Preparation of Semi-Activated Carbon Fibers

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Abstract−Preparation of semi-activated carbon fibers (SACFs) using a precursor consisting of coal tar pitch and phenolic resin coated on glass fiber was investigated. Stabilization of the fiber structure by crosslinking both the phenolic resin and coal tar pitch was essential to achieving high surface areas during high temperature activation. The phenolic resin was cured by using aqueous catalyst (hydrochloric acid/formaldehyde) followed by oxidative stabilization of the pitch. A surface area of 1,206 m^2/g based on the precursor was obtained through activation using carbon dioxide/steam at 880 °C. The pore size distribution was shown to be vary narrow using the Horvath-Kawazoe (HK) method.

Key words: Activated Carbon Fiber, Coal Tar Pitch, Phenolic Resin, Curing, Crosslinking, Aqueous Catalyst, Surface Area, Pore Size Distribution

INTRODUCTION

Growing concern over contamination of the environment has forced industry to develop responsible and effective methods for controlling the release of toxic contaminants in air and water. Activated carbons (ACs) made from coal or coconut shells have been of commercial interest for many years and are extensively used in modern industry [Mangun et al., 1998]. However, in general these activated carbons that have a low surface area and poor adsorption properties cannot be applied to industries such as environmental protection. Thus, high performance adsorbents are required. Recently, activated carbon fiber (ACF), which has a higher surface area and larger adsorption capacity than AC, has been developed and applied in some fields; however, its widespread use has been limited by cost considerations.

Economy et al. [1996] have developed a relatively low cost precursor consisting of phenolic resin coated on glass fibers which can be activated in a variety of means to produce materials with tailored pore structure and surface chemistry. The key to this approach is the use of low cost glass fibers coated with phenolic resins which could then be activated by using a simplified activation process with an operating range from 500 to 900 °C instead of the conventional process involving two steps carbonization and activation [Jeong et al., 1999].

This research was to evaluate the possibility of using coal tar pitch as a precursor because of its lower cost than phenolic resin. This paper describes a procedure for preparing SACFs from a mixture of coal tar pitch and phenolic resin. The effect of reaction time and temperature for curing the resin in the hydrochloric acid/formaldehyde solution as well as for oxidative crosslinking pitch was investigated. Thermogravimetric analysis (TGA), fourier-transform infrared (FT-IR), elementary analysis (EA), nitrogen isotherm and pore size distribution (PSD) were analyzed to observe physical and

chemical changes of SACFs.

MATERIALS AND METHOD

1. Materials

A coal tar pitch (115 °C of softening point) and a Novolac type phenolic resin (GP 2006) were supplied from Aristech Chemical and Georgia Pacific Co., respectively, and their ultimate analysis is given in Table 1. The E-glass type fiber (13 μm) was supplied from Crane Co. and its properties are summarized in Table 2. Quinoline was used to dissolve the coal tar pitch and phenolic resin. Hydrochloric acid and formaldehyde mixtures were prepared by using commercially available materials. Gases such as nitrogen, carbon dioxide and air were used as received. In this study, the precursor reagent consisted of coal tar pitch and phenolic resin in a 50/50 ratio by weight.

The coal tar pitch, phenolic resin and glass fiber were used as a raw material to manufacture SACFs. However, the carbon material such as coal tar pitch and phenolic resin were only consumed

Table 1. Ultimate analysis of the precursor (wt%)

Components	Coal tar pitch	Phenolic resin
Carbon	93.5	77.1
Hydrogen	4.1	5.7
Nitrogen	1.1	0.0
Oxygen*	1.4	17.0
Hydrogen/Carbon	0.52	0.89

*Calculated by mass difference.

Table 2. Properties of E-glass fiber

Density (g/cm³)	2.55
Tensile strength (kpsi)	500
Modulus of elasticity (×10^6 psi)	10.5
Melting temperature (°C)	<1725

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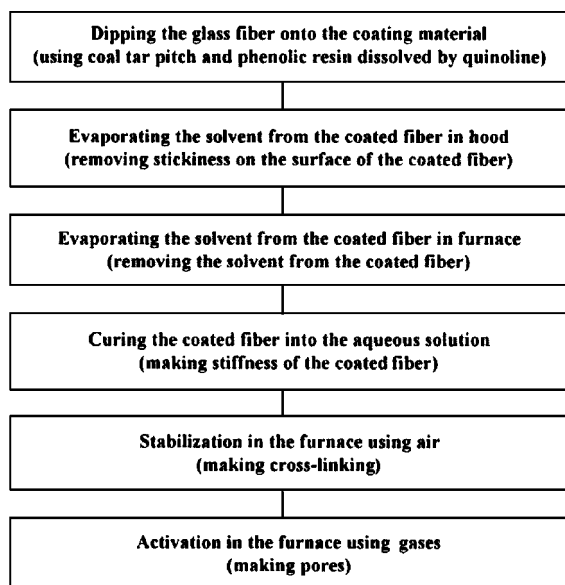E-mail: ihbaek@kier.re.kr

Fig. 1. Preparation procedure of SACFs.

Fig. 2. Experimental apparatus for gas activation.

to make porous carbon. Therefore, the raw material and the precursor are defined as coal tar pitch, phenolic resin and glass fiber, and coal tar pitch and phenolic resin, respectively, in this study.

2. Experimental Procedure and Apparatus

In order to permit a systematic study of the synthesis parameters, a protocol was developed for producing SACFs using coal tar pitch and phenolic resin as shown in Fig. 1. The major following steps are included: dipping the glass fiber into the coating solution; evaporating the solvent from the coated fiber; curing the coated fiber in the hydrochloric acid/formaldehyde solution; oxidative stabilization; activation. 25 grams of coal tar pitch and 25 grams of phenolic resin, respectively, were dissolved in 100 ml of quinoline with vigorous stirring. The glass fibers were impregnated with solution by dip coating. The coated fibers were kept overnight in a hood to reduce stickiness on the surface and then inserted into the furnace under nitrogen at 130 °C for 2 hr to remove excess quinoline. The curing of the coated fibers in the hydrochloric acid/formaldehyde solution was conducted under a variety of conditions including different compositions of hydrochloric acid and formaldehyde (0, 5, 10, 30 and 100 percent by volume). The temperature and time were optimized to achieve high stiffness of the coating material. The samples were then inserted into the furnace and stabilized with air in the temperature range from 200 to 350 °C and time from 1 to 5 hr. The heating experiment was carried out in a Lindberg furnace containing a 5 cm diameter quartz tube with glass end caps. Finally, oxidized samples were heated at a rate of 5 °C/min up to the desired activation temperature under nitrogen, and then the gas valve was switched from nitrogen to the desired activation gas. The activation was conducted in the temperature range from 600 to 880 °C for 3 hr. After activation, the carrier gas was switched to nitrogen and the furnace was cooled down to 200 °C before the sample was taken out. Activation using carbon dioxide/steam mixture was carried out by bubbling carbon dioxide into a water container as shown in Fig. 2. The samples were weighed at each step to determine weight change.
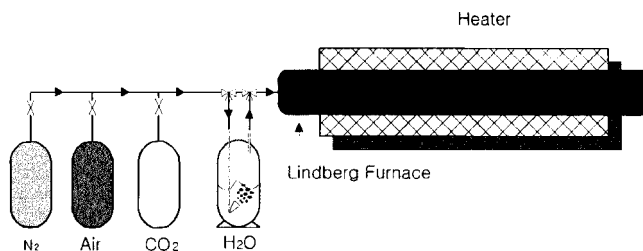
3. Analyses

The TGA (DuPont, Model 2950) was used in order to compare with direct weighing. About 20 mg of the coated or activated glass fiber was placed in a platinium crucible (2.8 mm height and 7.5 mm i.d), and heated up to 600 °C at a heating rate of 10 °C/min and then held for 30 min under air flow.

To understand the changes in molecular structure after oxidative stabilization, an FT-IR (Nicolet, Model 550) spectrometer was used. All the spectra were corrected for scattering by using a baseline range from 4,000 to 400 cm^{-1} and absorbance mode was used to observe the peaks.

EA (Exeter Analytical, Model 440) was performed. The nitrogen, carbon and hydrogen content were determined directly while the oxygen content was calculated by mass difference.

Specific surface area and PSD were determined from nitrogen adsorption at 77 K by using an automated adsorption apparatus (Quantachrome, Model ASIMP-LP). Before analysis, samples were outgassed under vacuum at 150 °C for 10 hr. Surface areas were determined by using the Brunaer-Emmett-Teller (BET) method (five point, $0.1 < P/P_o < 0.3$). Traditionally, activated carbons have been characterized by the B.E.T. method applying the adsorption isotherm to calculate surface area [Gregg and Sing, 1982]. Isotherm results in the appropriate ranges were used for PSD calculation via Barret-Joyner-Halenda (BJH) and Horvath-Kawazoe (HK) method [Russell and LeVan, 1994].

RESULTS AND DISCUSSION

1. Preparation of SACFs
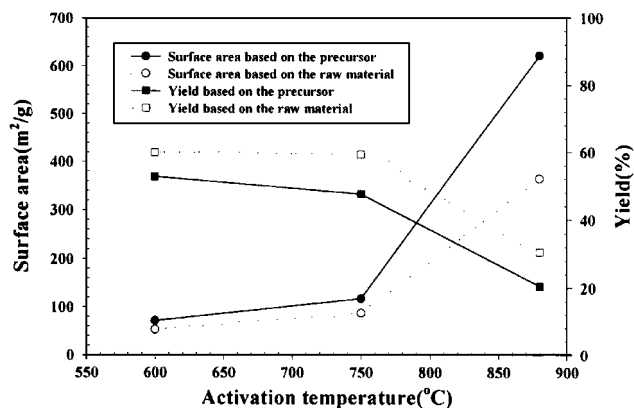
1-1. Curing using Aqueous Catalyst

Fig. 3. The effects of the activation temperatures without curing (oxidation at 300 °C for 2 hr under air, activation with 3 hr under CO_2/H_2O).

In a control experiment, the coated fiber was directly oxidized at 300 °C for 2 hr under air without curing the phenolic and then activated for 3 hr at various temperatures of 600 °C, 750 °C and 880 °C using carbon dioxide/steam as shown in Fig. 3. In the figure, the surface area increased with an increase in the activation temperature up to 622 m²/g based on the precursor.

To further increase the surface area of SACFs using pitch and phenolic resin as a precursor, alternative curing methods prior to oxidative stabilization were explored. The coated glass fibers were cured in the solution containing hydrochloric acid and formaldehyde [Economy et al., 1975]. In order to investigate the effects of different ratios of hydrochloric acid/formaldehyde on curing, the cured fibers were subsequently oxidized at 300 °C for 2 hr under air and further carbonized at 600 °C for 3 hr under nitrogen.

Fig. 4 shows the surface areas and yields according to different ratios of hydrochloric acid to formaldehyde at 25 °C for 20 hr. As shown in the figure, the highest surface area was obtained from curing an aqueous solution of 5 percent of hydrochloric acid and 95 percent of formaldehyde by volume (5/95% solution). However, the surface areas were slowly decreased with increasing volume of hydrochloric acid to formaldehyde. Also, the lowest surface area was appeared using only hydrochloric acid and formaldehyde, re-
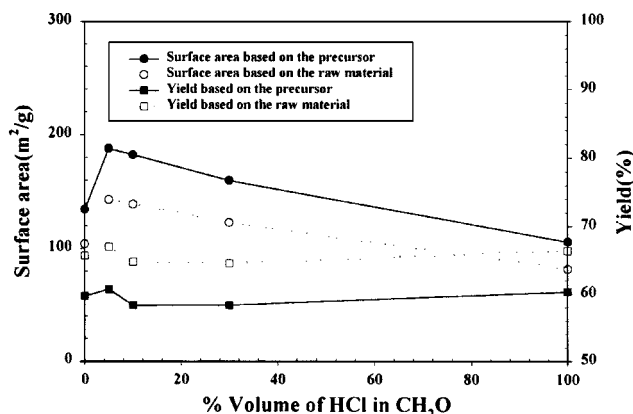

Fig. 4. The effects of HCl to CH₂O ratios at 25 °C for 20 hr (oxidation at 300 °C for 2 hr under air, carbonization at 600 °C for 3 hr under N₂).
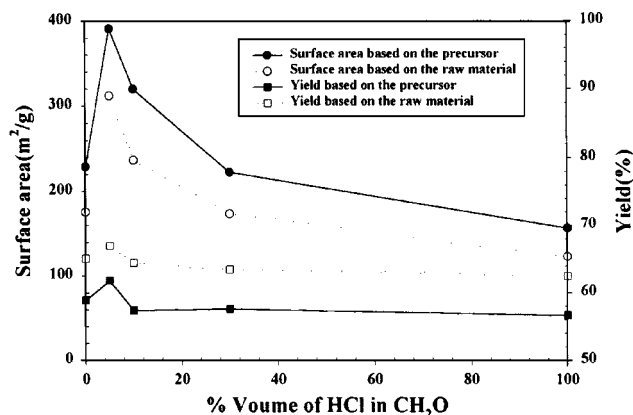

Fig. 5. The effects of HCl to CH₂O ratios at 60 °C for 20 hr (oxidation at 300 °C for 2 hr under air, carbonization at 600 °C for 3 hr under N₂).
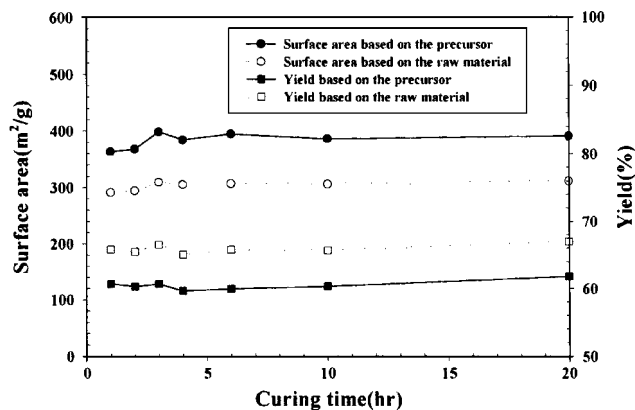

Fig. 6. The effects of the curing time at 60 °C using 5/95% solution (oxidation at 300 °C for 2 hr under air, carbonization at 600 °C for 3 hr under N₂).

spectively.

Fig. 5 shows the surface areas and yields using different ratios of hydrochloric acid to formaldehyde at 60 °C for 20 hr. The results as shown in Fig. 5 were very similar to those in Fig. 4. Thus it was of value to point out that the surface area obtained from the 5/95% solution clearly showed superiority over that from other conditions in this study. Increasing the curing temperature from 25 °C to 60 °C using 5/95% solution led to an increase in surface area from 190 to 391 m²/g.

Fig. 6 shows the surface areas and yields with different curing time at 60 °C using 5/95% solution. In this figure, the surface areas after 3 hr of curing were unchanged.

In summary, it was necessary to cure the coated fiber in the aqueous solution in order to increase the crosslink density prior to the oxidative stabilization process and eventually achieve a high surface area.

1-2. Oxidative Stabilization

Oxidation reactions are known to modify the structure of the precursor by developing a network of crosslinks between molecules, which prevents softening of the precursor during carbonization [Mochida et al., 1989].

Oxidative stabilization of the coated fiber was investigated under various temperatures and time to find the optimum conditions. Fig.
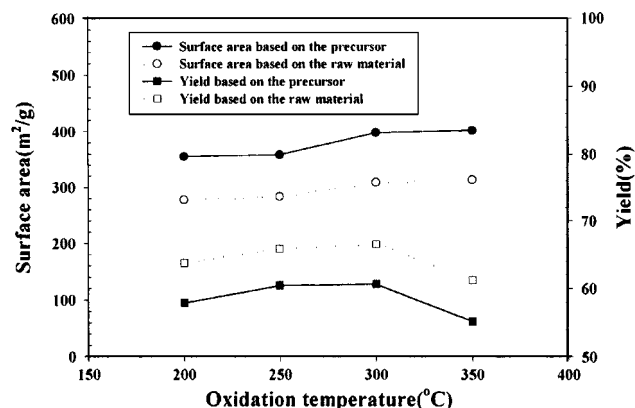

Fig. 7. The effects of oxidation temperatures with 2 hr (curing at 60 °C for 3 hr using 5/95% solution, carbonization at 600 °C for 3 hr under N₂).
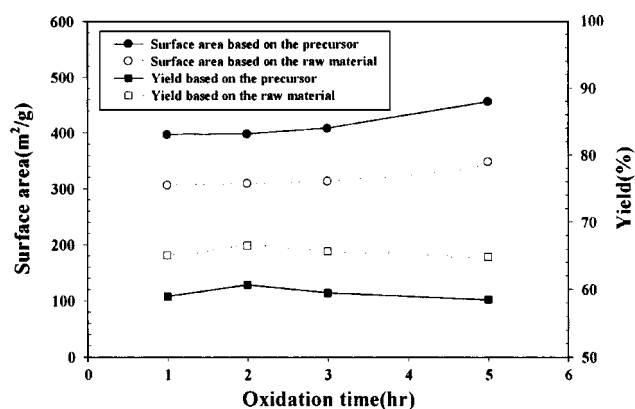
Fig. 8. The effects of oxidation time at 300 °C (curing at 60 °C for 3 hr using 5/95% solution, carbonization at 600 °C for 3 hr under N_2).
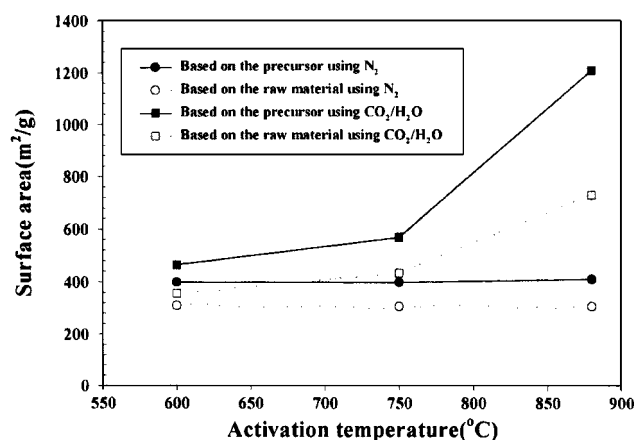

Fig. 9. The effects of activation temperatures with 3 hr (curing at 60 °C for 3hr using 5/95% solution, oxidation at 300 °C for 2 hr under air).

7 shows the surface areas and yields according to oxidation temperatures at 3 hr. Stabilization at 300 °C may favor the oxygenation of precursor components which had higher yield than at 350 °C, although with increasing oxidation temperature from 300 to 350 °C, the surface area was unchanged. Fig. 8 shows the surface areas and yields according to oxidation time at 300 °C. In this figure, similar surface areas were obtained with increasing oxidation time until 3 hr, while higher surface area was observed with increasing oxidation time up to 5 hr. The oxidation at 300 °C for 2 hr was adopted for the stabilization process in this study.

1-3. Activation

In this study, the surface area was assumed to be indicative of the activity of ACFs. Presumably, higher surface area ACs have a higher capacity for adsorption of contaminants than lower surface area ACs while selectivity is controlled by the pore size dimensions at very low concentrations [Gregg and Sing, 1982]. Activation was performed as shown in Fig. 9; the surface areas were slightly increased with increasing activation temperature under 750 °C. However, the steeper increasing of the surface area was found to be heated up 880 from 750 °C using carbon dioxide/steam. The surface area based on the precursor was 1,206 m^2/g at activation of

880 °C for 3 hr, although the yield rapidly decreased to 27.2 percent by weight. These detailed results are summarized in Table 3. The H/C ratios from EA revealed a slight increase of the carbon content together with a significant decrease in the hydrogen content as the heat treatment temperature increased, revealing the dehydrogenation reactions inherent to the aromatic condensation and cleavage of aliphatic side chain. It was interesting to point out that the activation reaction was markedly accelerated over 750 °C using only carbon dioxide/steam in all cases of this study.

2. Chemical Structure Characterization of Oxidized Fibers

FT-IR is a powerful tool for the detailed study of charred sample like oxidatively stabilized precursor because of high sensitivity due to its multiplex and throughput advantage. The reaction mechanism of the thermal-stabilization process of fiber derived from carbon materials under air and the effect of the co-polymerization have also been studied elsewhere using FT-IR [Shimada and Takahagi, 1986].

Fig. 10 shows FT-IR spectra for the coated fiber (a), the coated fiber with curing (b), the oxidized fiber without curing (c) and the oxidized fiber with curing (d). With curing and oxidation of the coat-

Table 3. The experimental results of SACFs at activation for 3 hr (curing at 60 °C for 3 hr, stabilization at 300 °C for 2 hr using air)

Activation		Coating ratio of the carbon coating after		Yield after activation		BET surface area		Elementary analysis[1]				
Gases	Temp. (°C)	Coating (%)	Activation (%)	Based on precursor (%)	Based on raw material (%)	Based on precursor (m^2/g)	Based on raw material (m^2/g)	C (%)	H (%)	N (%)	O[2] (%)	H/C ratio
N_2	600	85.1	77.6	60.7	66.5	398	309	74.6	1.4	0.7	0.9	0.22
	750	85.4	76.7	56.3	62.7	398	305	74.7	0.6	0.6	0.8	0.09
	880	85.4	74.8	50.7	57.9	409	306	72.8	0.4	0.7	0.9	0.06
CO_2 /H_2O	600	84.8	76.5	58.4	64.7	464	355	72.9	1.4	0.7	1.5	0.22
	750	85.3	76.5	56.1	62.6	567	434	73.2	1.0	0.6	1.7	0.16
	880	84.8	60.3	27.2	38.3	1206	727	57.6	0.4	0.7	1.7	0.08

*The precursor containing coal tar pitch and phenolic resin.

*The raw material containing coal tar pitch, phenolic resin and glass fiber.

[1]Total % based on the coating ratio of the precursor after activation.
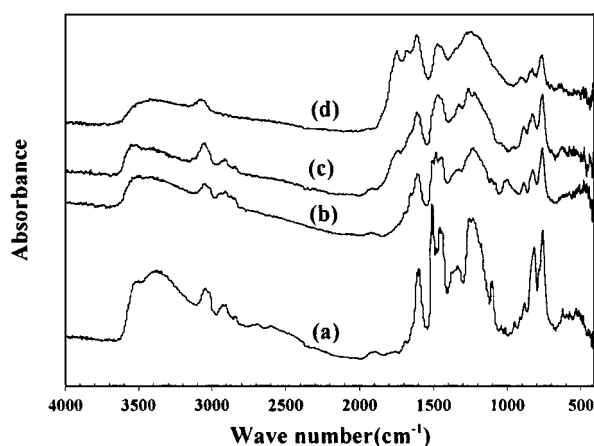
[2]Calculated by mass difference.

Fig. 10. FT-IR spectra according to various treatment: (a) the coated fiber, (b) the coated fiber with curing at 60 °C for 3 hr, (c) the oxidized fiber without curing, (d) the oxidized fiber with curing at 60 °C for 3 hr.

Fig. 11. PSD using BJH method (curing at 60 °C for 3 hr using 5/95% solution, oxidation at 300 °C for 2 hr under air, activation at 880 °C for 3 hr under CO_2/H_2O).

Fig. 12. PSD using HK method (curing at 60 °C for 3 hr using 5/95% solution, oxidation at 300 °C for 2 hr under air, activation at 880 °C for 3 hr under CO_2/H_2O).

ed fiber, the bands were observed to be increased in range from 1,800 to 1,600 cm^{-1} and completely disappeared and slightly weakened at 3,100-2,920 and 870-750 cm^{-1}.

Remarkable changes appeared between the fibers after oxidative stabilization without and with curing as shown Fig. 10c and d, in the two regions of 3,100 to 2,900 and 1,800 to 1,600 cm^{-1} which were ascribed to the C-H stretching of aliphatic and aromatic carbons and C=O stretching of carbonyls, respectively [Mochida et al., 1994]. The bands at 3,050 and 2,920 cm^{-1} were weakened and they disappeared after oxidative stabilization with curing, suggesting the condensation of aromatic rings and the oxidation of alkyl groups, respectively. In the banding range from 1,800 to 1,600 cm^{-1} created from the oxidative stabilization, bands at 1,775, 1,735, 1,770 and 1,660 cm^{-1} were ascribed to the formation of aromatic esters (Ar-O-CO-R), esters, unconjugated carbonyls and conjugated carbonyls (Ar-CO-Ar), respectively. Also, the C-H stretching of aromatic carbon in the band from 870 to 750 cm^{-1} decreased significantly as the curing and oxidative stabilization. It should be noted that oxidative structure was achieved by improving crosslinking structure through molecular association as well as the oxygenation and dehydrogenative condensation.

Eventually, it was clear that the chemical structures, indicating oxygen functional groups and aromatization of fibers only cured and oxidative stabilization without curing were slightly changed, in contrast to the oxidative stabilization with curing which obtained large changes. Thus, a higher surface area was obtained from activation using carbon dioxide/steam with curing prior to oxidative stabilization than that without curing as shown Fig. 3 and Fig. 9. It is very reasonable to point out that the stabilization, especially the oxidation and curing, both of which should be most relevant to developing crosslinking structure of the carbon fiber precursor, derived from the mixture involving coal tar pitch and phenolic resin.

3. PSD (pore size distribution)

Currently there is no direct method available for the structural evaluation of pores in fibers or in other solid carbons. However, indirect finding of pore structure is qualitatively supported by PSD calculations generated by applying the various methods to nitrogen adsorption data at 77 K.
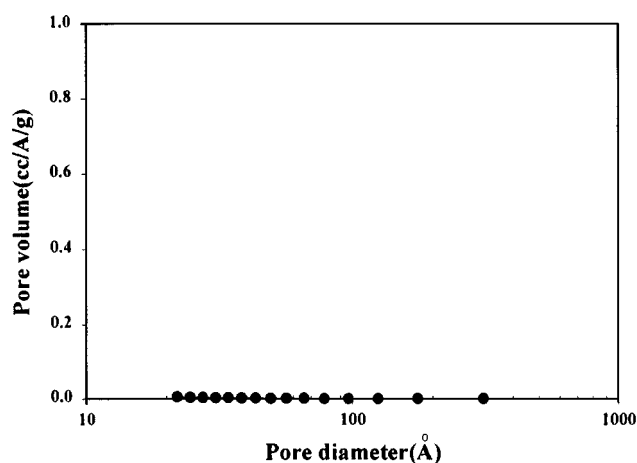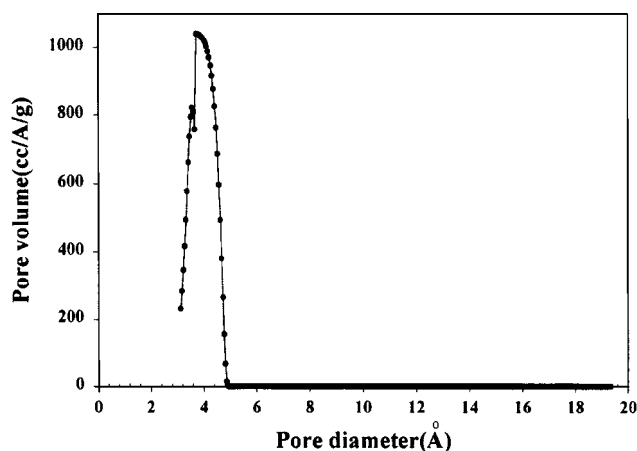
The meso-PSD was calculated by using the BJH method. The HK method enables the calculation of PSD of micropores from the low pressure region of the adsorption isotherm. Figs. 11 and 12 show the PSD using the BJH and HK methods, respectively. The PSD calculated from the BJH method indicated that only mesopore was not present. From calculating micro-PSD using the HK method, micorpores with 4 Å of average pore diameter were observed. The PSD of an AC is governed by two factors, namely, the structural uniformity of the precursor and the process conditions used in the activation. However, the precursor in this study was a highly crosslinked structure possessing a relatively uniform three-dimensional network as shown in Fig. 10(d). Thus, this structure would contributed to developing more narrower pores in SACFs [Economy and Lin, 1976].

CONCLUSIONS

The goal of preparing high surface area SACFs using coal tar pitch and phenolic resin coated on glass fiber was achieved. The

conditions included curing of the phenolic resin followed by oxidative stabilization of the pitch. The curing of the coated fiber involved treatment at 60 °C for 3 hr with a mixture of 5 percent of hydrochloric acid and 95 percent of formaldehyde. A higher surface area could be achieved on activation at 880 °C under carbon dioxide/steam with curing prior to oxidative stabilization, which one was observed to have micropores with 4 Å of average pore diameter through the HK method. Adsorption studies including equilibrium and kinetic data of those fibers should be further investigated in detail.

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