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Detection of low concentration oxygen containing functional groups on activated carbon fiber surfaces through fluorescent labeling

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Abstract

Covalent fluorescent labeling of surface species (FLOSS) was used to detect relatively low concentrations of surface functional groups (OH, COOH and CHO) on activated carbon fiber surfaces. The chromophores were attached to the surface through a reaction specific to each type of surface functional group. FLOSS indicated the presence of 8.7×10^{11} COOH groups/cm^2 and 1.3×10^{12} CHO groups/cm^2 on the ACF 25 fiber surface. Neither the infrared spectrum nor the X-ray photoelectron spectrum showed evidence of the existence of those low concentration groups. The concentration of OH groups on the fiber surface was lower than the detection limit ($\sim 10^{10}$/cm^2) of FLOSS under the present conditions. The FLOSS results for CHO and COOH groups were compared with the concentrations determined by Boehm titration (3.11×10^{13}/cm^2 for CHO and 1.05×10^{13}/cm^2 for COOH). The limited accessibility of the ACF surface to relatively large chromophores is one of the main reasons for the discrepancy between these two methods. FLOSS detects only exposed functional groups as opposed to functional groups hidden in small pores. This apparent limitation, however, highlights the surface sensitivity and specificity of FLOSS technique.

Keywords: Carbon fibers; X-ray photoelectron spectroscopy; Infrared spectroscopy; Spectrophotometry; Functional groups

1. Introduction

Many applications of carbon materials, including activated carbon, activated carbon fibers and carbon nanotubes, are based on the presence of oxygen containing surface functional groups [1–6]. For example, the dynamic adsorption of hexane by activated carbons under humid conditions was found to be mainly governed by the quantity of acidic surface functional groups [7]. It is reported that oxygen surface complexes, possibly lactone and carbonyl groups, were the active sites for Hg-0 capture [8]. An increase in the number of some acid functional groups and the surface wetting quality was helpful to enhancing microorganism fixing [9].

Several methods have been applied to detect and quantify oxygen functional groups on carbon surfaces [10–13]. Infrared spectroscopy (IR) [14–20], X-ray photoelectron spectroscopy (XPS) [2,7,14,15,20,21], thermal desorption spectroscopy (TPD) [14,17,22], elemental analysis [2,23,24] and Boehm titration [14,15,24–26] are the most frequently used methods. Although the Boehm titration is a valuable technique, it is limited to special functional groups [13,27]. TPD only provides the total number of groups without detailed information about their types. Quantitative analysis of XPS and IR is not straightforward [13]. The time-consuming titration [10], the difficulty in assigning the peaks, and the influence of experimental parameters (such as the heating rate in TPD) highlight the need for new methods. Furthermore, these techniques

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do not reveal the location of the functional groups. For example, they do not distinguish between functional groups located within small pores and functional groups located in large pores and on the external surface.

Some new methods, e.g., inverse gas chromatography (IGC) [28,29], diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [30], combining DRIFTS with transient kinetic (TK) and TPD techniques [31], and electrokinetic measurements (zeta potential) [32], have been applied to investigate the surface properties of activated carbons and carbon fibers. Scanning tunneling and atomic force microscopes (STM/AFM) have also been used to study surface functional groups in some cases [33].

Fluorescent labeling has been used to identify and quantify functionalities on self-assembly monolayers [34] and polymer surfaces [35,36]. In this study, we used fluorescent labeling to detect low concentrations of surface functionalities on carbon surfaces. The IR and XPS results for the activated carbon fiber are inconclusive due to low signal levels, which suggest low concentrations. The amount of functionalities determined by FLOSS was compared with the results of two other independent techniques (depletion and Boehm titration). The present experiments show that covalent fluorescent labeling of surface species (FLOSS) can effectively detect and quantify oxygen containing surface functional groups on activated carbon fibers.

2. Experimental

2.1. Materials and sample characterization

The commercially available activated carbon fiber, ACF 25, used in this study was supplied by American Kynol, Inc. Fibers were made by acid-catalyzed cross-linking of melt-spun novolac resin to form a fully cross-linked, three-dimensional, amorphous "network" polymer structure similar to that of thermo-setting phenolic resins. Kynol™ novoloid fibers were transformed into activated carbon fibers by a one-step process combining both carbonization and activation.[1] The specific surface area of the ACF 25 was measured by nitrogen adsorption at 77 K. The adsorption measurements were conducted with Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Corporation, Boynton Beach, FL).

The titration method suggested by Boehm [10] was used to determine the concentration of acidic groups on the ACF surfaces. Four samples of activated carbon fiber (~0.2 g each) were mixed with 25 ml solutions of 0.025 N of $NaHCO_3$, 0.025 N of Na_2CO_3, 0.025 N of NaOH, and 0.125 N of NaOH, respectively, for 24 h with continuous stirring. Ten milliliters of each filtrate was used for the titration of excess base by 0.025 N HCl. It is assumed that the lower concentration NaOH neutralizes carboxylic, phenolic and lactonic groups; Na_2CO_3 neutralizes carboxylic and phenolic groups; $NaHCO_3$ only neutralizes carboxylic groups. Total acidity, including phenolic, lactonic, carboxylic and carbonyl groups, was determined by the higher concentration NaOH solution.

UV–Vis absorbance was determined on a Varian CARY 100 bio UV–Vis spectrophotometer with a 1 cm quartz cell.

IR spectra were recorded, at 4 cm^{-1} resolution, on a Brüker Tensor 27 spectrometer equipped with a DTGS detector. Five hundred scans were averaged for each spectrum. Two KBr pellets were pressed into a tungsten grid. Approximately 0.8 mg of activated carbon fiber, suspended in hexane solution, was deposited on one pellet through the drop and dry method. The other pellet was used as a reference.

XPS was performed on a Physical Electronics Model 550, equipped with a cylindrical, double pass energy analyzer. The ACF sample was attached to a tantalum surface by a conductive silver paste (LADD Research Industries).

2.2. Covalent attachment of chromophores to different functional groups on activated carbon fiber surfaces

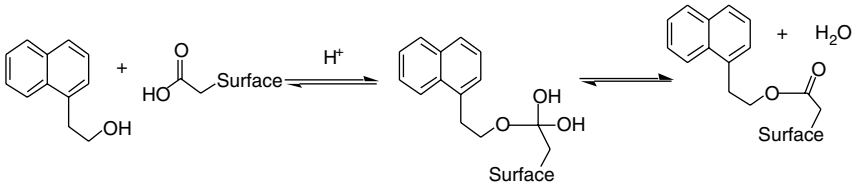
Three chromophores with appropriate functionalities were selected to covalently label CHO, COOH and OH groups, respectively, as shown in Schemes 1–3 in Fig. 1. Solutions were prepared of 1-pyrenemethylamine (95%, Aldrich) in ethanol (ACS grade, Pharmaco), triphenylmethylchloride in DMF (ACS grade, Baker) and 1-napthaleneethanol (99%, Aldrich) in acetonitrile (ACS grade, Fisher). The first two reactions were performed at room temperature for 2 h. The last reaction was refluxed for 2 h with a catalytic amount of hydrochloric acid (CMOS grade, Baker).

In order to differentiate the fluorescence signals of chemisorbed chromophores from physisorbed chromophores, control experiments, using naphthalene, triphenylmethane and pyrene instead of 1-1-napthaleneethanol, triphenylmethylchloride and pyrenemethylamine, were performed. Post reaction cleanings following the chromophore grafting were performed by rinsing the sample several times with neat solvents used in each reaction to get rid of physisorbed molecules.

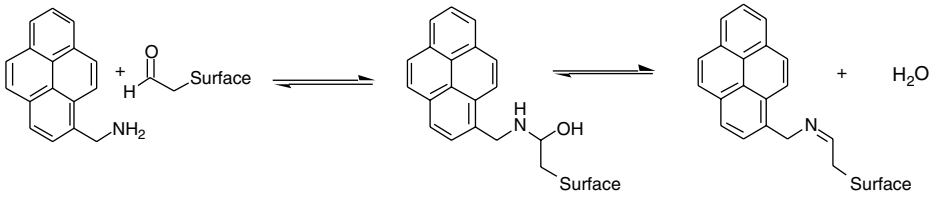
Sample fibers were dispersed in the reaction solvent after the post reaction cleaning. Fibers were deposited on a silicon (1 1 1) (n type, 25–40 Ω cm) wafer through drop and dry method. Silicon wafers were previously cleaned with RCA SC1 (NH_4:H_2O_2:H_2O, 1:1:4) at 80 °C for 45 min. Fluorescence measurements were performed on a Jobin Yvon Horiba Spex Fluorolog 3 with 5 nm band pass and 3 scan averages with samples oriented at a 45° incident angle to the incident excitation beam and at normal incidence to the collection optics. Detection was accomplished using a PMT. Fluorescence signals for all samples were corrected for lamp fluctuations by recording the ratio of the sample fluorescence signal to the source reference photodiode.

[1] http://www.kynol.com.

Scheme 1 Attachment of 1-napthaleneethanol to COOH



Scheme 2 Attachment of 1-pyrenemethylamine to CHO



Scheme 3 Attachment of triphenylmethylchloride to OH

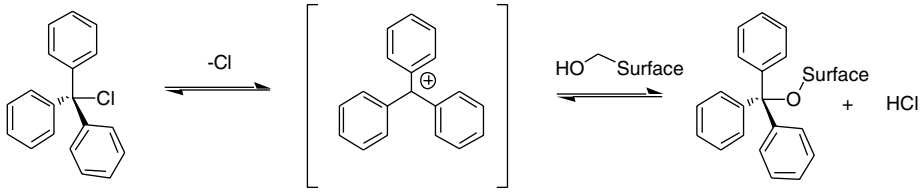


Fig. 1. Reaction schemes of covalent attachment of chromophores to different functional groups.

2.3. Depletion experiment

After the reaction (Scheme 2), the amount of pyrenemethylamine left in the reaction solution, as opposed to chromophores bound to the fibers, was determined using UV absorption at 324 nm. The reacted fibers were rinsed four times with neat solvent and the supernatant solution was transferred to a volumetric flask every time by pipette after the fibers settled to the bottom of the reaction container. In this manner only chemisorbed chromophores were retained by the fibers.

3. Results and discussion

3.1. Fluorescent labeling of surface functional groups

The presence of COOH groups on fiber surface is indicated in the data shown in Fig. 2. The dominant peak near 340 nm is associated with monomer emission of naphthaleneethanol [34]. One open question was whether this peak came from chemisorption (naphthaleneethanol that reacted with COOH groups) or from non-specific physisorption of chromophores on the fiber surface. Estimation of residual, non-specific adsorption on the fiber surface was made by repeating the functionalization experiment with unsubstituted naphthalene. The spectrum from this control is also shown in Fig. 2 (dashed line). The absence of a monomer peak at 340 nm for the fiber mixed with naphthalene suggests that the peak in the spectrum of the naphthaleneethanol reacted sample really corresponds to chemisorbed chromophores. Dimer emission has been reported to occur near 365 nm and near 400 nm [37]. The intensity of the dimer emission peaks in these regions of our naphthaleneethanol reacted fiber spectra suggests that some chromophore aggregation occurs on the surface. This is not inconsistent with the FLOSS result that the concentration of COOH groups is low, as dimer formation reflects local concentration. The presence of dimers suggests that the naphthaleneethanol clusters and therefore that not all COOH groups are isolated.

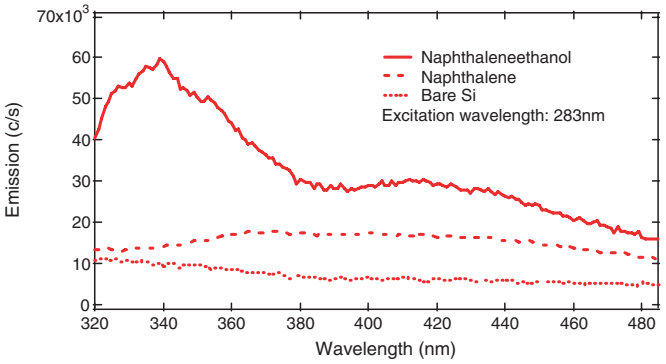


Fig. 2. FLOSS for COOH groups. Emission spectra of naphthaleneethanol (solid), naphthalene (dashed) reacted activated carbon fiber on silicon and bare silicon (dotted line).

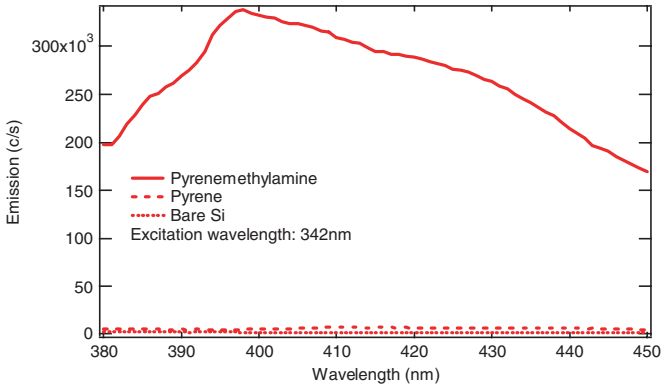


Fig. 3. FLOSS for CHO groups. Emission spectra of pyrenemethylamine (solid), pyrene (dashed) reacted activated carbon fiber on silicon, and bare silicon (dotted line).

The fiber used in our study was derived from a phenol–aldehyde polymer. It is reasonable to expect residual aldehyde groups from the raw material. The presence of CHO groups on the fiber surface is revealed by the fluorescence spectra that resulted from covalent attachment of 1-pyrenemethylamine to CHO, as shown in Fig. 3. The dominant peak near 398 nm is associated with monomer fluorescence [34]. The lack of emission peak at 398 nm for physisorbed-unfunctionalized chromophore (pyrene) suggested that the peak in 1-pyrenemethylamine spectrum is from chemisorbed fluorophores.

The detection of OH was performed using triphenylmethylchloride, which is known to react with hydroxyl groups [34]. The fluorescence spectrum for fibers exposed to triphenylmethylchloride is shown in Fig. 4. The fibers exposed to non-functionalized chromophore (triphenylmethane) showed almost the same signal level (Fig. 4).

3.2. XPS and IR data

XPS was used to detect functionalities on activated carbon fiber surfaces. The difference in binding energies for atoms in various environments is very small and deconvolution of the peaks is necessary to analyze XPS data

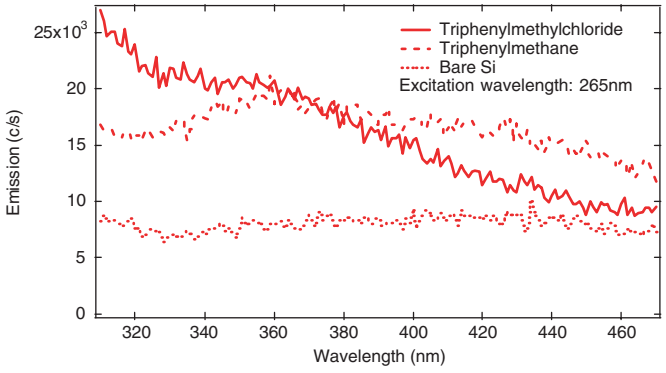


Fig. 4. FLOSS for OH groups. Emission spectra of triphenylmethylchloride (solid), triphenylmethane (dashed) reacted activated carbon fiber on silicon and bare silicon (dotted line).

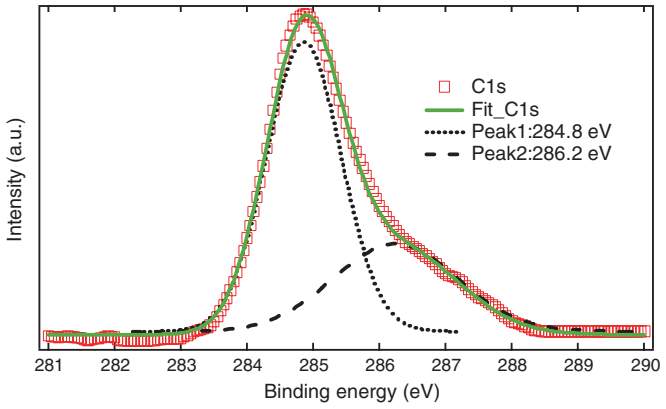


Fig. 5. C1s XPS spectrum of activated carbon fiber (□ is experimental data; the solid line is the fit to the experimental data; the dotted line is the 284.8 eV peak contribution; the dashed line is the 286.2 eV peak contribution).

[10,38]. The curve fitting and deconvolution of C1s region XPS spectra of ACF 25 are shown in Fig. 5. The dominant peak at 284.8 eV was assigned to graphitic carbon in the fiber [15,20,38]. However, the asymmetric shape of the peak suggests the existence of another peak as shown in the deconvolution. The 286.2 eV peak was assigned to the carbon in –C–O– structures [15,20,38]. The binding energy of carbon in carbonyl groups is 287.5–288.1 eV [20]. No obvious evidence of carbonyl groups was detected in the C1s XPS.

The O1s feature shown in Fig. 6 is composed of two peaks. One is at 533.4 eV, which corresponds to oxygen in –C–O– groups [38]. The smaller peak with higher binding energy of 535.6 eV was assigned to chemisorbed oxygen and/or oxygen in the remaining fiber moisture [20]. The oxygen double bond carbonyl peak was expected to be at 530.4–530.8 eV [20]. Existence of carbonyl groups, that could either be characteristic of aldehyde or carboxylic acid functionalities, could not be detected by XPS in this case.

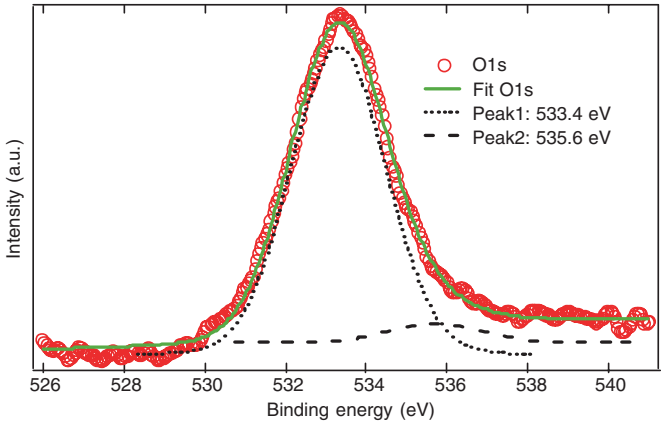


Fig. 6. O1s XPS spectrum of activated carbon fiber (○ is experimental data; the solid line is the fit to the experimental data; the dotted line is the 533.4 eV peak contribution; the dashed line is the 535.6 eV peak contribution).

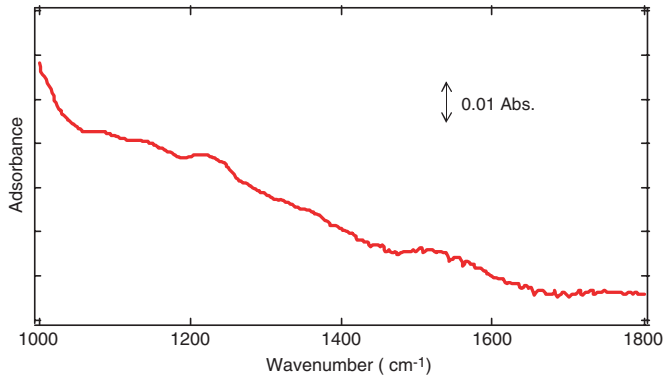


Fig. 7. Transmission IR spectra of activated carbon fiber in the range of 1100–1800 cm^{-1}.

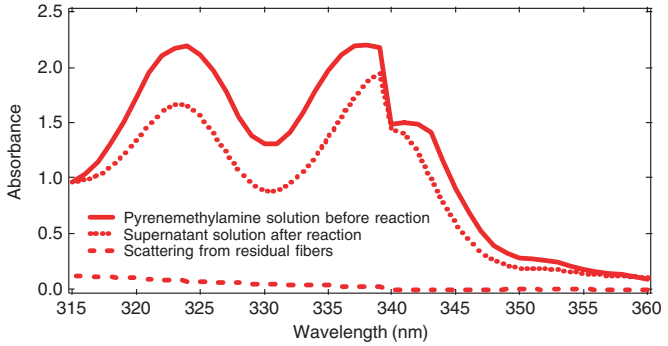


Fig. 8. UV–Vis spectra of pyrenemethylamine solution before and after reaction.

The infrared spectrum from 1100 to 1800 cm^{-1}, shown in Fig. 7, does not reveal any evidence of carbonyl groups (usually in the 1700 cm^{-1} region) on the fiber surface [18,39]. The IR results are in good agreement with the XPS results. The peak in the 1200–1250 cm^{-1} region was associated with ether type structures (C–O–C). The peak in the 1500–1600 cm^{-1} region is assigned to aromatic C=C bands and various substitution modes of the aromatic ring [39]. The amount of fiber used for the transmission IR experiment was limited by the high absorbance of carbon materials [10] and loss of light due to scattering process. While more ACF would have resulted in a greater fractional IR absorbance, loss of light due to scattering would render the experiment detector noise limited.

3.3. Quantification of functional groups by FLOSS

Quantification of functional groups by FLOSS (±20%) was carried out by establishing a calibration curve formed by measuring the peak fluorescence intensities for known amounts of chromophores on a silicon surface coated with a self-assembled monolayer of alkylsiloxane [34]. We assumed that the functional groups are homogeneously distributed on the fiber surface and that the fiber is homogeneously distributed on the silicon wafer.

Fibers exposed to naphthaleneethanol give a signal of 60,000 counts/s in Fig. 2, which corresponds to 8.7×10^{11} COOH groups/cm^2 of fiber surface based on the calibration curve provided in our previous paper [34]. The results are determined knowing the mass of ACF deposited on the Si wafer, typically ~5 μg, and the specific surface area of this sample (1950 m^2/g).

Fibers reacted with functionalized pyrene molecules gave a signal of 340,000 counts/s (Fig. 3) which corresponds to 1.3×10^{12} CHO groups/cm^2 of fiber surface. Similar calculations were performed for OH groups. The signal level shown in Fig. 4 is 18,000 counts/s at 400 nm where the triphenylmethane emission peaks. The intensity is close to the zero level on the calibration curve [34]. Therefore, the concentration of the OH group on the fiber was below the present detection limit of FLOSS (~10^{10} molecules/cm^2).

In order to compare the number of functionalities determined by FLOSS with data from another independent technique, UV-Vis depletion experiments were performed. UV spectra of the supernatant of the pyrenemethylamine solution before and after reaction with the ACF are shown in Fig. 8. The reaction induced change in solution absorbance at 324 nm is 0.47 O.D., corrected for scattering from residual fiber ~0.07 O.D. The molar extinction coefficient of pyrenemethylamine at 324 nm was determined to be 26,500 mol^{-1} L cm^{-1}. The amount of chromophore reacted with fibers was determined to be 1.6×10^{12} (±15%) molecules/cm^2 of fiber surface, corresponding to a density of aldehyde groups on the fiber surface of about 1.6×10^{12}/cm^2. This number is in good agreement with the data determined by FLOSS, which is $1.3 \times 10^{12}/cm^2$.

The Boehm titration results (±7%) shown in Table 1 suggest that there are 1.1×10^{13} carboxyl groups/cm^2 of fiber surface and 3.1×10^{13} carbonyl groups/cm^2 of fiber surface. The total acid determined by the Boehm titration includes phenolic, lactonic, carboxylic and carbonyl groups [27]. Since the precursor of the fiber is a phenol–aldehyde polymer,[2] it is likely that the carbonyl groups determined by Boehm titration correspond to aldehyde groups.

Compared with Boehm titration, FLOSS underestimated the total amount of both COOH (8.7×10^{11} vs 1.1×10^{13}) and CHO (1.3×10^{12} vs 3.1×10^{13}) groups on the fiber surface. Several issues could contribute to this discrepancy. First, the narrowest diameter of chromophores, as calculated (Chemsketch, Advanced Chemistry Development Inc.), is around 10 Å for naphthaleneethanol molecule. This neglects the solvent shell that might be necessary for reaction. Meanwhile, the pore size distribution analysis suggest that pores larger than 10 Å account for less than 50% of the total surface area as shown in Fig. 9. Thus not all the functional groups were accessible to the chromophores while the bases used in Boehm titration are small enough to diffuse into most micropores.

The pores of fibers are important in applications that involve separations, for example. However, for many other

[2] http://www.kynol.com.

Table 1
Surface acidic functional groups of activated carbon fiber determined by Boehm titration

Surface functional groups based on surface area (number/cm^2 ACF 25)				
Phenolic	Lactonic	Carboxylic	Carbonyl	Total acidic
2.5×10^{12}	4.2×10^{12}	1.1×10^{13}	3.1×10^{13}	4.8×10^{13}

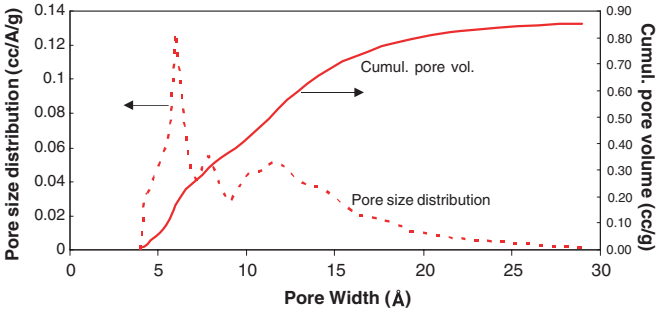


Fig. 9. Pore size distribution and cumulative pore volume of ACF 25.

applications, e.g., composite material formation, the larger pores and external surface are the key components. The sensitivity of FLOSS to these surfaces provides a unique application of FLOSS. The aldehyde groups determined by pyrenemethylamine are expected to be even more underestimated compared with carboxylic acid groups, which are determined by naphthaleneethanol, because pyrenemethylamine is larger than naphthaleneethanol. Therefore, it is reasonable to expect that the FLOSS data would give lower values than the Boehm titration approach for the analysis of COOH group.

4. Conclusions

FLOSS is an effective method to detect and quantify low concentrations of functional groups on carbon surfaces, especially when IR and XPS data are not conclusive regarding the existence of COOH and CHO groups. The presence of COOH and CHO groups was indicated by the fluorescence signal from covalently bound chromophores. The surface concentration of OH groups was estimated to be less than 10^{10} molecules/cm^2 of fiber surface. Compared with other methods, i.e., Boehm titration, FLOSS is surface sensitive and is valuable for determining specific functional groups. FLOSS is not limited to COOH, CHO and OH groups studied here. Other groups can be detected by selection of suitable chromophores. While FLOSS may be well adapted to probing functionalities on exposed surfaces and insider larger pores, the size of the chromophores clearly puts a limit on the smallest pores accessible.

Acknowledgements

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