Printed in the Republic of Korea
ANALYTICAL SCIENCE & TECHNOLOGY
Vol. 20, No. 4, 296-301, 2007

Surface analysis of rayon-based carbon nanofibers and activated carbon fibers

Youn Jung Kim[1], Sang Hoon Ryu[2], Woo Taik Lim[1] and Sik Young Choi[1]★

[1]Department of Applied Chemistry, Andong National University, # 388 Songcheondong, Andong 760-749, Korea
[2]Center for Scientific Instruments, Andong National University, # 388 Songcheondong, Andong 760-749, Korea
(Received June 21, 2007; Accepted June 28, 2007)

레이온을 이용한 카본나노섬유와 활성카본섬유의 표면 특성분석

김연정[1] · 류상훈[2] · 임우택[1] · 최식영[1]★

[1]안동대학교 응용화학과, [2]안동대학교 공동실험실습관
(2007. 6. 21. 접수. 2007. 6. 28. 승인)

요 약: 카본 나노섬유(CNFs)는 높은 비표면적(100~200 m^2/g)과 순도를 갖는 물질로서 2 nm 이하의 기공을 형성하지 않는 물질이다. 그러므로 이 물질은 촉매 지지체로서의 활용 가치가 우수한 물질이다. 활성 카본섬유(ACFs)는 첨단기술 산업 분야의 유독가스 제어에 많이 이용되어지고 있다. 레이온을 이용한 카본 나노섬유(CNFs)와 활성 카본섬유(ACFs)는 소재 표면에 다양한 온도와 공기량을 조절함으로서 열적 산화 방법인 열화학을 이용하여 제조하였다. 카본 나노섬유(CNFs)는 공기 주입 상태에서 600 °C 이상으로 반응시켰으며, 온도와 공기량을 점차적으로 증가시키면서 카본 나노섬유(CNFs)을 성장시켰다. 활성 카본섬유(ACFs)는 800 °C 상에서 72시간 반응시켜, 2,662 m^2/g (BET)의 비표면적과 1.41 cm^3/g의 부피를 갖는 소재를 제조하였다. 이와 같은 방법으로 제조된 활성 카본섬유(ACFs)는 기공크기가 10 nm이하 되는 비표면적이 전체 표면적의 99 %을 차지 하며, 2 nm 이하 되는 비표면적이 전체 표면적의 60 %을 차지 하였다.

Abstract: Carbon nanofibers (CNFs) are non-microporous materials with a high surface area (100~200 m^2/g) and high purity. Therefore, the material has a high potential for use as catalyst support. Activated carbon fibers (ACFs) are of increasing concern with regard to the levels of toxic air pollutants emitted from high-technology industry. Rayon-based CNFs and ACFs was subjected to thermal oxidation under a wide variety of temperature and air conditions to modify the surface properties. Rayon-based CNFs and ACFs were prepared by using thermal chemistry. CNFs were synthesized at temperatures above 600 °C in an air atmosphere and grew with increased temperature and air conditions. After heating at 800 °C for 72 hr, carbonized rayon with ACFs had 2,662 m^2/g (BET) of surface area and 1.41 cm^3/g of pore volume. The resulting ACFs had a 99 % surface area in which pore size was 10 nm or less, and a 60 % surface area in which pore size was 2 nm or less.

Key words: Activated carbon fibers, carbon nanofibers, rayon

★ Corresponding author
Phone : +82-(0)54-820-5457, 5674 Fax : +82-(0)54-822-5452
E-mail: sychoi@andong.ac.kr

www.kci.go.kr

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 lowered permissible limits. Activated carbon fibers (ACFs), which are fibrous carbon materials with imperfect graphite crystalline structure arranged along the fiber axis, have been widely used in adsorption processes to solve the problems described above.[1] ACFs are better than granular activated carbons which have surface area of 800~1,200 m^2/g (BET), in terms of the adsorption capacity of organic compounds and the high adsorption efficiency.[2-4] Commercial ACFs are generally prepared from various organic material such as polyacrylonitrile (PAN), rayon, and resins.

This adsorbent is prepared from natural or synthetic raw material, with the precursor having an impact on surface groups and pore-size distribution.[5,6] The raw material is carbonized in a temperature range of 800~1,000 °C in order to remove the non-carbonaceous components and to develop a limited porous volume.[1-4] The carbonaceous material is then reacted with steam or CO_2 at 800~1,200 °C in order to increase its specific surface area, up to 2,000 m^2/g, and its porous volume.[7] Activated fibers are highly microporous materials which have micropores directly connected to the external surface and diameters ranging from 5 to 21 Å.[8,9] Micropores dominate in activated carbon fiber, which exhibits a higher adsorption capacity and faster adsorption kinetics than granular activated carbon (GAC). Furthermore, ACFs are easier to use than GAC since they can be manufactured in various forms: cloth, felt, etc. Consequently, ACFs are more suitable for use as an adsorbent for the removal of indoor VOC.[10,11]

The preparation of rayon-based carbon fiber by thermal activation involves the thermal decomposition of the organic material with the porosity later being developed by reaction with carbon dioxide or steam.[12-17] In the particular case of viscous rayon, the carbonization (pyrolysis) of the organic material produces a loss of around 82 % of the original weight and a considerable loss in flexibility and strength. An alternative route to the preparation of activated carbon cloth from viscous rayon can be chemical activation, consisting of the impregnation of the material with chemicals to alter the course of pyrolysis.

Carbon fibers can be produced essentially from three organic materials: rayon, polyacrylonitrile (PAN), and pitch (isotropic or anisotropic). Bacon and Smith determined mechanical properties heat treated at 1,900 °C for 5 min. in the temperature range of 20 °C~1,900 °C for a rayon-based carbon fiber (VYB105 and VYB70 from Union Carbide Corp.).[18] Mostovoi *et al*. measured the mechanical properties of a PAN-based carbon fiber (VMN-RK high temperature carbon fiber) in the temperature range of 20~2,000 °C. Tanabe *et al*. examined a pitch-based carbon fiber (HM 70 from Petoca Co.) in the temperature range of 20~1,300 °C.[19,20] The majority of studies tests only one fiber at each temperature. The reaction times have not been sufficiently studied. Furthermore, the conditions of an air atmosphere at high temperatures was not investigated nor discussed with respect to structural features.

The aim of the present study is to discuss the effects of different chemicals on the pyrolysis of rayon and to characterize the resulting rayon surfaces. The growth and the specific surface area of rayon-based CNFs and ACFs were studied with regard to reaction temperature and reaction time, respectively. Especially, rayon-based carbonized condition was then reacted without steam or CO_2 at 800 °C in order to increase its specific surface area up to 2,000 m^2/g. This work was done for the further environmental studies.

2. Experimental

The rayon fabric was supplied by Acordis Ltd. (Netherlands) with fiber diameters from 7 to 10 μm. The samples were heat-treated in a horizontal tubular furnace equippedwith a gas flow control system, quartz chamber, and thermocouples. About 1 g of

www.kci.go.kr

sample was used in each batch. The heat treatment was carried out at 600, 700, 800 and 900 °C for 2 hr with a direct temperature in 400 cc air atmosphere. After heat treatment, the samples were cooled in flowing nitrogen gas until they reached ambient temperature. A Specific Surface Area Analyzer (ASAP 2010, USA) was used to measure nitrogen adsorption isotherms at -196 °C in the relative pressure (p/p_0) range of 0.06 to 0.2. Before measurement, all samples were degassed at 300 °C for 8 hr and then high-purity (99.99%) nitrogen was used in the measurement. The specific surface area of the samples were evaluated using the standard BET method.[21,22] The morphologies of the synthesized CNF and ACF materials were imaged using a Field Emission Scanning Electron Microscope (FE-SEM, JSM-6700F, Japan). The experimental conditions are shown in *Table* 1.

Table 1. Experimental conditions for reaction and synthesis

Variables	Conditions
Reaction temperatures and time	Carbonization : 500 °C, 1 hr CNFs : Over 600 °C, 2 hr ACFs : 800 °C, 2~72 hr
Sample weight	1.00 g

3. Results and Discussion

3.1. Rayon-based carbon nanofibers (CNFs)

Fig. 1 shows the FE-SEM photographs of Rayon-based CNFs thermally treated for 2 hr at 500, 600, 700, and 800 °C. CNFs were synthesized on the rayon surface at temperatures over 600 °C. The size of the CNFs was relatively uniform (40 nm). The length of CNFs increased with higher temperatures. It is interesting to note temperature influences the length of the CNFs for samples heated for the same

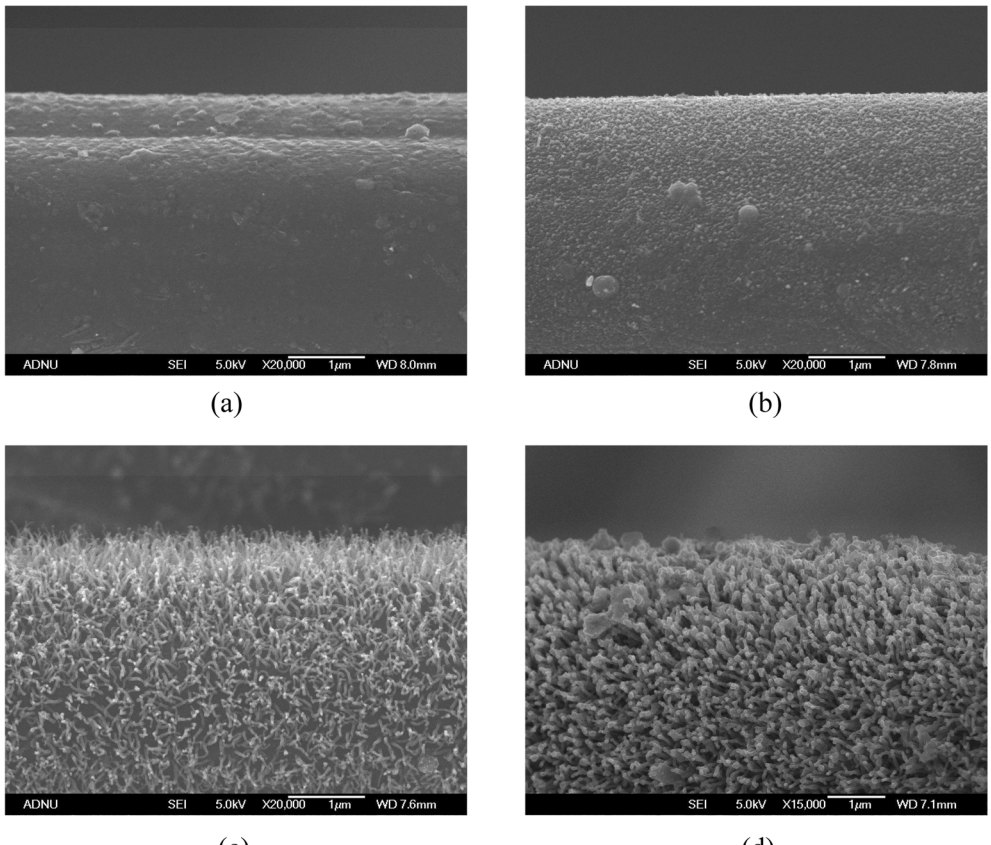

Fig. 1. The morphologies of carbon nanofibers heated at 500 °C (a), 600 °C (b), 700 °C (c) and 800 °C (d) for 2 hr.

www.kci.go.kr

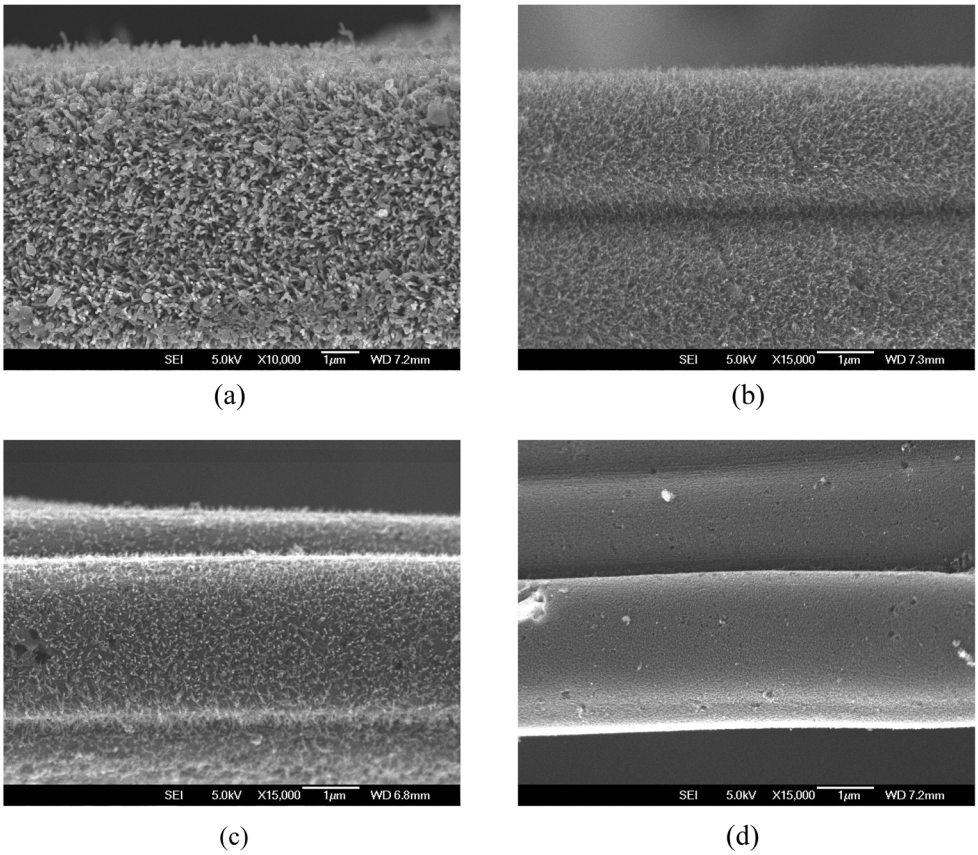

Fig. 2. The morphologies of active carbon fibers heated from 2 hr to 72 hr at 800 °C (a) 2 hr, (b) 24 hr, (c) 48 hr and (d) 72 hr.

400 cc air atmosphere in 1 g of rayon sample.

3.2. Rayon-based activated carbon fibers (ACFs)

The surface morphologies of the rayon based ACFs samples are shown in *Fig.* 2. The diameter of ACFs was in the range of 5~10 μm with some CNFs onthe surface. The presence of the CNFs was not favorable to the formation ofstructures with a high surface area because the microporous area was induced within the rayon fibers. The surface of the rayon treated at 800 °C for 2 hr was covered with CNFs with a diameter of 40 nm. However CNFs were not observed on the rayon treated at 800 °C for 72 hr. Only nano-scaled pores were observed on this surface. For longer reaction times at 800 °C, the microporous area increased but CNFs decreased. An increase of reaction time lead to the improvement of the activation in ACFs.

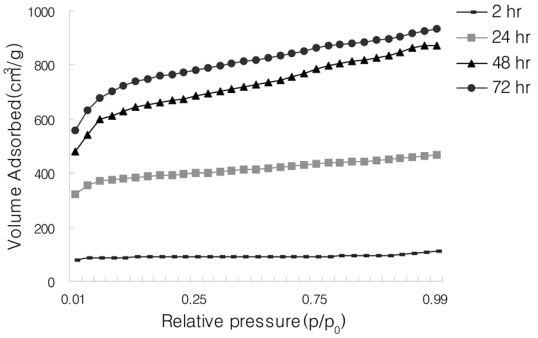

Fig. 3. Nitrogen adsorption isotherms of ACFs 2 hr to 72 hr at 800 °C.

3.3. Nitrogen adsorption isotherms and surface composition of ACFs

The nitrogen adsorption isotherm is a standard tool for the characterization of porous materials. Valuable

www.kci.go.kr

Table 2. Porous structure parameters of the thermal-treatment samples

Sample	S_{BET}[a] (m^2/g)	S_{mic}[b] (m^2/g)	V_t[c] (cc/g)	V_{mic}[d] (cc/g)
800°C-2hr	303	265	0.16	0.12
800°C-24hr	1336	1046	0.71	0.48
800°C-48hr	2320	1389	1.33	0.63
800°C72hr	2662	1793	1.41	0.81

[a]Standard specific surface area. [b]Micropore (less than 2 nm) area. [c]Total pore volume. [d]Micropore (less than 2 nm) volume.

information about the surface area, pore structure of adsorbent, and heat of adsorption can be determined from the adsorption isotherm.[23] Nitrogen adsorption isotherms of the rayon-based ACFs samples measured at -196 °C are presented in *Fig.* 3. All samples exhibit a type I isotherm according to IUPAC classification[24] which shows that the dominant pores in these samples are micropores. All samples show high volume adsorbed at low press (p/p_0), that means to develop micropore area. The 800 °C-72 hr sample was developed in the highest micropore area.

The porous structure parameters of the thermal-treated samples under study are listed in *Table* 2. The specific surface area and the total pore volume of the thermal-treated samples at 800 °C improved significantly with reaction times, but the CNFs decreased as shown in *Fig.* 2. This showed that the surface area was related on rayon fibers. From these results, it can be seen that ACFs also formed inside the rayon fibers. The total pore volume of the 800 °C-72 hr sample was 8.8 times that of the 800 °C-2 hr sample. The microporous surface area of the 800 °C-72 hr sample was 6.8 times that of the 800 °C-2 hr sample. Porous structure parameters of the all samples were alsoin accordance with their nitrogen adsorption isotherms.

4. Summary

In this study, we have described interesting CNFs growth and ACFs on rayon. The CNFs and ACFs were subjected to thermal treatment under a wide variety of conditions to modify the surface properties. CNFs were observed at temperatures above 600 °C for 2 hr. The average diameter of the CNFs was 40 nm. An increase in the reaction time at 800 °C was found to enhance surface area and micropore volume. In conclusion, CNFs and ACFs have been produced through thermal-treatment methods of rayon at 600~800 °C. The formation and growth of CNFs was usually dependant upon conditions such as temperature and air control. Using rayon ACFs were fabricated with a high specific surface area in which 99 % of the pore size range was less than 10 nm.

Acknowledgement

This work was supported by a grant from 2004 Special Research Grant of Andong National University, grant number 2004-0185.

References

1. R. Bacon and W. H. Smith, *Extended abstracts In Conference on Industrial Carbon and Graphite London*, **2**, 203-21 3(1965).
2. P. R. Anderson and H. J. Fan, *Separation and Purification Technology*, **45**, 61-67 (2005).
3. N. Diban, G. Ruiz, A. Urtiaga and I. Ortiz, *Journal of Food Engineering*, **78**, 1259-1266 (2007).
4. V. Marinovic, M. Ristic and M. Dostanic, *Journal of Hazardous Materials*, **117**, 121-128 (2005).
5. G. E. Mostovoi, N. N. Dergunov, Y. N. Rabotnov and Y. P. Anufriev, *Mekh. Polim.*, **4**, 626-630 (1977).
6. Y. Tanabe, E. Yasuda, A. R. Y. Bunsell, M. Favry, Inagaki and M. J. Sakai, *Mater. Sci.*, **26**, 1601-1604 (1991).
7. Z. H. Huang, F. Kang, Y. P. Zheng, J. B. Yang and K. M. Liang, *Carbon*, **40**, 1363-1367 (2002).
8. A. C. Pastor, F. Rodrìguez-Reinoso, H. Marsh and M. A. Martìnez, *Carbon*, **37**, 1275-1283 (1999).
9. Z. H. Huang, F. Kang, K. M. Liang and J. Hao, *Journal of Hazardous Materials*, **98**, 107-115 (2003).
10. Z. H. Huang, F. Kang, Y. P. Zheng, J. B. Yang and K. M. Liang, *Carbon*, **40**, 1363-1367 (2002).
11. F. Feng Li and J. Niu, *Atmospheric Environment*, **41**,

www.kci.go.kr

2344-2354 (2007).
12. Q. L. Wu, S. Y. Gu, J. H. Gong and D. Pan, *Synthetic Metals*, **156**, 792-795 (2006).
13. J. K. Park, D. H. Cho and T. J. Kang, *Carbon*, **42**, 795-804(2004).
14. G. Pan, N. Muto, M. Miyayama and H. J. Yanagida, *Mater. Sci.*, **27**, 3497-3501 (1992).
15. H. A. Katzman, P. M. Adams, T. D. Le and C. S. Hemminger, *Carbon*, **32**, 379-391 (1994).
16. L. Zhao and B. J. Jang, *Mater. Sci.*, **30**, 4535-4540 (1995).
17. L. Zhao and B. J. Jang, *Mater. Sci.*, **32**, 2811-2819 (1997).
18. C. Sauder and J. Lamon, *Carbon*, **42**, 715 (2004).
19. Z. Ma, J. Shi, Y. Song, Q. Guo, G. Zhai and L. Liu, *Carbon*, **44**, 1298-1352 (2006).
20. F. Y. I. Mochida and Y. Nishimura, *Carbon*, **38**, 741-747 (2000).
21. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, **57**, 603 (1985).
22. Q. Jiang and Y. Zhao, *Microporous and Mesoporous Mater*, **76**, 215-219 (2004).
23. H. Rong, Z. Ryu, J. Zheng and Y. Zhang, *Journal of Colloid and Interface Science*, **261**, 207 (2003).
24. D. B. Hibbert, *TrAC Trends in Analytical Chemistry*, **24**, 281-284 (2005).

www.kci.go.kr