FRACTAL NETWORKS OF CARBON NANOPORES

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Introduction

It is well documented in the literature [1,2] that the morphology and, therefore, the adsorptive properties of activated carbons largely depend on the activation process. However, until now, there was no fundamental relation between morphology and activation process [2]. In the present communication, we show, by means of small-angle X-ray scattering (SAXS), that steam activation of a common char yields the formation of a fractal network of nanopores. The existence of a fractal nanopore network may confer to these activated carbons new interesting properties which will be discussed.

Experimental

The activated carbons (H series) investigated in the present study were prepared [3] from a char obtained from olive stones by carbonization in N_2 at 1123K for 2 hours. The samples were activated under a constant steam flow (100 ml min^{-1}) at 1023K. Under these conditions, the activation rate is close to 1% h^{-1}. The burn-off (expressed as a weight percentage) is indicated in the sample reference: H0, H8, H22, H37, H52 and H74.

Small-angle X-ray scattering (SAXS) measurements were performed at the Sandia National Laboratories-University of New Mexico Scattering Laboratory in Albuquerque, NM. Data for momentum transfer q smaller than about 0.03 $Å^{-1}$ were measured on a Bonse-Hart scattering system. A pinhole scattering system was used for investigations at larger q values. The pinhole data were adjusted in intensity to the desmeared Bonse-Hart ones, after corrections for background.

The intensity I(q) scattered by a fractal surface [4] or by a fractal volume [5] are described by the following power laws:

$$I \propto q^{D_S-6} \quad (1)$$

$$I \propto q^{-D_V} \quad (2)$$

in which D_S and D_V are respectively surface and volume fractal dimensions.

Results and Discussion

It was already shown [6] that, in the low-q range, all samples exhibit a surface fractal dimension close to or slightly larger than 2. Thus, this presentation will be focused on the results obtained for q-values above about 10^{-3} $Å^{-1}$. Figure 1 shows the log-log plot of the SAXS data obtained for H0 and H52.

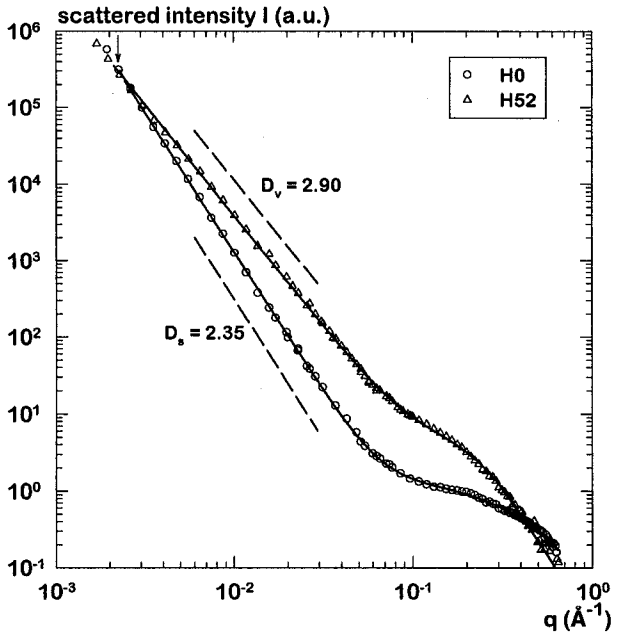

Figure 1. SAXS curves obtained for the initial char H0 and the char activated by steam at 52% burn-off (H52). Continuous lines are fits to Eq. 4 and 3b, respectively. The arrow indicates the value of q_c for H52

A linear regression between a lower limit q_c and an upper limit close to 6×10^{-2} yields a slope equal to -3.65, in the case of H0. The absolute value of the exponent is larger than 3, inferring from Eq. 1 a surface fractal with D_s = 2.35. All other samples exhibit volume fractal characteristics (Eq. 2) since the absolute value of the slope range between 2.85 and 2.90 (H37, H52 and H74) or is equal to 3 (H8 and H22). These features are attributed to a fractal pore network. This structure can be modeled [6] as

3-dimensional stacks of 2-dimensional invasion-percolation networks (for which one predicts D = 2.89 [7]) along graphitic planes.

The size L_{max} of the network is determined from the lower q-value ($q = q_c$) of the fractal range ($L_{max} = 2\pi/q_c$). The width L_{min} of the channels belonging to the fractal pore network can be determined from the fit to the data to the following equation:

$$I(q) = K\,[f(q)]^2\,S(q) \qquad (3)$$

in which:
- K is a constant for a given system (arbitrary units)
- the form factor is approximated (Guinier approximation) as: $[f(q)]^2 \cong \exp[-1/5\,(qr_1)^2]$, with $r_1 = L_{min}/2$
- S(q) is the structure factor, with $S(q) = 1 + (qr_1)^{-D_v}$ [5]

Thus, Eq. 3 writes:

$$I(q) = I_1\,[1 + (qr_1)^{-D_v})]\,\exp[-1/5\,(qr_1)^2] \qquad (3a)$$

The three parameters corresponding to the best fit are determined by using the Marquardt-Levenberg algorithm in SigmaPlot® (weight = $1/[I(q)]^2$).

sample	L_{max} (nm)	L_{min} (nm)	D_v	ϕ_{SAXS}	ϕ_{N_2}	L_2 (nm)
H0		0.85	-	-	≈ 0	2.02
H8	78	1.64	3	-	0.33	0.78
H22	205	1.38	3	-	0.43	(0.34)
H37	238	1.52	2.87	0.52	0.46	0.84
H52	296	2.12	2.90	0.61	0.51	1.02
H74	343	2.10	2.85	0.47	0.56	0.96

Table 1. Parameters obtained from the fit to Eq. (4) for H0 and to Eq. (3b), for activated samples (determination of ϕ_{SAXS} and ϕ_{N_2} is explained in text).

However, it appears that Eq. 3a cannot fit the data up to the largest q-value. An analytical expression for the whole curve (between q_c and 0.66 $Å^{-1}$) is given by Eq. 3b:

$$I(q) = I_1\,[1 + (qr_1)^{-D_v})]\,\exp[-1/5\,(qr_1)^2] + I_2\exp[-1/5\,(qr_2)^2]$$

from which a second family of non correlated objects which scatter independently from the fractal pore network, is inferred. The values of D_v, $L_{min} = 2r_1$ and $L_2 = 2r_2$, are collected in Table 1. For CO_2 activated samples, the analysis of N_2 adsorption provided by Monte Carlo simulation [8] shows the existence of two families of micropores, located around 2.4 and 1.2 nm respectively. A similar treatment will allow to decide whether the second family of scattering objects obtained in the present study consists of non-correlated micropores or carbon grains.

By definition, the volume fraction ϕ_{SAXS} of the fractal network is equal to $(L_{max}/L_{min})^{D_v-3}$. Even if the second family of scatterers are micropores, its contribution to I(q) is about ten times smaller than that of the fractal pore network. Thus, one may compare, ϕ_{SAXS} to ϕ_{N_2} defined as the ratio of the total specific volume of adsorbed nitrogen V_{N_2} to the total specific volume of the sample $V_t = V_{N_2} + 1/\rho_{carbon}$ ($\rho_{carbon} \cong 2$ g/cm^3). Table 1 shows fair agreement between the two series of values.

The data obtained for the non-activated sample H0, can be fitted to the following equation:

$$I(q) = I_o\,q^{D_s-6} + I_1\exp[-1/5\,(qr_1)^2] + I_2\exp[-1/5\,(qr_2)^2] \quad (4)$$

describing the total intensity scattered by three independent scatterers: a fractal surface and two families of non-correlated objects, the first one being likely pores accessible to CO_2 at 273K but not to N_2 at 77K [3].

Conclusion

Steam activation produces a fractal network of channels with an average channel diameter of 2 nm. By virtue of the high fractal dimension of 2.9 of the network, on length scales of 2-300 nm, the channels criss-cross the solid in a nearly space-filling manner and generate a high porosity of 0.5. Since all the porosity resides in these channels, the solid may be regarded as a matrix of branched carbon nanotubes and may compete with isolated nanotubes, in terms of its potential for gas storage and phase transitions in confined geometries. A distinct advantage of the fractal network is that transport through the branched, interconnected channels is much more rapid than transport in and out of isolated tubes.

References

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