Surface chemistry of polyacrylonitrile- and rayon-based activated carbon fibers after post-heat treatment

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Abstract

Polyacrylonitrile- and rayon-based activated carbon fibers (ACFs) subject to heat treatment were investigated by means of elemental analyzer, and X-ray photoelectron spectroscopy (XPS). The total ash content of all ACFs was also analyzed. The adsorption of benzene, carbon tetrachloride and water vapor on ACFs was determined to shed light on the role of surface chemistry on gas adsorption. Results show that different precursors resulted in various elemental compositions and imposed diverse influence upon surface functionalities after heat treatment. The surface of heat-treated ACFs became more graphitic and hydrophobic. Three distinct peaks due to C, N, and O atoms were identified by XPS, and the high-resolution revealed the existence of several surface functionalities. The presence of nitride-like species, aromatic N-imines, or chemisorbed nitrogen oxides was found to be of great advantage to adsorption of water vapor or benzene, but the pyridine-N was not. Unstable complexes on the surface would hinder the fibers from adsorption of carbon tetrachloride. The rise in total ash content or hydrogen composition was of benefit to the access of water vapor. Modifications of ACFs by heat treatment have effectively improved adsorption performance.

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Keywords: Carbon fibers; Heat treatment; X-ray photoelectron spectroscopy (XPS); Adsorption

1. Introduction

There has been increasing concern over the levels of toxic air pollutants emitted from high-technology industry. The industry has been prompted to seek more effective methods of pollution control in view of the lowered permissible limits. Activated carbon fibers (ACFs), which are fibrous carbon materials with imperfect graphite crystalline structure arranged along the fiber axis [1], have been widely used in adsorption processes to solve the problems described above. ACFs are better than granular activated carbons in terms of the adsorption capacity of organic compounds and the high sorption rates [1]. The ACF adsorbents can be converted into a wide variety of textile forms and non-woven materials, with low hydrodynamic resistance, to be used in thin layers for treatment of high gas flow rates. Thus these materials will increase adsorption efficiency, permit far greater flexibility and simplify the sorption process designs.

Commercial ACFs are generally prepared from various precursors such as polyacrylonitrile (PAN), rayon, resins, and pitches [1], which cause their final products possess different properties [2]. ACFs with different pore texture and surface composition had different adsorption and desorption behaviors for polar and non-polar vapors [3,4]. The pore texture of ACFs depends on the nature of the precursors, the impregnants, flow rate of the reacting gas, maximum heat treatment temperature (HTT) and heating rate [5]. Needle-shaped voids have been observed to exist between crystallites on the surface of PAN fibers [6]. The surface chemistry of carbons is determined by the distribution and the nature of the surface functional groups (SFGs) and the heteroatoms. Carbon–oxygen complexes, the most important SFGs [7], are thought to be located near the edges of the polyaromatic sheets in carbon [8]. Chemical and spectroscopic analyses have identified the presence of many SFGs on the carbon surface [1], and the carbonyl and alcohol groups were the most abundant carbon–oxygen functional groups [9]. Lahaye [10] and Boehm [11] have reviewed the most frequently used methods for the characterization of surface oxides.

Carbon and oxygen were the most abundant elements at the pitch- and PAN-based carbon fiber surface [12] and...
fibers contained a considerable amount of nitrogen, which was supposed to affect carbon adsorption [9] or increase catalytic activity [13]. A number of different N functional groups have been observed on the activated carbon [9], where pyridinic-N was the most active. Above 600 °C, pyrrolic-N disappeared gradually and was converted into pyridinic-N and quaternary-N. Furthermore, the ratio of pyridinic-N/quaternary-N would remain constant up to 1000 °C [14,15]. After pyrolysis, N atoms could be incorporated into the graphene layers replacing carbon atoms, and eventually present in six-member rings located at the edges of the graphene layers as pyridinic-N or in the interior as quaternary-N [14,16].

X-ray photoelectron spectroscopy (XPS) is an effective and powerful technique for investigation of the surface functionalities of carbon fibers as illustrated by a number of studies [e.g., 17]. Valence band XPS has the ability to distinguish some subtle chemical differences, and the combination of XPS data from different regions could indicate differences in chemical composition with depth into the surface [18]. The sampling depth for an XPS measurement on carbon fibers was reported to be only about 10–15 nm [19]. The XPS spectra of C 1s and O 1s indicated that carbonyl groups were introduced to the surface at low oxidation potentials, and the concentration of alcohol–ether groups increased at high oxidation potentials [20]. However, the OH and C–O oxygen atoms in the carboxyl groups could not be easily distinguished if the XPS experiments were carried out at room temperature [21]. Moreover, addition of a defect peak to the pristine C 1s profile appeared imperative in the fitting when the treatment destroyed the crystalline order of the carbonaceous materials [22]. This spectroscopic method has been extensively employed to study the surface carbon–oxygen complexes and elemental composition before and after surface treatments.

Treatment of carbon fibers prior to their uses is known to increase the scope and variety of applications. A number of treatment methods have been investigated to modify the carbon [8,18,23–29]. Surface treatment of ACFs can affect adsorption of organic substances through the modification of pore volume distribution and surface chemistry. Porous carbon materials should be treated at an appropriate temperature to avoid loss of porosity. SFGs may partially block the pore entrances, altering the diffusion rate of vapor molecules through the pore system [30]. As HTT increased, thermal decomposition of carbon–oxygen complexes within the pore structure resulted in a hydrophobic pore surface [25]. Consequently, the micropore surface area became more accessible to the adsorbate; in addition, very narrow pores blocked by hydrogen bonding and oxygenated functions became more open [31]. After ACF was treated above 1100 °C, the degree of graphitization increased significantly, partially attributed to the release of the C=O groups [25].

Compared with that of graphite or diamond, the surface chemistry of polycrystalline carbon has not yet been well characterized [32]. In order to extend the aspects of their applications, ACFs have usually been modified by a number of surface treatments. For instance, Yue et al. [31] investigated the effects of post-oxidation heat treatment on PAN-based ACFs, where the post heating adsorption characterization for Ag⁺, NaOH, and I₂ solutions was reported. Shin et al. [25] used FTIR to analyze the surface oxides of pitch-based ACFs after post-heat treatment. However, there is little information in literatures on characterizing the carbon, oxygen, and nitrogen surface groups on ACFs after post-heat treatment as well as their correlations to vapor adsorption. Therefore, the objectives of the present research are to increase the understanding of the effects of post-heat treatment on the surface chemical constituents of PAN- and rayon-based ACFs, to identify the possible surface functional groups as well as to investigate how these chemical properties influence their adsorption characterization for gaseous pollutants. Surface analytical methods including elemental analysis, total ash measurement, and XPS experiment have been used to characterize the changes in the carbon surface and determine the relationship between the surface chemistry and adsorption capacity after heat treatment.

2. Experimental

2.1. Activated carbon fibers

Two commercial types of ACFs manufactured by Taicarbon Inc. were selected in this study. One was the polycrylonitrile (PAN)-based, woven activated carbon fabric (AW1108) and the other was rayon-based, non-woven activated carbon felt (AM1132). Both pristine ACFs had a BET (Brunner, Emmett, and Teller) surface area of ca. 1100 m² g⁻¹; the densities of AW1108 and AM1132 were 0.2 and 0.09 g cm⁻³, respectively, provided by the manufacturer.

2.2. Heat treatment

The as-received ACF samples were heat-treated in a horizontal tubular furnace. About 20 g of the pristine samples were used in each of the batch. The heat treatment was carried out at 600, 850, or 1100 °C for 1 h by a heating rate of 10 °C min⁻¹ in nitrogen atmosphere [25,33,34]. After heat treatment, the samples were cooled in flowing nitrogen gas until they reached ambient temperature. The PAN-based ACF samples of as-received ACF, and those treated at 600, 850, or 1100 °C are denoted by AW1108, AW1108-600, AW1108-850, and AW1108-1100, respectively, in the text. Similarly, the rayon-based ACF samples are identified as AM1132, AM1132-600, AM1132-850, and AM1132-1100, respectively. According to the N₂ adsorption isotherms obtained by ASAP 2010 (V4.02), the AW1108-series samples yielded a BET surface area of 1100.3, 1209.2, 1227.3, and 1083.8 m² g⁻¹, respectively, while the AM1132-series had a BET surface area of 1087.0, 1280.5, 1317.4, and 1307.8 m² g⁻¹, respectively.

2.3. Elemental analysis

Elemental analysis was carried out using Elementar Vario EL III (Heraeus). The carbon (C), hydrogen (H), and nitrogen (N) contents of the ACFs of interest were determined directly using the thermal conductivity detector (TCD), and the oxygen (O) content was then obtained by difference.

2.4. Measurement of total ash content

The total ash contents of ACF samples were determined by burning a portion of each ACF sample in air at 650 ± 25 °C for 16 h until constant weight of the residue was reached. The detailed procedures followed the ASTM D2866-94 method [35]. The weight percentage of the residue from the original sample (as-received or heat-treated) is defined as the total ash content.

2.5. X-ray photoelectron spectroscopy (XPS) analysis

X-ray photoelectron spectroscopy (XPS), also referred to as electron spectroscopy for chemical analysis (ESCA), was employed to determine the number
and type of functional groups present on the surface of the ACF samples. The XPS spectra of all samples were obtained using a spectrophotometer (VG Scientific ESCALAB 250). A twin anode Mg X-ray source ($h = 1253.6$ eV) was used for this analysis, at a power of 15 kV at 400 W. The survey scans were collected from the binding energy of 0–1000 eV with a step size of 1 eV, in order to identify the elements present on the surface and in the sub-superficial zone of the ACFs. The XPS survey spectra exhibited prominent peaks due to carbon, nitrogen, and oxygen only; consequently, the high-resolution XPS measurements were configured to include these three elements. The high-resolution spectra of C 1s, N 1s, and O 1s were acquired over 277–292, 394–418, and 522.5–542.5 eV, with a step size of 50, 70, and 50 meV, respectively.

For calibration purposes, the C 1s electron binding energy corresponding to graphitic carbon was set at 284.5 eV [9]. Atomic ratios were calculated from the XPS spectra after correcting the relative peak areas by sensitivity factors according to the transmission characteristics of the Physical Electronics SCA [36]. A nonlinear least squares curve-fitting program (XPSPEAK software, Version 4.1) was used for XPS spectral deconvolution. A Shirley type background was chosen to be subtracted prior to quantification. After the baseline was subtracted, curve fitting was performed using an asymmetrical Gaussian–Lorentzian sum function fitting program under an optimized peak shape. This peak-fitting procedure was repeated until an acceptable fit was obtained. It is assumed that the surface composition does not vary significantly along the tow of fibers, and that fiber heterogeneity is present but at a much smaller scale than the analysis area probed by the X-ray beam.

2.6. Adsorption experiments

Three widely used adsorbates, i.e., benzene (C$_6$H$_6$), carbon tetrachloride (CCl$_4$), and water vapor (H$_2$O) were selected to determine the adsorption capacities on as-received and heat-treated ACF samples. The saturated uptakes of adsorbates on ACFs at 25 °C were determined according to the ASTM D3467-94 method [37], where nitrogen gas was used as the carrier gas. The concentration of organic vapor was controlled to approximately 5000 ppmv (C$_6$H$_6$) or 8500 ppmv (CCl$_4$) quantified by gas chromatography (HP 6850). The water vapor content was measured as relative humidity using a hygrometer (Rotronic A2), controlled at about 55%.

3. Results and discussion

3.1. Elemental composition

Elemental analysis was carried out to obtain the compositions of C, H, N, and O atoms in the bulk fibers. As seen from Table 1, element C was the most abundant constituent in as-received AW1108 (74.2 wt.%) and AM1132 (58.4 wt.%). The C content climbed as HTT increased, and the rate of change hit a peak when HTT increased from 850 to 1100 °C. It should be noted that AM1132-series samples contained more O atoms, compared with the AW1108-series. Because the O content was obtained by difference and AM1132 was a rayon-based activated carbon felt, the high O level could be partially attributed to the additives in the coalaceous of the fibers in a tow. The H composition in the AM1132-series (3.58–4.26 wt.%) appeared to be twice as that in the AW1108-series (1.81–2.64 wt.%). In contrast, the AW1108-series samples contained more N atoms (3.50–4.69 wt.%) than the AM1132-series (2.19–2.95 wt.%).

One reason is that the basal structure of PAN-based ACFs (AW1108) possessed C=N, while the unit of cellulose in rayon (AM1132) had relatively high amounts of H and O atoms. Compared with the C content, the amounts of H or N atoms were low and erratic within both bulk ACFs. Data for the treated ACFs indicate that a more graphitic but less hydrophilic surface was obtained by heat treatment.

3.2. Total ash content

All AM1132-series samples had a higher percentage of total ash content than the AW1108-series, as shown in Fig. 1. It could be ascribed to the fact that rayon-based activated carbon felts comprised fibrous tows which were made up of several coallesced fibers, where different binder materials were employed for different applications. The total ash contents of both ACF-series increased generally with HTT because the previous heat treatment had partially removed the carbon–oxygen complexes from the ACF surface, thus promoting the thermal stability in ACFs. Compared with untreated ACFs, an increment of 186%...
or 88% in total ash content was observed in AW1108-1100 or AM1132-1100, respectively. This also elucidates that the removal of non-graphitic carbons resulted in the disruption to the bonding in the aromatic ring structure, but probably the heteroatoms or a portion of additives remained still in the samples after heat treatment.

3.3. Surface functional groups

3.3.1. Survey spectra of XPS

The nature of surface functionalities fixed on the surface of all ACF samples was studied by XPS, which revealed the composition of the most external surface of the ACFs. Data from the XPS survey spectra of the AW1108-series (Fig. 2) and AM1132-series (Fig. 3) indicate that the major peaks in the spectra were due to the C 1s and O 1s photoelectrons, and a smaller N 1s peak was also discernible. Table 2 summaries the elemental compositions (at.%) on the surface of ACF samples or over the sampling depth of several atomic layers from the surface. The percentage of graphitic carbon content and other bonding states in PAN-based ACFs hit a peak at AW1108-850 (94.4 at.%), while that in rayon-based ACFs presented a steady increase with HTT. The intensity of O 1s for both ACFs plunged significantly as ACFs were heat-treated, which gave an explanation for the dramatic decrease in O/C atomic ratio after heat treatment, and the ratios continued to decrease as HTT increased. However, because the degree of C degradation of PAN-based ACFs was higher than that of the oxygen complexes on the surface at 1100 °C, a slight increase in O/C atomic ratio on AW1108-1100 was observed. Data from N/C atomic ratios on both ACFs indicate that the loss in surface N occurred after HTT of 600 °C, even though it seemed to be behaving erratically with HTT.

Compared with those shown in Table 1, the O atoms for the PAN-based ACFs were present primarily on the surface of as-received fibers. However, the relative percentages of O atoms on the surface decreased significantly after heat treatment. On the contrary, the O atoms in the rayon-based ACFs existed mainly within the fiber core; thus, removal of oxygen on the external surface only resulted in a slight loss in the bulk oxygen content. The surface N composition on AW1108 was relatively consistent with the result obtained from the bulk matrix, which implies homogeneous distribution of N atoms in the pristine PAN-based ACFs. Though there were more surface N present on rayon-based ACFs (AM1132-series) than on PAN-based ones (AW1108-series), a peak of N, both in the bulk and on the surface, was observed at HTT of 600 °C, indicating that a net amount of N atoms was introduced into both ACFs as they were heat-treated at 600 °C under flowing nitrogen gas. The relationships between the relative O/C and N/C mole ratios by XPS and the matrix composition by elemental analysis for AW1108-series and AM1132-series samples were shown in Fig. 4. Fig. 4a reveals that the effect of heat treatment on carbon–oxygen composition on the surface of PAN-based ACFs was more significant

![Fig. 2. XPS survey spectra of: (a) AW1108, (b) AW1108-600, (c) AW1108-850, and (d) AW1108-1100.](image1)

![Fig. 3. XPS survey spectra of: (a) AM1132, (b) AM1132-600, (c) AM1132-850, and (d) AM1132-1100.](image2)

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (at.%)</th>
<th>N (at.%)</th>
<th>O (at.%)</th>
<th>N/C (%)</th>
<th>O/C (%)</th>
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<td>AW1108</td>
<td>74.4</td>
<td>3.95</td>
<td>21.6</td>
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<td>29.0</td>
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<td>AW1108-600</td>
<td>86.3</td>
<td>5.24</td>
<td>8.49</td>
<td>6.07</td>
<td>9.84</td>
</tr>
<tr>
<td>AW1108-850</td>
<td>94.4</td>
<td>1.16</td>
<td>4.46</td>
<td>1.23</td>
<td>4.73</td>
</tr>
<tr>
<td>AW1108-1100</td>
<td>89.9</td>
<td>2.14</td>
<td>7.94</td>
<td>2.38</td>
<td>8.83</td>
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<tr>
<td>AM1132</td>
<td>74.2</td>
<td>5.95</td>
<td>19.8</td>
<td>8.02</td>
<td>26.8</td>
</tr>
<tr>
<td>AM1132-600</td>
<td>82.7</td>
<td>7.65</td>
<td>9.66</td>
<td>9.25</td>
<td>11.7</td>
</tr>
<tr>
<td>AM1132-850</td>
<td>86.8</td>
<td>3.31</td>
<td>9.90</td>
<td>3.81</td>
<td>11.4</td>
</tr>
<tr>
<td>AM1132-1100</td>
<td>90.9</td>
<td>3.93</td>
<td>5.14</td>
<td>4.32</td>
<td>5.65</td>
</tr>
</tbody>
</table>
than that in the bulk. However, the effects of rayon-based ACFs on the surface and in the bulk were rather consistent. It should be noted that, in Fig. 4b, the change in profile with progressive HTT observed on PAN-based fibers was very similar to that observed on rayon-based fibers, which indicates that N reactivity is independent of the fiber matrix. Consequently, within the XPS sampling depth, the N in the rayon-based ACFs was primarily located near the surface; but under HTT of 850 or 1100 °C, the surface N on both ACF-series would disappear at a rapid pace.

3.3.2. C 1s peak

The high-resolution XPS spectra of the C 1s region are illustrated in Fig. 5. Carbon atoms differ in their binding energies depending on whether they are linked to one O atom by a single bond, a double bond, or two oxygen atoms [11]. As with all carbons, the C 1s signals exhibited an asymmetric tailing, which was partially due to the intrinsic asymmetry of the graphite peak or to the contribution of oxygen surface complexes. Deconvolution of the C 1s spectra gives at most six individual component groups that represent graphitic carbon (CG1, 284.5 eV), and carbon present in phenol, alcohol, ether or C=N groups (CG2, 286.1–286.3 eV), carbonyl or quinine groups (CG3, 287.3 eV), carboxyl, lactone, or ester groups (CG4, 289.1 eV), carbonate groups (CG5, 290.6 eV), and plasmon or shake-up satellite peaks due to π–π* transitions in aromatic rings (CG6, 291.6 eV) [38].

Table 3 summarizes the calculated percentages of graphitic and functional carbon atoms. Besides graphitic carbon, phenolic, and carbonyl groups were the most predominant functionalities on the surface of the AW1108-series. Although carbonyl groups were the most abundant (19%) on as-received PAN-based fibers, their contents decreased with HTT. Many oxygen atoms were removed when AW1108 was heat-treated at 850 °C, which accounted for the highest content of graphitic carbons (86.9%) and the lowest amount of phenolic, carbonyl, and carbonate groups. Compared with AW1108-850, AW1108-1100 showed an increase in all oxygen-containing groups mentioned above on the surface, which could partially be attributed to the significant degradation of graphene layers. Corresponding to the complete decomposition of carboxyl groups, a very slight contribution of plasmon to the C 1s peak was observed on the surface of AW1108-600, which implies that the graphene structure behaved a bit unstable at 600 °C. The most abundant oxygen-containing groups on the surface of the AM1132-series were phenolic groups, with high intensities; while no carbonyl groups

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percent of total intensity</th>
<th>Percent of the intensity of [O]s</th>
<th>Binding energy (eV)</th>
<th>284.5 (CG1), graphite</th>
<th>286.1–286.3 (CG2), C–OH</th>
<th>287.3 (CG3), C=O</th>
<th>289.1 (CG4), C=O</th>
<th>290.6 (CG5), CO2, CO2</th>
<th>291.6 (CG6), plasmon (or π — π*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AW1108</td>
<td>100</td>
<td>100</td>
<td>66.2</td>
<td>12.0</td>
<td>19.0</td>
<td>1.82</td>
<td>1.03</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>AW1108-600</td>
<td>90.7</td>
<td>81.3</td>
<td>69.6</td>
<td>11.1</td>
<td>4.96</td>
<td>1.22</td>
<td>0.601</td>
<td>–</td>
<td>0.0828</td>
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<tr>
<td>AW1108-850</td>
<td>111</td>
<td>42.9</td>
<td>86.9</td>
<td>6.30</td>
<td>5.18</td>
<td>2.74</td>
<td>1.58</td>
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<td>–</td>
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<tr>
<td>AW1108-1100</td>
<td>107</td>
<td>62.8</td>
<td>80.1</td>
<td>10.4</td>
<td>5.43</td>
<td>1.47</td>
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</tr>
<tr>
<td>AM1132</td>
<td>93.9</td>
<td>105</td>
<td>62.2</td>
<td>30.3</td>
<td>–</td>
<td>5.43</td>
<td>2.06</td>
<td>–</td>
<td>–</td>
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<tr>
<td>AM1132-600</td>
<td>103</td>
<td>90.0</td>
<td>70.1</td>
<td>24.5</td>
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<td>3.34</td>
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<td>23.9</td>
<td>–</td>
<td>4.10</td>
<td>1.47</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>AM1132-1100</td>
<td>83.9</td>
<td>77.8</td>
<td>68.6</td>
<td>24.8</td>
<td>–</td>
<td>5.85</td>
<td>0.708</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

The total surface oxygen-containing functions [O]s include CG2, CG3, CG4, and CG5 groups.

* The value is normalized to the corresponding area of untreated AW1108 sample.

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Fig. 4. Relation between the relative mole ratio by XPS and the matrix composition by elemental analysis for AW1108- and AM1132-series samples. (a) O/C ratio and (b) N/C ratio.
were resolved. The variations in % intensity for most peaks in the AM1132-series showed patterns similar to the AW1108-series with HTT.

Total intensities of C 1s peak and [O]s for all samples are also displayed in Table 3, whereas the values, in percent, are normalized to the corresponding area of untreated AW1108 samples. [O]s is defined as the sum of the functional groups denoted by $C_{G2}$, $C_{G3}$, $C_{G4}$, and $C_{G5}$. As seen from the data, the intensity of C 1s in AW1108 was greater than that in AM1132, so was the graphite composition, which implies that the carbon purity of PAN-based ACFs was superior to rayon-based ones. Contrary to the amount of C 1s, the [O]s content of AM1132 was higher than that of AW1108, mostly coming from phenolic groups, which reveals that the surface basal structure of rayon-based fibers contained a higher density of oxygen. These situations remained even though the ACFs have been heat-treated. The data show extensively a progressive removal of surface oxides after heat treatment on both ACFs. The XPS analysis suggests that the surface oxides on the ACFs heat-treated at 600 °C would decompose from carboxyl groups into carbonate groups or result in the $\pi-\pi^*$ transitions in aromatic rings. After heating up to 850 °C, a large amount of oxygen atoms in AW1108 would evolve into air, probably in terms of the forms of CO or CO$_2$.

3.3.3. O 1s peak

To gain a better understanding of the results noted above, high-resolution O 1s spectra (Fig. 6) of the heat-treated ACFs, corresponding to binding energies between 522.5 and 542.5 eV, were compared with the corresponding spectra of as-received ACFs. The optimum curve fitting of the O 1s peak of all fibers
was achieved, and four different O functionalities as well as a contribution of chemisorbed water were identified, as reported in the studies of Zielke et al. [21,39]. The peak at 531.1 eV (OG1) corresponds to the carbonyl oxygen atoms; the peak at 532.3 eV (OG2) to the carbonyl oxygen atoms in esters, amides and anhydrides as well as oxygen atoms in hydroxyls or ethers; the peak at 533.3 eV (OG3) to the ether oxygen atoms in esters and anhydrides; and the peak at 534.2 eV (OG4) to the oxygen atoms in the carboxyl groups. The contribution of water was located at 536.1 eV (OG5), which was found in most cases, even with dried fibers. There were two additional small groups occurring in the deconvolution of O 1s spectra of AW1108-850 (at 526 eV, OG6) and AM1132-600 (at 528.1 eV, OG7), respectively. However, the interpretation of these two peaks is very difficult due to the paucity of appropriate literature data.

For both types of fibers, the intensity of O 1s spectra decreased promptly when heat-treated at 600 °C. After that the O 1s level changed with HTT and behaved erratically: PAN-based fibers hit the bottom at HTT of 850 °C; but the O 1s concentration on rayon-based fibers was removed continuously after heat treatment, with a smaller loss between 600 and 850 °C. The calculated percentages of functional O atoms are shown in Table 4. For PAN-based ACFs, the relative concentration of carbonyl groups (OG1) to the O 1s hit a peak at AW1108-850 (68.5%), which accounted for the dramatic drop in OG2 or the complete loss of OG3 and OG4 due to the removal of ether oxygen atoms in esters and anhydrides or the -OH in the carboxyl groups. Correspondingly, it resulted in an increase in chemisorbed water and the formation of an undefined peak at 526 eV. Compared with AW1108-850, AW1108-1100 showed an increase in the relative concentrations of OG2, OG3, or OG4, which agreed with the result obtained from the deconvolution of C 1s spectra. Results conclude that in PAN-based fibers the removal of carbonyl oxygen atoms in amides and oxygen atoms in hydroxyls or ethers has primarily occurred beginning at 600 °C; while that of ether oxygen atoms in esters and anhydrides and the -OH in the carboxyl groups...
Table 4
Results of the curve fitting of the O 1s region, values given in % of individual total intensity

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percent of total intensity</th>
<th>Percent of the sum of O_{G1}–O_{G4}</th>
<th>Binding energy (eV)</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>531.1 (O_{G1}), C=O</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>532.3 (O_{G2}), R−O−C=O, O=C−NH_{2}, O=C−O−C=O, C−OH, R−O−R</td>
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<td>533.3 (O_{G3}), C−OH, R−O−C=O</td>
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<td>534.2 (O_{G4}), O=C−O−C=O</td>
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<td></td>
<td></td>
<td>536.1 (O_{G5}), H_{2}O</td>
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<td>27.1</td>
<td>4.11</td>
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<tr>
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<td>118</td>
<td>39.2</td>
<td>21.7</td>
</tr>
<tr>
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<td>60.1</td>
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<td>50.6</td>
<td>51.1</td>
<td>15.9</td>
</tr>
<tr>
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<td>25.9</td>
<td>27.1</td>
<td>44.3</td>
<td>9.44</td>
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</table>

The value is normalized to the corresponding area of untreated AW1108 sample.

Generally, about 20–30% of chemisorbed water remained on the AW1108-series. In the AM1132-series, still the carbonyl groups (O_{G1}) were the most abundant functionalities. O_{G2} concentration decreased promptly after heat treatment and disappeared completely at 850°C, while a small rise was observed on AM1132-1100. A similar pattern of variation occurred in the carboxyl groups (O_{G4}), which became exhausted at 600 °C. However, the O_{G3} contribution to O 1s had a steady decrease with HTT. A relatively low concentration of chemisorbed water (2.78%) was observed on AM1132. However, the level increased significantly after heat treatment and there was a maximum on AM1132-850. As a result, the smaller surface O 1s concentration in AM1132 than in AW1108 could be attributed to weak chemisorbed water on the surface of rayon-based fibers. Excluding the chemisorbed

Fig. 7. High-resolution fitted N 1s spectra of the AW1108-series ACFs.
water from O 1s, the relative percentage was increased from 95.5% to 118% (column 3 in Table 4). These findings imply that C–OH and R–O–R functionalities were gradually removed beginning at 600 °C, resulting in a sudden rise in chemisorbed water (24.3%). The C–OH and R–O–R continued to disappear at 850 °C, though carboxyl groups appeared to be reincorporated on the surface. Similarly, the loss of carbonyl groups was observed at 1100 °C. As PAN-based carbon fibers had highly polar nitrile groups, the chemisorbed water (O_G5) concentration on AW1108 was about eight folds of that on AM1132. In addition, AM1132 had over two folds of carbonyl oxygen atoms in esters, amides, anhydrides, and oxygen atoms in hydroxyls or ethers (O_G2), which was because the basal units of rayon fibers contained a number of C–OH and R–O–R functionalities. According to the above reason and Table 3, the deconvolution between carbonyl oxygen atoms (O_G1) and carbonyl oxygen atoms in esters, amides, anhydrides, and oxygen atoms in hydroxyls or ethers (O_G2) probably had misleading.

3.3.4. N 1s peak

The high-resolution N 1s spectra for the AW1108-series (Fig. 7) and AM1132-series (Fig. 8) were obtained to identify the distribution of N functionalities by the curve-fitting procedures. Contrary to C 1s and O 1s spectra, the shape of N 1s profiles was relatively irregular. According to the existing literature data[9,40,41], the N 1s spectra were decomposed into seven identified components: the peak at 395.7 eV (N_G1) ascribed to nitride-like species or aromatic N-imines; the peak at 398.4 eV (N_G2) attributed to pyridine-like structures; the peak at 400.1 eV (N_G3) to the nitrogen atoms in pyrrolic or amine moieties; the peak at 401.2 eV (N_G4) containing a contribution from quaternary or protonated nitrogen; the peak at 402.4 eV (N_G5) to the nitrogen atoms in pyridine-N oxides; the peak at 404 eV (N_G6) attributed to shake-up satellites; and the peak at 405 eV (N_G7) ascribed to chemisorbed nitrogen oxides. There was one extra small group in the 393.7–394.4 eV region observed on AW1108-850, AM1132-600, AM1132-850, and AM1132-1100. Owing to limited literature information, it was very difficult to give a solid interpretation.

For the AW1108-series, the calculated percentages of functional N atoms (Table 5) indicated that pyridine-type N groups (N_G2) reached a plateau between 600 and 850 °C. However, an extensive decrease in unstable pyrrole or pyridone (N_G3) and shake-up satellites (N_G6) was observed as heat treatment was applied, responsible for an increase in pyridine-type N (N_G3), quaternary N (N_G4) and chemisorbed nitrogen oxides (N_G7). Once heat-treated at 850 °C, the chemisorbed nitrogen oxides would probably translate to pyridine-N oxides (N_G5) and thus result in shake-up satellites. This implies that when the carbon matrix was condensing, nitrogen atoms might be incorporated in the graphene layers replacing carbon atoms. The N 1s peak on as-received AM1132 was much weaker than that

Fig. 8. High-resolution fitted N 1s spectra of the AM1132-series ACFs.
on AW1108 due to their precursors; however, the data obtained from AM1132-600 and AM1132-850 revealed a significant rise in N 1s intensity. This rise came mostly from the presence of nitride-like species or aromatic N-imines (NG1), and an increase in chemisorbed nitrogen oxides (NG7). The levels for most N functionalities decreased after heat treatment, except for NG1 and NG7. Specifically, pyrrole or pyridone groups (NG3) have progressively decomposed with HTT on the AM1132-series, at a slower rate than that on the AW1108-series; and the shake-up satellites (NG6) even disappeared completely after heat treatment. It should be noted that a great increment in chemisorbed nitrogen oxides (NG7) was observed on rayon-based carbon fibers (AM1132-series) after heat treatment, which was supposed to incorporate and bond −NO2 into the graphene layers, in contrast to that on PAN-based fibers. Nevertheless, after heat treatment at 1100 °C, a majority of N atoms were eventually present in the six-member rings located at the edges of the graphene layers as pyridinic-N (NG2) where N is linked to sp2 carbon atoms, or in the interior as quaternary-N (NG4) where N is linked to three sp2 carbon atoms.

### 3.4. Adsorption characteristics

The uptakes of C6H6, CCl4, and H2O on as-received and heat-treated ACFs at the given condition are shown in Table 6. The correlation coefficients between the parameters of interest and the equilibrium adsorption amounts of C6H6, CCl4, and H2O on as-received and heat-treated ACFs were present by a polar plot in Fig. 9. In that the solid symbols represent a positive correlation, and the empty symbols denote a negative correlation; the directed distance from the origin indicates the absolute value of correlation coefficient. The BET surface area of as-received and heat-treated carbon fibers exhibited a positive medium-to-high correlation to gas adsorption. The total ash content was also positively medium-to-high-related to the adsorption amounts. The % intensity of C 1s was advantageous but that of O 1s was disadvantageous to CCl4 uptake. It should be noted that the elemental H composition was highly positive-associated with the H2O adsorption, which reveals that the existence of H atoms was prone to the adsorption of polar adsorbates due to hydrogen bonding.

The presence of the nitride-like species or aromatic N-imines (NG1) and chemisorbed nitrogen oxides (NG7) on the surface of

<table>
<thead>
<tr>
<th>Sample</th>
<th>AW1108-600</th>
<th>AW1108-850</th>
<th>AW1108-1100</th>
<th>AM1132-600</th>
<th>AM1132-850</th>
<th>AM1132-1100</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6H6 (5000 ppm)</td>
<td>34.5</td>
<td>33.8</td>
<td>29.6</td>
<td>36.0</td>
<td>40.1</td>
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<tr>
<td>CCl4 (8500 ppm)</td>
<td>43.8</td>
<td>66.7</td>
<td>81.0</td>
<td>69.1</td>
<td>79.8</td>
<td>101</td>
</tr>
<tr>
<td>H2O (55%)</td>
<td>35.8</td>
<td>27.9</td>
<td>21.2</td>
<td>33.8</td>
<td>56.0</td>
<td>50.3</td>
</tr>
</tbody>
</table>

Table 6

Equilibrium adsorption capacities of the activated carbon fiber samples
ACFs would be of benefit to the adsorption capacities of C6H6,
CCl4, and H2O. The H2O uptake increased with higher con-
tents of carbon present in phenol, alcohol, ether or C=N groups
(CG2). On the other hand, the pyridine-like N structures (NG2)
was strongly disadvantageous to the adsorption of C6H6 and
H2O, so was N shake-up satellites (NG6) to CCl4 adsorption.
The presence of the carbonate groups (CG5) and the ether oxygen
atoms in esters and anhydrides (OG3) on the surface was sup-
posed to hinder partially carbon fibers from C6H6 adsorption.
The CCl4 adsorption capacity was moderately deteriorated by
the existence of the carbonyl or quinine groups (CG3), the ether
oxygen atoms in esters and anhydrides (OG3) and the nitrogen
atoms in pyrrolic or amine moieties (NG3). As a result, the C
1s and O 1s present on the surface of the carbon fibers would
strongly control CCl4 adsorption. There seemed to be no strong
evidence supporting that C 1s and O 1s as well as associated
functionalities had an influence upon gas adsorption, the real effects of
individual N functional groups could be finally emerged after
spectra deconvolution. The N functionalities with complicated
or less stable molecular structures were speculated to prohibit
the adsorption. However, the presence of nitride-like species,
aromatic N-imines, or chemisorbed nitrogen oxides appeared to
be of benefit to the adsorption of water vapor or benzene. In
particular, the adsorption of water vapor was more accessible to
the rise in total ash content or in hydrogen composition. As a
result, the modifications in surface chemistry of ACFs by heat
treatment contribute effectively an improvement on adsorption
performance.

4. Conclusions

The results indicate that PAN-based fibers containing a higher
purity of carbon than rayon-based fibers had a much lower total
ash content. On the other hand, the change in total ash content
with HTT for each type of ACFs behaved relatively consistent
with their C atomic % obtained by elemental analysis. The vari-
ations in % intensity of XPS spectra implied the increase in
the degree of graphitization and the decrease in the O content
with progressive HTT, in that different types of O functional
groups removed at different temperatures. However, the composi-
tions of carbon–oxygen complexes identified from C 1s and O
1s spectra seemed not to correspond to each other very much.
After heat treatment, the variation of N percentages in the car-
bon matrix was similar to that on the surface. It should be noted
that extra N functionalities were supposed to introduce onto the
surface or incorporate into the interior of the carbon matrix at
600 ◦C. After heat treatment of 1100 ◦C most N atoms were
present at the edges of the graphene layers as pyridinic-N or
chemisorbed nitrogen oxides, and partly located in the inte-
rior as quaternary-N. The decrease in surface carbon–oxygen
complexes could improve the uptake of carbon tetrachloride.
In spite of no strong evidence supporting that N 1s or bulk N con-
tent had an influence upon gas adsorption, the real effects of
individual N functional groups could be finally emerged after
spectra deconvolution. The N functionalities with complicated
or less stable molecular structures were speculated to prohibit
the adsorption. However, the presence of nitride-like species,
aromatic N-imines, or chemisorbed nitrogen oxides appeared to
be of benefit to the adsorption of water vapor or benzene. In
particular, the adsorption of water vapor was more accessible to
the rise in total ash content or in hydrogen composition. As a
result, the modifications in surface chemistry of ACFs by heat
treatment contribute effectively an improvement on adsorption
performance.

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References

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