Colloid Polym Sci (2004) 283: 237–242
DOI 10.1007/s00396-004-1139-7

ORIGINAL CONTRIBUTION

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Surface modification of activated carbon and fullerene black by Diels–Alder reaction

Received: 5 December 2003
Accepted: 1 April 2004

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Abstract Activated carbon and fullerene black react with cyclopentadiene at room temperature or slightly elevated temperature. At higher temperature a retro-Diels–Alder reaction takes place. The reaction with the diene and the retro-Diels–Alder reaction could be repeated. As a consequence of the reaction with cyclopentadiene or other suitable dienes and the retro reaction, the surface structure of different carbons changed considerably. The surface area of micropores on fullerene black was much higher than for the original sample. The influence on the surface area of porosity is reported for two different types of carbon.

Keywords Activated carbons · Surface treatment · Brunauer–Emmett–Teller surface area · X-ray scattering · Adsorption properties

Introduction

A huge number of different reactions with different fullerenes and acivated carbon were studied in the last few years. The carbons react with dienes under mild conditions and Diels–Alder adducts are formed [1]. Experiments indicated that in the reactions of fullerenes with cyclopentadiene or 1,3-cyclohexadiene there is a correlation between the reactivity of fullerene and the strain in the carbon lattice [2, 3]. When fullerenes and certain kinds of carbons are heated in air, first oxygen uptake occurs, while other types of carbon exhibit the usual oxidation reaction resulting in a monotonous decrease of the mass with increasing temperature [4, 5]. Obviously, there must be certain changes of the structure of the reactivated carbons. It was assumed that such kinds of reaction may occur owing to the strain among the carbon rings, analogously to the reactivity of fullerenes. Furthermore, it was observed that a retro-Diels–Alder reaction of the different adducts occurs at about 220 °C. The Diels–Alder adducts formed on the carbon surface then yield diene $-(-C=C-)-$ groups in the interfacial carbon structure. After the retro-Diels–Alder reaction the coupling with cyclopentadiene may be repeated. In this paper we present data on the change of different surface parameters a consequence of Diels–Alder and retro-Diels–Alder reactions for two different carbons, i.e. activated carbon and extracted fullerene black. Control experiments were made with graphite.

Materials and methods

Preparation of the samples

Activated carbon (DARCO G-60) and fullerene black, the graphite soot from fullerene synthesis (obtained from MER Co., Tucson, AZ, USA) were extracted with toluene several times to remove even traces of soluble fullerenes.

Freshly distilled cyclopentadiene (120 ml) was added to 12 g solid carbon and then refluxed for 1 h in an Ar stream. After filtering, the solid was washed first with toluene and subsequently with acetone and then dried at room temperature in an Ar stream. A 1 + g portion of the dried sample was removed for study of the surface parameters; the rest was heated for 2 h at 220 °C in an Ar stream. A 1-g portion of this sample was removed for surface studies and with the rest the Diels–Alder and the retro-Diels–Alder reactions were repeated several times keeping the sample-to-reagent ratio the same as in the first reaction**.** The samples prepared were notated activated carbon AC0–AC5 and after heating AC1H–AC5H, and for fullerene black FS0–FS5 and after heating FSH1–FSH5.

Nitrogen adsorption

N_2 adsorption isotherms were determined at 77 K in a Micromeritics Gemini 2375 automated sorptometer. Prior to the measurement the carbon samples were dried in vacuo (10^{-2} torr) for 2 h. The adsorption and desorption branches of the isotherms were determined. Analysis of the isotherms yielded the following structural parameters[6]: specific surface area, determined by the Brunauer–Emmett–Teller equation; micropore surface, determined using de Boer's *t* method; specific external surface area, determined by a combination of the previously mentioned methods; maximal pore volume, derived from the adsorption saturation value of the isotherm.

Small-angle X-ray scattering

Small-angle X-ray scattering (SAXS) was measured by Cu Kα X radiation ($\lambda = 0.1542$ nm) generated in a PW 1830 generator. The primary beam was directed through a Ni filter into a compact Kratky camera, type KCEC/3, in which the width of the beam was 20 mm and its thickness was 80 µm. The measurements were done in air for 4–6 h. The intensity of the scattered radiation was measured by a proportional detector (slit width 100 µm) controlled by a PW 1710 microprocessor, and scattering data controlling software, at angles $2\Theta = 0.05$–7°. Absorption intensities (A_s, A_b) were determined by the so-called moving slit method [7, 8, 9, 10].

The density of the carbon samples within the powder sample container was measured using a Micromeritics 1305 gas multivolume pycnometer from a separate measurement.

Results and discussion

The adsorption isotherms of activated carbon samples are shown in Fig. 1. The specific surface area of the modified activated carbons was increased by the reaction with cyclopentadiene and subsequent heating. The data listed in Table 1 clearly reveal that the increased surface area was mainly due to an increase of the micropore surface. In general, the specific surface area and the pore

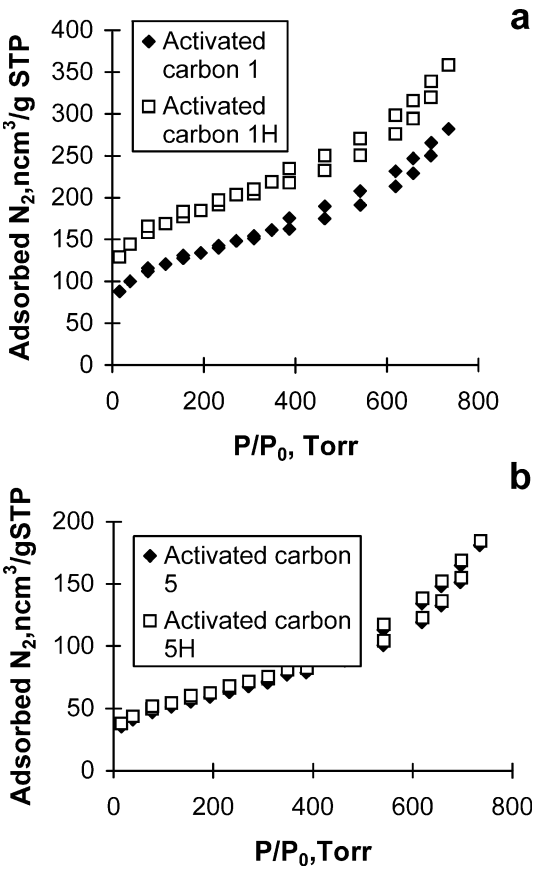

Fig. 1 a Nitrogen adsorption–desorption isotherms on activated carbon after the first surface treatment and after heating (*1H*). **b** Nitrogen adsorption–desorption isotherms on activated carbon after the fifth surface treatment and after heating (*5H*)

Table 1 Nitrogen sorption on activated carbon

Sample	a^{S}_{BET} (m^2/g)	a^{S}_{ext} (m^2/g)	a^{S}_{mp} (m^2/g)	V_{por} (cm^3/g)
AC0[a]	911	476	423	0.227
AC1	661	421	240	0.126
AC2	421	330	91	0.047
AC3	375	311	64	0.033
AC4	326	281	44	0.023
AC5	271	249	22	0.011
AC1H	715	441	275	0.144
AC2H	536	377	159	0.083
AC3H	436	334	103	0.054
AC4H	374	303	71	0.037
AC5H	328	280	48	0.025

[a] Original sample

volume of the carbons were increased by surface reactions, but remained below the values of the unmodified carbon (911 m^2/g). When the surface reaction was repeated five times, the isotherms of treated and heated samples were very similar, indicating that repeated reactions did not cause significant differences (Fig. 1b).

Adsorption isotherms of fullerene black subjected once to Diels–Alder reaction and its heated form are shown in Fig. 2. Clearly the adsorption capacities increased significantly as a result of heating. When the treatments were repeated several times, no significant difference occurred between the isotherms of the non-heated and heated samples (Fig. 2b).

Isotherms of modified graphite before and after heat treatment (Fig. 3) indicated that heat treatment only modestly increased the specific surface area. The compact structure of graphite does not allow extensive rearrangements to occur.

The specific surface area of the micropores, a^{S}_{mp}, calculated by de Boer's t method [6] is plotted against the number of treatments in Fig. 4.The micropore surface area was considerably reduced by the surface reactions, the pores were practically clogged up but the surface area was also increased by heat treatment. The maximal pore volumes as a function of the number of treatments was also reduced (Tables 1, 2).

The results of SAXS measurements on activated carbon and fullerene black samples are presented as log I versus log h representations (Fig. 5) (see Eqs. 1, 2, 3 in the Appendix). As there were no large differences in scattering intensities, the so-called Porod representation of the analysis of scattering curves was chosen because the structural differences underlying the X-ray scattering characteristics of various samples become visible (Fig. 6a, see Eq. 4 in the Appendix). At low values of the scattering vector the Ix h^3 intensities for sample AC1H are higher than the corresponding ones for sample AC1 (treated). Linear extrapolation of these functions yielded the Porod constants K_p from which the correlation lengths and specific surface areas were calculated (Table 3).

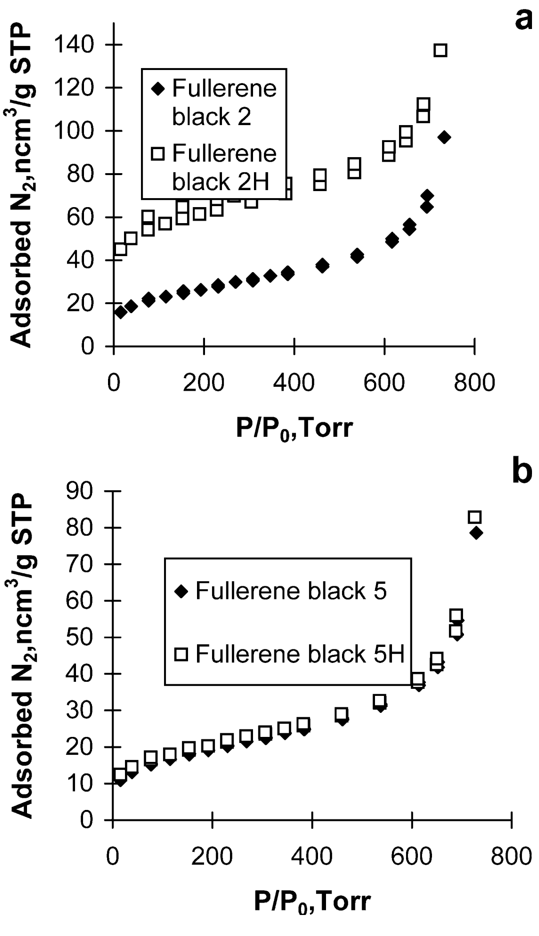

Fig. 2 **a** Nitrogen adsorption–desorption isotherms on fullerene black after the second surface treatment and after heating (*2H*). **b** Nitrogen adsorption–desorption isotherms on fullerene black after the fifth surface treatment and after heating (*5H*)

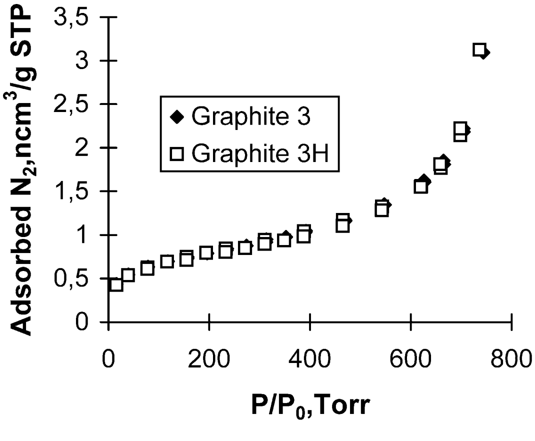

Fig. 3 Nitrogen adsorption–desorption isotherms on graphite after the third surface treatment and after heating (*3H*)

The correlation length l_c providing information on the distances between inhomogeneities within the samples can be calculated from the scattering function (see

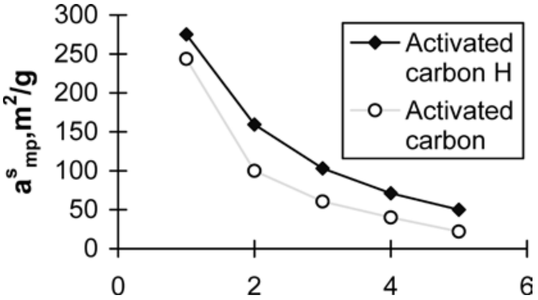

Fig. 4 The specific micropore surface area as a function of the number of surface treatments and after heating (*H*)

Table 2 Nitrogen sorption on fullerene black samples

Sample	a^{S}_{BET} (m^2/g)	a^{S}_{ext} (m^2/g)	a^{S}_{mp} (m^2/g)	V_{por} (cm^3/g)
FS0[a]	185.7	102.5	83.2	0.0437
FS1	81.2	82.7	0	0
FS2	92.3	83.5	8.8	0.0043
FS3	71.4	71.8	0	0
FS4	56.9	41.1	15.8	0.0082
FS5	64.1	60.1	3.9	0.0019
FS1H	324.9	139.3	185.7	0.097
FS2H	261.5	127.8	133.7	0.07
FS3H	155.6	96.5	59.1	0.031
FS4H	76.3	63.4	12.9	0.0066
FS5H	69.7	57.9	11.8	0.0061

[a] Original sample

Eq. 5 in the Appendix [11, 12, 13, 14]). The value of this parameter for activated carbon samples AC0, AC1 and AC1H was in the range 12.4–14.2 nm, whereas the distance between inhomogeneities in the fullerene black samples FS0, FS1and FS1H was 25.3–28.7 nm. The specific surface areas of the samples were also calculated from the SAXS data. In the case of activated carbon samples, these were in excellent agreement with Brunauer–Emmett–Teller surface areas calculated from nitrogen adsorption measurements. The differences between the FS samples were also clearly visible on the Porod representations (Fig. 6 b). Table 3 clearly shows that the specific surface area of the sample also reaches a maximum; the Porod constant was high. This is especially obvious in the case of sample AC1H: the increase of the specific surface area from 661 to 715 m^2/g by heat treatment (Table 1) was also indicated by the X-ray scattering data. The same holds for the correlation lengths, which are characteristic of structural discontinuities, and these varied between 12.4 and 14.2 nm.

The specific surface areas of fullerene black samples (FS) calculated from Porod constants also indicated the increase on heating and the correlation length as well as the statistical length, a parameter characteristic of the thickness of solid phases, decreased from 23.4 to 12.9 nm, indicating a well-defined increase in the degree of dispersion. Structural changes owing to the heat treatment were also evident from the changes of the mass fractal dimension D_{m} (see Eq. 6 in the Appendix). In the case of

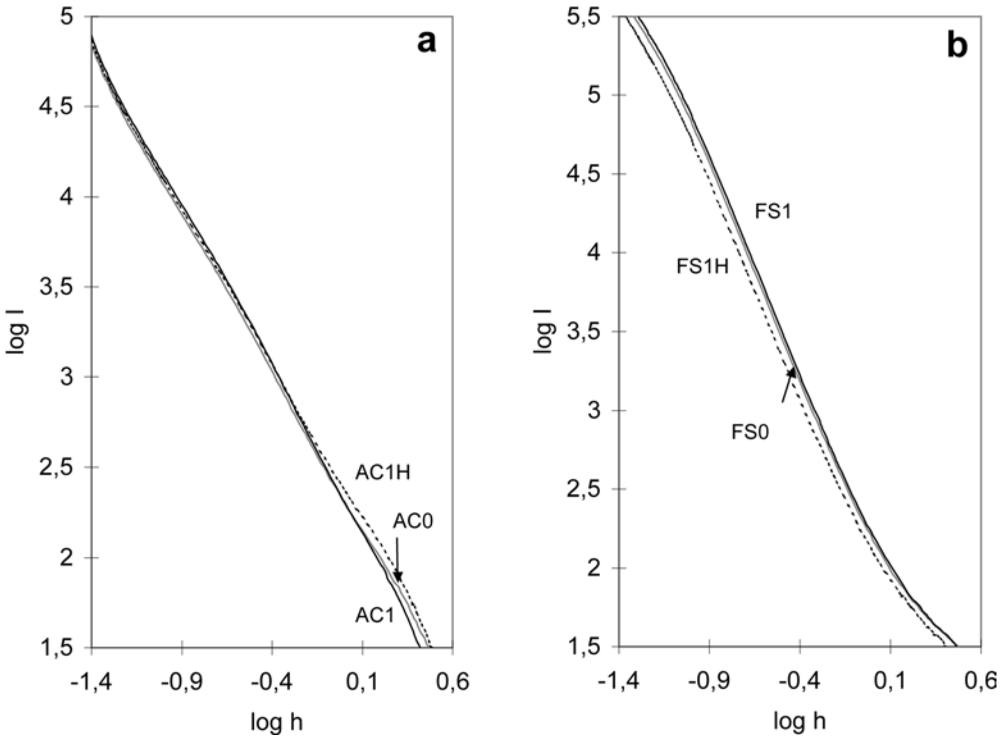

Fig. 5 **a** Small-angle X-ray scattering curves on different carbons: original activated carbon (*AC0*); activated carbon after the first surface reaction (*AC1*); activated carbon after the first surface reaction and heating (*AC1H*). **b** Small-angle X-ray scattering curves on different fullerene samples: original fullerene black (*FS0*); fullerene black after the first surface reaction (*FS1*); fullerene black after the first surface reaction and heating (*FS1H*)

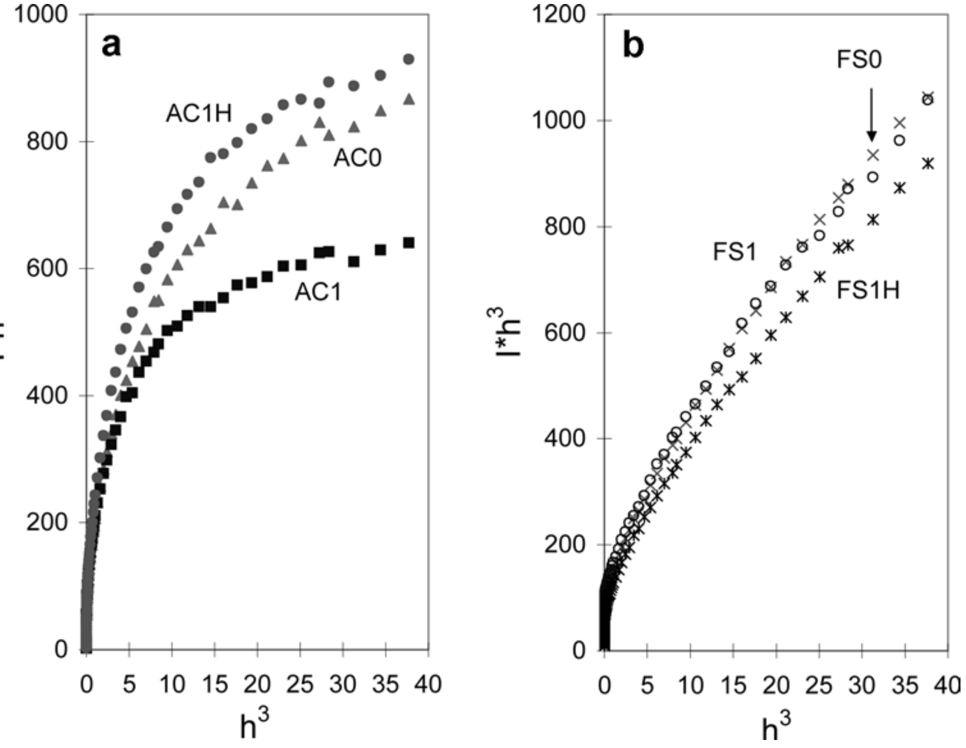

Fig. 6 a The Porod representation on activated carbon samples (notation as in Fig. 5a). **b** The Porod representation on fullerene black samples (notation as in Fig. 5b)

Table 3 Small-angle X-ray scattering (*SAXS*) experiments on activated carbon and fullerene black samples

SAXS parameters	Samples				
	AC0	AC1	AC1H	FS0	FS1
K_p (cps/nm^2)	590.3	418.7	535.5	131.6	117.2
K_p/M_1	0.564	0.350	0.473	0.059	0.044
l_c(nm)	12.39	14.26	12.40	28.75	26.56
S_p(m^2/g)	928	657	740	95	69
l_1(nm)	2.39	3.38	3.00	23.42	32.25
D_m	2.69	2.73	2.69	2.85	2.90
$a^S_{BET}(N_2)$	911	661	715	185.7	81.2

activated carbon samples (AC) such changes were not significant but the fractal dimension of the FS samples increased from 2.90 to 2.99. These observations establish that the surface reactions and changes resulting from heat treatment can be described with parameters related to structural inhomogeneities calculated from SAXS.

Acknowledgement The authors wish to thank the Hungarian National Scientific Fund OTKA T02522 T033004 and M36688 for scientific support.

Appendix: SAXS by disperse porous systems

When X-rays are scattered by colloidal particles owing to differences in electron density caused by inhomogeneities, the intensity of scattered radiation is a function of the scattering vector $\mathbf{h} = 4\pi/\lambda \sin\Theta$ [7, 8, 9]:

$$I(h) = \eta^2(0) V \int_0^\infty 4\pi r^2 \gamma_0(r) \frac{\sin hr}{hr} \mathrm{d}r, \tag{1}$$

where V is the volume of the system in which X-rays are scattered by electrons. $\eta^2(0)$ is defined by [7, 8, 9]

$$\eta^2(0) = \frac{1}{V} \int_0^\infty [\rho_e(r) - \rho_e]^2 \, \mathrm{d}^3 r, \tag{2}$$

where $\rho_e(r)$ is the local electron density at a given point r and ρ_e is the average electron density.

The correlation function contains significant information on the geometry and structural arrangement of the scattering particles. The function is calculated from the scattering function [7, 10]. The following relationship holds for the tailing region of the scattering function (the so-called Porod range) [7]:

$$I(h) = \eta^2(0)\, 2\pi \frac{S}{h^4}, \tag{3}$$

where S is the surface area of the particles. The specific surface area of the particles (relative to unit volume V) is [7].

$$\frac{S}{V} = \pi \frac{\lim\limits_{h\to\infty} I(h)\, h^4}{Q} = \pi \frac{K_p}{Q}, \tag{4}$$

where K_p is the tail-end constant.

The correlation length is calculated directly from the scattering function by the following integration [7, 8, 9]:

$$l_c = \pi \frac{\int\limits_0^\infty I(h)\, h\, dh}{Q}. \tag{5}$$

From the middle section of the scattering curve the mass fractal dimension D_m of the particles can be determined [10, 11], when the scattering curve is linear in a relatively wide range of h:

$$\log I(h) = p \log h. \tag{6}$$

From the value of the tangent p, D_m is calculated by the relationship $D_m = |p| + 1$ (for $1 \leq D_m \leq 3$).

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