19-2 *(PVA/MgO)	15.7	1.03 (N_2)	SM $486 \pm\ 38$ (3)	590	320	47	0.097 ± 0.008	Micropore volume 0.23 $cm^3\ g^{-1}$

* Poly(vinyl alcohol) carbonized with MgO

Supplementary References

1 T. A. Centeno, F. Stoeckli, *Carbon*, 2010, **48**, 2478-2486.

2 T. A. Centeno, M. Hahn, J.A. Fernández, R. Kötz, F. Stoeckli, *Electrochem. Commun.*, 2007, **9**, 1242-1246.

3 E. Fernandez, D. Hugi-Cleary, V. López-Ramón, F. Stoeckli, *Langmuir*, 2003, **19**, 9719 -9723.

4 F. Stoeckli, in *Porosity in carbons. Characterization and applications*, (Ed: J. Patrick), Arnold, London, **1995**, pp. 67-92.

5 F. Stoeckli, A. Lavanchy, *Carbon*, 2000, **38**, 475-477.

6 J.A. Fernández*,* T. Morishita, M. Toyoda, M. Inagaki, F. Stoeckli, T.A. Centeno, *J. Power Sources*, 2008, **175**, 675-679.

7 R.C. Bansal, J.B. Donnet, F. Stoeckli, *Active Carbon,* Marcel Dekker, New York, **1988**, pp. 119

8 M.M. Dubinin, *Carbon*, 1989, **27**, 457-467.

9 F. Stoeckli, *Russ. Chem. Bull. Int. Ed.*, 2001, **50**, 2265-2270.

10 G.O. Wood, *Carbon*, 2001, **39**, 343-356.

11 F. Stoeckli, V. López-Ramón, D. Hugi-Cleary, A. Guillot, *Carbon*, 2001, **39**, 1115-1116.

12 T. Ohba, T. Suzuki, K. Kaneko, *Carbon*, 2000, **38**, 1892- 1896.