



# Influence of activation temperature on adsorption characteristics of activated carbon fiber composites

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## Abstract

In this work, the effect of activation temperature on adsorption properties of activated carbon fiber-reinforced phenolic resin matrix composites has been investigated. The composites were manufactured via a molding process with unwoven carbon fabrics and phenolic resin. The green body mold was heated at 125°C to cure the phenolic resin and they were carbonized in an inert environment at 1000°C for 2 h. They were then activated by CO<sub>2</sub> gas at 700, 800, 900 and 1000°C for 2 h, denoted as ACFC-700, ACFC-800, ACFC-900 and ACFC-1000. The specific surface area and the pore structure were evaluated from nitrogen adsorption data at 77 K, and the acid–base values on the surface were determined by titration methods. As a result, the activation temperatures had a major influence on adsorption characteristics and surface properties of the composites. © 2001 Published by Elsevier Science Ltd.

**Keywords:** A. Activated carbon; Carbon/carbon composite; C. BET surface area; D. Adsorption properties, Surface properties

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## 1. Introduction

Since their initial development for the aerospace and military aircraft industry, carbon fibers are receiving increasing interest from the high strength materials community due to their light-weight, high mechanical strength, fatigue endurance, thermal resistance and safety during a long life time. In recent years, activated carbon fibers (ACFs) have drawn great attention and are widely used in various fields, such as water treatment and the removal of toxic gases, due to their superior adsorption properties [1–3].

The structural properties of ACFs rely on them containing micropores in a significant proportion which in turn depends on the manufacturing process [4,5]. It is well known that the activation process is essential to high performance ACFs, and the activation conditions are largely considered as two different courses, depending on the nature of the raw materials used. The physical or thermal activation process is carried out at a temperature between 800 and 1000°C in the presence of suitable oxidizing gases such as steam, carbon dioxide, oxygen or

any mixture of these gases [6–9]. In the chemical activation process, the raw material is impregnated with the chemical activating agents such as phosphoric acid, sulfuric acid, or nitric acid, and consecutively pyrolyzed at a temperature between 400 and 600°C in the absence of air [10–12]. During activation, the enlargement of pore diameters and development of microporous structures are therefore introduced in the carbonized carbon, resulting in an increase of extremely large specific surface areas. Also, the functional groups of the carbon surface are created during the activation process, which results in adsorption selectivity for polar organic or inorganic adsorbates [13–17]. However, the constitution of surface functional groups of ACFs has not been clarified in periodicals and monographs.

Recently, development of a porous carbon monolithic composite material for on-board water recovery units include applications in both military and recreational vehicles and removal of volatile organic compounds (VOCs) with high flow rates and low VOCs concentrations was reported [18–22]. However, details of the composite manufacturing method and activation procedure are not yet known. It was claimed that ACFCs possess an open internal structure, which presents little resistance to the flow of fluids, and allows direct access of contacting fluid

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to the surface of the composites. Consequently, they offer a potential solution to the problems of removing VOCs diluted in a large volume of air. Also, the composites are used in catalytic support and other industrial applications requiring high strength and corrosion resistance materials in severe conditions [23–25].

In this work, we study the influence of activation temperature on structural properties, such as specific surface area and porosity by burn-off and on surface properties, such as pH and acid–base value of the activated carbon fiber composites (ACFCs) prepared from mixtures of oxidative PAN-based carbon fabrics and phenolic resin binder.

## 2. Experimental

### 2.1. Sample preparation

The composites used for preparing activated carbon fiber composites were manufactured via a molding process with oxidized PAN-based carbon fabric (plain type) and phenolic resin (resole-type) at a ratio of 7:3 by weight. After curing the composites by following steps in Fig. 1, they were carbonized in an inert environment at 1000°C for 2 h and then activated by CO<sub>2</sub> gas at a heating rate of 5°C min<sup>-1</sup> to each temperature of 700, 800, 900 and 1000°C for 2 h. The CO<sub>2</sub> flow rate was maintained at 30 ml min<sup>-1</sup> by means of a metering valve and measured using calibrated rotameters. The composites were denoted as ACFC-700, ACFC-800, ACFC-900 and ACFC-1000 with respect to the activation temperatures.

### 2.2. Surface area and pore structure

Specific surface areas and pore structures of each sample were measured by nitrogen gas adsorption at 77 K using ASAP 2400 instrument from BET-method [26]. Prior to analysis, the sample was out-gassed at 298 K for 6 h to obtain a residual pressure of less than 10<sup>-3</sup> Torr. The pore size distribution involved subdividing the adsorbed amount

in the range of the relative pressure ( $P/P_0$ ), 0–0.05, 0.05–0.30 and 0.30–0.90, corresponding broadly to adsorption in micropores, mesopores, and macropores or external surface, respectively. The amount adsorbed was converted to liquid volume by assuming a molar volume of liquid nitrogen of 35 cm<sup>3</sup> mol<sup>-1</sup>.

### 2.3. Iodine adsorption capacity

Iodine adsorption capacity represents the number of milligrams of adsorbed iodine per gram of dried carbon adsorbent. Common to all procedures, weighed quantities of each sample were shaken with measured quantities of KI/I<sub>2</sub> solutions in stoppered flasks. After filtering off the ACFCs, the filtrate was titrated with standard sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) solution. Change in total I<sub>2</sub> content divided by the sample weight gave the amount adsorbed at each filtrate concentration. For the iodine adsorption capacity, about 0.1, 0.3, 0.5 and 1.0 g of each sample was accurately weighed and 50 ml of 0.1 N iodine solution was added. They were then filtrated after 15 min vibrating at room temperature, and the residual iodine concentration was determined by 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> titration. The iodine number is defined as the amount of iodine adsorbed in mg g<sup>-1</sup> when the equilibrium concentration is 0.02 N total iodine, hence the ACFCs weight must be selected to bring the final concentration near 0.02 N [27].

### 2.4. Surface properties

The surface pH of ACFCs was measured according to the ASTM D 3838. About 1.0 g of each sample was added to 20 ml distilled buffer solution (pH 7.0, 25°C), and the mixture was shaken for 12 h. The pH was measured after filtration with a nylon membrane filter (0.45 µm in diameter).

The acid and base values on the surface were determined by Boehm's titration technique [28]. In the case of an acidic value, about 1.0 g of sample was added to 100 ml of 0.1 N NaOH solution and shaken for 24 h. After filtration with a nylon membrane filter (0.45 µm in

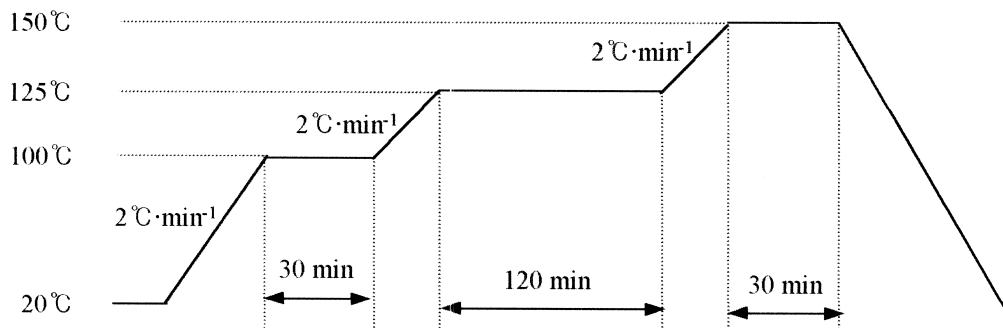


Fig. 1. Curing process of ACFC.

diameter), the mixture was titrated with 0.1 *N* HCl standard solution, using 0.01 *M* phenolphthalein solution as indicator. Likewise, a basic value was determined by converse titration.

### 3. Results and discussion

#### 3.1. Adsorption surface and pore structures

The adsorption surface characteristics of the ACFCs are listed in Table 1, which shows that the specific surface area and porous texture are well developed with increasing activation temperature. For the ACFC-700, specific surface area is very small being almost identical with the geometric surface area. This discrepancy can be attributed to an activated diffusion effect associated with a slow diffusion of adsorbate molecules through very narrow pore entrances or constrictions.

Fig. 2, shows the variation in burn-off of ACFC-series as a function of activation temperature. The weight loss was determined from a change in weight before and after activation. At elevated temperatures, carbon monoxide is produced by reaction of the carbon constituent in the carbonized fiber and phenolic resin reacted with carbon dioxide, which leads to a decrease in the weight of resultant activated carbon fiber composites.

The specific surface areas for ACFC studied have been plotted as a function of burn-off value, as seen in Fig. 3. For activated carbon fiber composites made of the sample carbonized at 1000°C, the surface areas were just below 600 m<sup>2</sup> g<sup>-1</sup> at about 58% burn-off. For the activation temperatures, the specific surface area is decreased. This ACFC-1000 result indicates that the low surface area is attributed to the formation of new graphite basal planes and the refilling of the pores developed by the attack of carbon dioxide during activation of the carbonized fiber.

The adsorption isotherms of ACFCs for N<sub>2</sub> gas at liquid N<sub>2</sub> temperature were shown in Fig. 4. All of the isotherms have two characteristic regions; one below the relative

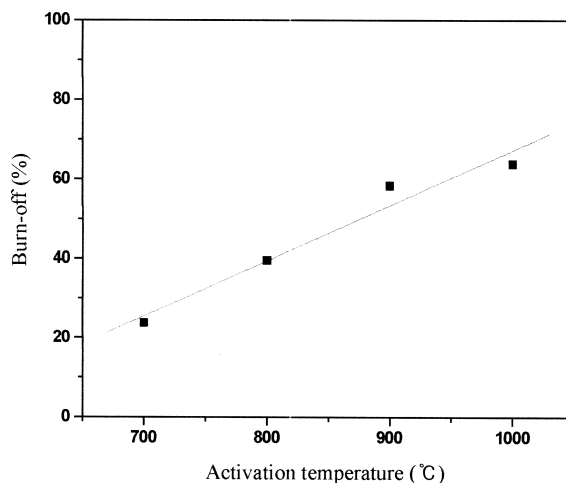


Fig. 2. Burn-off of activated carbon fiber composites with increasing activation temperature.

pressure ( $P/P_0 < 0.05$ ), where a substantial increase of the adsorbate uptake is observed with increasing  $P/P_0$ . This is indicative of microporosity in all samples. While, at  $P/P_0$  values larger than about 0.05, very little gas adsorbed with increased relative pressure indicated that minimal meso- or macropore structure in the ACFCs studied. For ACFCs, the isotherms are of Type-I according to the BET classification, with little adsorption occurring at  $P/P_0$  above 0.05, and the adsorption processes are reversible.

The development of a pore structure of ACFCs studied with activation temperature was shown in Fig. 5. With increasing activation temperature, the average pore diameter of samples decreases, as expected. Apparently, the PAN fibers are not very reactive to CO<sub>2</sub> at 700°C, but are consumed readily with increasing activation temperature.

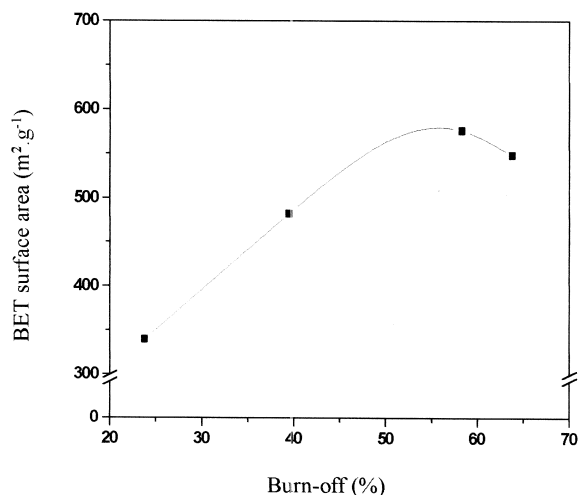


Fig. 3. Specific surface area vs. burn-off of activated carbon fiber composites.

Table 1

Adsorption characteristics of ACFCs with different activation temperature

Samples	I.N. <sup>a</sup> (mg g <sup>-1</sup> )	<i>S</i> <sub>BET</sub> <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	<i>V</i> <sub>T</sub> <sup>c</sup> (cm <sup>3</sup> g <sup>-1</sup> )	<i>D</i> <sub>p</sub> <sup>d</sup> Å
ACFC-700	376	340	0.26	28.5
ACFC-800	517	482	0.29	24.2
ACFC-900	605	576	0.34	17.6
ACFC-1000	562	548	0.30	19.2

<sup>a</sup> Calculated with linear plotted at residual iodine=0.02 *N* in Fig. 7.

<sup>b</sup> Specific surface area determined from BET-method.

<sup>c</sup> Total micropore volume from α<sub>s</sub>-method.

<sup>d</sup> Average pore diameter.

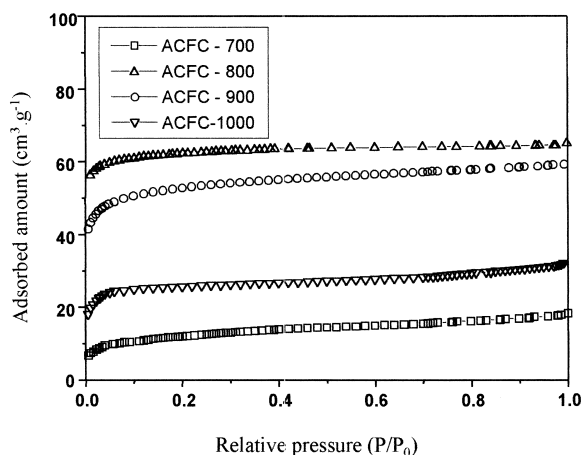


Fig. 4. Isothermal  $N_2$  gas adsorption of activated carbon fiber composites studied.

The increase in both specific surface area and total pore volume, combined with a very slight decrease in pore diameter, suggest that  $CO_2$  activation did not etch the fiber. The large number of micropores in ACFCs seems reasonable because the fibril structures of PAN fiber are conducive to large pore volumes. The typical diameter size in PAN fibers is around 5–10  $\mu m$ . From the extensive folding and fibril nature of these crystals, there are likely to be a large fraction of micropores less than 20 Å, confirmed by Fig. 5.

Moreover, the S.E.M. examination in Fig. 6 reveals a substantial decrease in some fiber diameters, indicating that the fibers are consumed readily by a process of gasification of their external surface. These results show that the ACFCs are gasified under conditions where diffusion of  $CO_2$  to the fiber exterior and through the pore

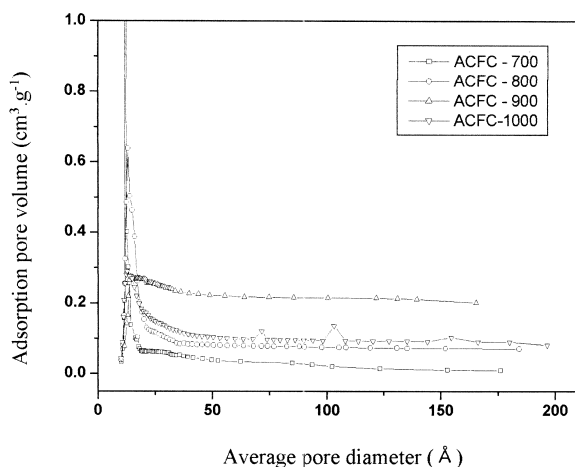


Fig. 5. Pore volume distribution of activated carbon fiber composites as a function of activation temperature.

structure as well as inhibition by carbon monoxide affect the rate and the development of micropore texture. Although, the contribution of the pores, of mesopore size, to the total surface area was small, these results suggest the implication of obtaining the mesoporous activated carbon fiber composites by controlling the preparation conditions. With further burn-off, the fiber itself is consumed, thus destroying the pore structure. Following the above reaction from the periphery of the fiber to its core, increasing the fiber loss weight, the total volume of pores being created or developed is reduced.

### 3.2. Iodine adsorption properties

Fig. 7 presents the isothermal adsorption, and the iodine number is found to correlate with carbon surface area of pores larger than 10 Å in diameter. In view of the results of this study, it appears that the amount adsorbed at 0.02  $N$  (0.11 mmol  $l^{-1}$  free iodine) is a fractional part of the saturation capacity. Also, the limitation on surface area of pores greater than 10 Å diameter is a compensating factor which accounts for the steric hindrance effect, i.e., in aqueous phase adsorption, the KI apparently hinders pore filling by the iodine, hence surface adsorption occurs primarily. Further, the molecules have more than normal void volume between them, such as occurs when rigid spheres are packed into relatively small cylinders.

### 3.3. Surface properties

The variation of surface properties for activated carbon fiber composites with different activation temperatures is shown in Table 2. The results of the Boehm's titration shows that surface natures of ACFC-700 and ACFC-800 are amphoteric with slight acidic properties, whereas ACFC-900 and ACFC-1000 have basic properties, respectively. This is probably due to the existence of surface functional groups by the activation temperatures. When the activation temperature was lower than 800°C, the carbon-oxygen surface complexes formed are less stable and develop acid surface functional groups which are hydrophilic in character. On the other hand, the activated carbon fiber composites activated at higher temperatures (above about 800°C) develop basic surface functional groups due to surface carbon-oxygen resonance structure which is more stable and forms the electron pair donor structure. Also these results indicate that the acid and base values are largely depended on pH of the activated carbon fiber composites measured.

## 4. Conclusion

The ACFCs showed different specific surface area, porosity and surface nature, depending on the activation temperature. The evolution of pore size, pore volume and

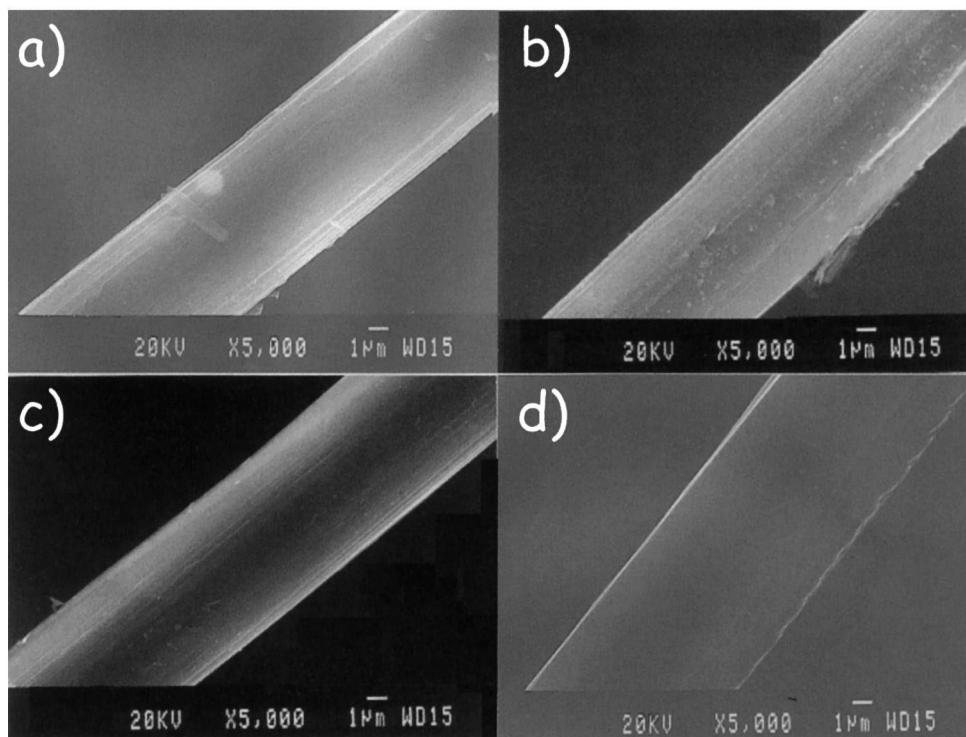


Fig. 6. S.E.M. photographs of activated carbon fiber composites with activation temperature: a, ACFC-700; b, ACFC-800; c, ACFC-900; d, ACFC-1000.

specific surface area could be easily observed in increasing the burn-off with activation temperature. Among them, the ACFC-900 produced the well-developed pore structure from adsorption characteristics. The pore structures were developed by gasification of the pore walls of the resin in increasing micropore volume. A marginal decrease of the

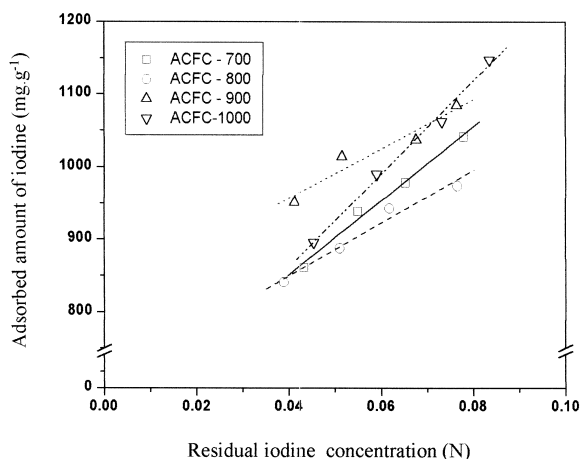


Fig. 7. Isothermal iodine adsorption properties of activated carbon fiber composites.

Table 2  
Surface properties of ACFCs studied

Samples	pH	Acid value mequiv g <sup>-1</sup>	Base value mequiv g <sup>-1</sup>
ACFC-700	6.8	180	90
ACFC-800	6.9	135	70
ACFC-900	7.2	80	55
ACFC-1000	7.4	65	50

BET surface area was observed in this activation system. The activation temperature also influenced the surface nature of the ACFCs. When the temperature was less than 800°C, the surface developed acidic properties, but was basic when greater than 900°C.

## References

- [1] Donnet JB, Bansal RC. In: Lewin M, editor. Carbon fibers, Vol. 5, New York: Marcel Dekker, 1990, pp. 259–60.
- [2] Suzuki M. Activated carbon fiber: Fundamentals and applications. Carbon 1994;32:577–86.
- [3] Donnet JB, Qin RY, Park SJ, Ryu SK, Rhee BS. Scanning tunnelling microscopy study of activated carbon fibres. J Mater Sci 1993;28:2950–4.

- [4] Merraoui ME, Tamai H, Yasuda H, Kanata T, Mondori J, Nadai K, Kaneko K. Pore structures of activated carbon fibers from organometallics/pitch composites by nitrogen adsorption. *Carbon* 1998;36:1769–76.
- [5] Park SJ, Kim KD. Influence of activation temperature on surface structure changes and adsorption properties of PAN-based carbon fibers. *Polymer (Korea)* 1998;22:994–8.
- [6] Blanco-López MC, Martínez-Alonso A, Tascón JMD.  $N_2$  and  $CO_2$  adsorption on activated carbon fibres prepared from Nomex chars. *Carbon* 2000;38:1177–82.
- [7] Li Z, Kruk M, Jaroniec M, Ryu SK. Characterization of structural and surface properties of activated carbon fibers. *J Colloid Interface Sci* 1998;204:151–6.
- [8] Shigeno Y, Evans JW, Yoh I. Infiltration of microporous activated charcoal by pyrolysis of  $CH_4$  and its effect on enhancement of resistance against oxidation. *ISIJ International* 1997;37:733–47.
- [9] Lebeda R, Skubiszewska-Zięba J, Bogillo VI. Influence of gasification catalyzed by calcium and steam activation on the porous structure of activated carbons. *Langmuir* 1997;13:1211–7.
- [10] Benaddi H, Bandosz TJ, Jagiello J, Schwarz JA, Rouzaud JN, Legras D, Béguin F. Surface functionality and porosity of activated carbons obtained from chemical activation of wood. *Carbon* 2000;38:669–74.
- [11] Evans MTB, Halliop E, MacDonald JAF. The production of chemically-activated carbon. *Carbon* 1999;37:269–74.
- [12] Ahmadpour A, King BA, Do DD. Comparison of equilibria and kinetics of high surface area activated carbon produced from different precursors and by different chemical treatments. *Ind Eng Chem Res* 1998;37:1329–34.
- [13] Bansal RC, Donnet TB, Stoeckli F. In: *Active carbon*, New York: Marcel Dekker, 1988, pp. 1–26.
- [14] Lahaye J. The chemistry of carbon surfaces. *Fuel* 1998;77:543–7.
- [15] Tessmer CH, Vidic RD, Uranowski LJ. Impact of oxygen-containing surface functional groups on activated carbon adsorption of phenols. *Environ Sci Technol* 1997;31:1872–8.
- [16] Menendez JA, Phillips J, Xia B, Radovic LR. On the modification and characterization of chemical surface properties of activated carbon: In the search of carbons with stable basic properties. *Langmuir* 1996;12:4404–10.
- [17] Park SJ, Donnet TB. Evaluation of distribution function of adsorption site energies based on the Fermi–Dirac’s Law in a monolayer. *J Colloid Interface Sci* 1997;188:336–9.
- [18] Derbyshire F. Activation and micropore structure determination of carbon fiber composite molecular sieves. In: 8th annual fossil energy materials conference, Tennessee, USA: Oak Ridge National Laboratory, 1994, pp. 137–43, Extended abstracts.
- [19] Klett JW, Burchell TD. Carbon fiber carbon composites for catalyst supports. In: 22nd biennial conference on carbon, UC San Diego, California, USA, American Carbon Society, 1995, pp. 124–5, Extended abstracts.
- [20] Gadkaree KP, Jaroniec M. Pore structure development in activated carbon honeycombs. *Carbon* 2000;38:983–93.
- [21] Lee JC, Park MJ. Effect of hold time on reaction of silicon monoxide with activated carbon fiber composites. *Carbon* 1999;37:1075–80.
- [22] Lee JC, Lee BH, Kim BG, Park MJ, Lee DY, Kuk IH, Chung H, Kang HS, Lee HS, Aim DH. The Effect of carbonization temperature of PAN fiber on the properties of activated carbon fiber composites. *Carbon* 1997;35:1479–84.
- [23] Matsuo T, Nishi T. Activated carbon filter treatment of laundry waste water in nuclear power plants and filter recovery by heating in vacuum. *Carbon* 2000;38:709–14.
- [24] Liang C, Sha G, Guo S. Carbon membrane for gas separation derived from coal tar pitch. *Carbon* 1999;37:1391–7.
- [25] Imamura R, Matsui K, Ozaki J, Oya A. Ammonia deodorization ability of activated carbon fibers prepared from phenolic resin incorporating phosphorus in the network structure. *Carbon* 1999;37:997–9.
- [26] Brunauer S, Emmett PH, Teller E. Adsorption of gases in multimolecular layers. *J Am Chem Soc* 1938;60:309–19.
- [27] Juhola AJ. Iodine adsorption and structure of activated carbons. *Carbon* 1975;13:437–42.
- [28] Boehm HP, Diehl E, Heck W, Sappok R. Oberflächenoxyde des Kohlenstoffs. *Angew Chem* 1964;76:742–51.