Effect of Oxidation Treatment on Surface Fractal Dimension of Activated Carbon Fiber

Zheng-Hong Huang, Feiyu Kang*, Jun-Bing Yang, Kai-Ming Liang, Hui Zhao† and Bao-Zhong Dong†
Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, P. R. China
†*Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100080, P. R. China*

(Received September 12, 2001; CL-010897)

Viscose rayon based activated carbon fibers (ACFs) were oxidized in different ways, resulting in changes of surface fractal dimension, which might be found in ACFs with low and high specific surface areas treated under the same condition.

Both pore structure and surface chemistry of microporous carbon play an important role on the adsorption for inorganic gas and polar volatile organic compound (VOC). Oxidation treatment in the gas or liquid phase may modify the chemical and physical characteristics of microporous carbon,[1–4] resulting in the modification of the adsorption performance of adsorbent. As a matter of fact, the surface roughness and irregularities of the porous solids were also changed. Since the concept of fractal was introduced as the characteristic parameter of porous materials by P. Pfeifer *et al*.,[5,6] it has been helpful to evaluate quantitatively the geometrical irregularity of solid surfaces. The surface fractal dimension of various porous carbon materials has been determined by organic vapor adsorption,[7–10] high-resolution N_2 adsorption[10–13] and small-angle X-ray scattering[14,15] as well as electron microscopy and image processing.[16] However, few researchers[17] studied the effect of oxidation on the fractal dimension of porous carbon.

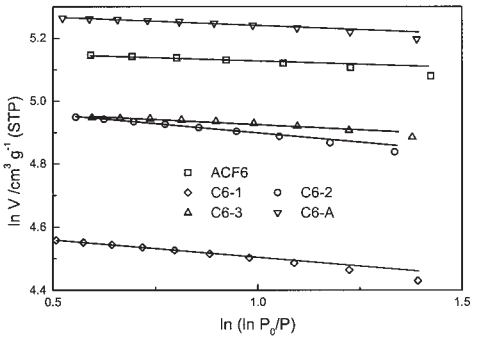
The aim of this work is to study the effect of different oxidation treatments on micropore structure as well as surface fractal dimension of viscose rayon based activated carbon fibers (ACF) with different specific surface areas though they were treated under the same condition.

The original materials were two viscose rayon based ACF samples with different specific surface areas and they were denoted as ACF6 and ACF14 referring to its surface area. The following samples were prepared through different oxidation treatments: samples of C6-1 and C14-1, treated with conc. HNO_3 at 393 K for an hour; C6-2 and C14-2, treated with 30 wt% H_2O_2 at 363 K for an hour; C6-3 and C14-3, treated with conc. HNO_3 at room temperature for an hour; C6-A and C14-A, oxidized with air at 673 K for an hour. The samples treated with oxidizing solution were thoroughly washed with distilled water and dried in a vacuum oven at 393 K for 12 hours. The pore textures and the surface chemistry of samples were characterized by N_2 adsorption method at 77 K and X-ray photoelectron spectroscopy (XPS), respectively. The details were described previously.[18]

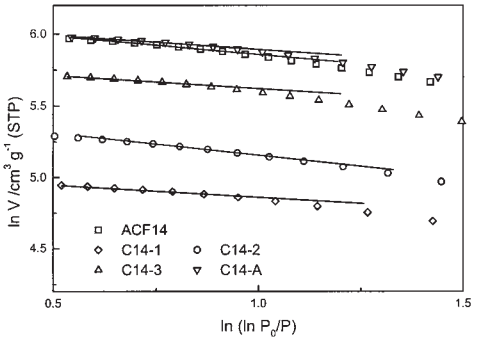
The surface fractal dimension, $D_{s,N}$, can be calculated from the nitrogen adsorption isotherms according to the following fractal Frenkel-Halsey-Hill (FHH) equation.[13,19]

$$\ln V = \text{constant} + \frac{D_{s,N} - 3}{3}[\ln(P_0/P)]$$

where V is the gas volume at STP adsorbed at equilibrium pressure P and P_0 is the saturation pressure of the adsorbate. The equation holds well at the lower end of the isotherm, representing the early stages of the multilayer buildup, where the van der Waals attraction force, i.e. gas/solid interaction is dominating. The previous fractal analysis[20] showed that the fractal exponent (D-3)/3 provides more realistic results than (D-3), thus being used in present study. Figure 1 shows the ln V vs ln(ln P_0/P) plots for the nitrogen adsorption isotherms of ACF samples. All plots exhibit good linear relationships, from which the $D_{s,N}$ value can be determined, as shown in Table 1 and 2. The BET specific surface areas of original samples are 640,1460 $m^2\,g^{-1}$. The lower specific surface area is, corresponding to narrower median micropore size, the higher fractal dimension is, corresponding to rougher surface.



(a)



(b)

Figure 1. ln V vs ln (ln P_0/P) plots for the nitrogen adsorption isotherms of (a) ACF6 series; (b) ACF14 series.

Different oxidation treatment resulted in changes of fractal dimension. In the case of ACF6 series, the $D_{s,N}$ value of C6-1 and C6-2 was lower than that of ACF6, in contrast, the $D_{s,N}$ of C6-3 and C6-A was higher than that of ACF6. It is well known that the presence of slitlike micropores of different sizes in porous carbons increases significantly the geometrical irregularity of their surfaces and the value of the surface fractal dimension.[11] As the fractal dimension increases, the micropore size distribution

Table 1. Surface fractal dimension $D_{s,N}$ and $D_{s,X}$ of ACF6 series

	ACF6	C6-1	C6-2	C6-3	C6-A
$D_{s,N}$	2.84	2.65	2.66	2.92	2.87
$D_{s,X}$	2.69	2.41	2.24	2.71	2.69

Table 2. Surface fractal dimension $D_{s,N}$ of ACF14 series

	ACF14	C14-1	C14-2	C14-3	C14-A
$D_{s,N}$	2.26	2.41	2.24	2.51	2.54

becomes more hyperbolic, and the volume fraction of small micropore increases.[21] In addition, the surface functional groups are situated at the intermicrographite junctions, giving rise to the rough pore wall and resulting in the increase of the fractal dimension.[22] It is known from our previous study[18] that the amount of the functional groups on ACF surface increased after oxidation treatment, BET specific surface areas and micropore volumes of ACFs oxidized by oxidizing solution decreased, in contrast, those of ACFs oxidized by air increased due to gasification by air. For C6-1 and C6-2, their fractal dimensions decreased due to destruction and widening of the micropores by drastic oxidation.[23] For C6-A, gasification by air promoted the increase of the volume fraction of small micropore, resulting in the increase of its fractal dimension. Whereas for C6-3, moderately oxidation fixed oxygen containing functional groups on the entrances of microporosity, resulting in the increase of its fractal dimension, even higher than that of C6-A. It was the prevention of mass transport due to a high concentration of oxygen in narrow pore entrances that the capacity and the adsorption rate of C6-3 for VOC decreased drastically.[18]

In the case of ACF14 series, the $D_{s,N}$ value of C14-2 decreased and the $D_{s,N}$ of C14-3 and C14-A increased as comparing with the original sample for the above reasons. It is noted that the $D_{s,N}$ of C14-1 was higher than that of ACF14. The volume fraction of small micropore in ACF14 was lower than that of ACF6, thus, the contribution of the surface functional groups to the increase of $D_{s,N}$ was significant. It can be seen that the $D_{s,N}$ value of C14-2 decreased slightly.

In addition, SAXS measurements were performed for ACF6 series. The SAXS method on the determination of the surface fractal dimension was developed by Bale and Schidt.[24] Simply speaking, the intensity of radiation scattered on a fractal surface is proportional to a negative power of the wave vector q:

$$I \propto q^{-(6-D_{s,X})}$$

The $D_{s,X}$ can be easily obtained from the slope of the measured intensity as a function of wave vector in log-log coordinates for the range of logarithm values between -1.2 and -0.9.[14] The scattering curves of the samples are plotted in log-log scale in Figure 2 and the $D_{s,X}$ values are listed in Table 1. A similar trend for the SAXS data was observed and the adsorption measurement results were confirmed. It is noted that the $D_{s,X}$ values are smaller than the $D_{s,N}$ values. Similar report can be seen elsewhere.[15] This might be ascribed to no drying the samples prior to SAXS measurement. Kaneko and co-worker found that water adsorption swells the micropores.[25]

In conclusion, oxidation treatment produced the destruction and widening of porosity as well as the increase of oxygen containing functional groups, resulting in change of surface fractal dimension of ACF sample. The oxidized ACF with different treatments exhibited different surface fractal dimensions, indicating differences of geometrical irregularity. The ACF samples with low and high specific surface areas treated under the same condition exhibited different changes of surface fractal dimensions due to the different pore structures of original samples.

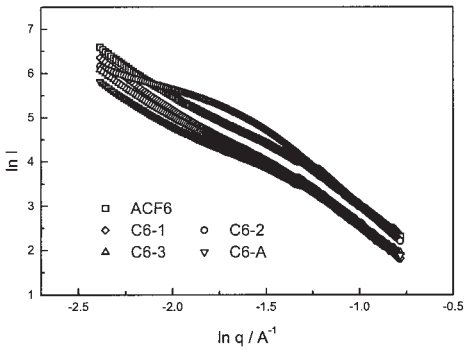


Figure 2. ln I vs ln q plots of the SAXS curves for ACF6 series.

References and Notes

1 Y. Otake and R. G. Jenkins, *Carbon*, **31**, 109 (1993).
2 B. K. Pradhan and N. K. Sandle, *Carbon*, **37**, 1323 (1999).
3 E. D. Dimotakis, M. P. Cal, J. Economy, M. J. Rood, and S. M. Larson, *Environ. Sci. Technol.*, **29**, 1875 (1995).
4 M. Polovina, B. Babić, B. Kaluderović, and A. Dekanski, *Carbon*, **35**, 1047 (1997).
5 P. Pfeifer and D. Avnir, *J. Chem. Phys.*, **79**, 3558 (1983).
6 D. Avnir, D. Frain, and P. Pfeifer, *Nature*, **308**, 261 (1984).
7 S. Blazewicz, A. Swiatkowski, and B. J. Trznadel, *Carbon*, **37**, 693 (1999).
8 P. Pfeifer and D. Avnir, *J. Chem. Phys.*, **79**, 3556 (1983).
9 M. Sato, T. Sukegawa, and T. Suzuki, *Chem. Phys. Lett.*, **181**, 526 (1991).
10 B. J. Trznadel and A. Światkowski, *Adsorp. Sci. Technol.*, **17**, 303 (1999).
11 K. Kaneko, M. Sato, T. Suzuki, Y. Fujiwara, K. Nishikawa, and M. Jaroniec, *J. Chem. Soc., Faraday Trans.*, **87**, 179 (1991).
12 N. R. Khalili, M. Pan, and G. Sandí, *Carbon*, **38**, 573 (2000).
13 I. M. K. Ismail and P. Pfeifer, *Langmuir*, **10**, 1532 (1994).
14 R. Diduszko, A. Swiatkowski, and B. J. Trznadel, *Carbon*, **38**, 1153 (2000).
15 K. László, A. Bóta, L. G. Nagy, G. Subklew, and M. J. Schwuger, *Colloids Surf., A*, **138**, 29 (1998).
16 K. Oshida, K. Kogiso, K. Matsubayashi, K. Takeuchi, S. Kobayashi, M. Endo, M. S. Dresselhaus, and G. Dresselhaus, *J. Mater. Res.*, **10**, 2507 (1995).
17 K. Tsutsumi, Y. Matsushima, and A. Matsumoto, *Langmuir*, **9**, 2665 (1993).
18 F. Kang, Z.-H. Huang, K.-M. Liang, J.-B. Yang, and H. Wu, *Adsorp. Sci. Technol.*, in press.
19 P. Pfeifer, Y. J. Wu, M. W. Cole, and J. Krim, *Phys. Rev. Lett.*, **62**, 1997 (1989).
20 N. R. Khalili, M. Pan, and G. Sandí, *Carbon*, **38**, 573 (2000).
21 M. Jaroniec and R. K. Gilpin, *Carbon*, **31**, 325 (1993).
22 M. Sato, T. Sukegawa, T. Suzuki, and K. Kaneko, *J. Phys. Chem. B*, **101**, 1845 (1997).
23 C.Moreno-Castilla, M. A. Ferro-García, J. P. Joly, I. Bautista-Toledo, F. Carradco-Marín, and J. Rivera-Utrilla, *Langmuir*, **11**, 4386 (1995).
24 H. D. Bale and P. W. Schidt, *Phys. Rev. Lett.*, **53**, 596 (1984).
25 K. Kaneko, Y. Fujiwara, and K. Nishikawa, *J. Colloid Interface Sci.*, **127**, 298 (1989).