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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

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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 PAN-based

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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 I_2 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 polyacrylonitrile (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 (Brunauer, Emmett, and Teller) surface area of ca. $1100\,m^2\,g^{-1}$; 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 N_2 adsorption isotherms obtained by ASAP 2010 (V4.02), the AW1108-series samples yielded a BET surface area of 1110.3, 1209.2, 1227.3, and $1083.8\,m^2\,g^{-1}$, respectively; while the AM1132-series had a BET surface area of 1087.0, 1280.5, 1317.4, and $1307.8\,m^2\,g^{-1}$, 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