금속함유 탄소섬유의 탄화 및 활성화 거동

최영옥, 양갑승
전남대학교 응용화학공학부

Carbonization and Activation Behaviors of Metal Containing Carbon Fibers

Young Ok CHOI, Kap Seung YANG
Faculty of Applied Chemistry, Chonnam National Univ., Kwangju, Korea

1. Introduction

The efficiency of the adsorption of adsorbents depends on both pore size and shape. In other to adsorb hydrated ion in application of electric double layer capacitor (EDLC), mesopore is necessary[1,2]. Tamai et al.[3] reported that an increased portion of mesopore was introduced through addition of metal or organometallic compound in the precursor and following activation of the carbon fibers with steam.

In the present study, Lewis acid ($FeCl_3$) and Br_2 were used in oligomerization of coal tar to prepare precursor pitches with softening point of 250-300 ℃. The precursor pitches were spun into fibers and followed by stabilization, carbonization, and finally activation. The behaviors of metal in the carbonization procedure were traced by using transmission electron microscope(TEM) and scanning electron microscope (SEM) and the results were correlated with pore size distribution of the ACF.

2. Experimental

The coal tar pitch (softening point, 110 ℃) was dissolved in tetrahydrofuran (THF) and the soluble portion (TSP) was recovered by separation by filtration. 3 wt.% of $FeCl_3$ was evenly dispersed in the TSP and followed by oligomerization in the presence of 15 wt.% of Br_2 at 180 ℃. Elemental analysis data of the TSP was summarized in Table 1.

Table 1. Elemental analysis of TSP

	Softening Temp. (℃)	Elemental content (%)					C/H ratio
		C	H	N	S	O(diff.)	
TSP	85	91.79	4.31	0.94	0.53	2.25	1.79

The precursors were grinded to be fine powder and spun through one hole nozzle (L/D=2, D=0.2mm) by using pressurized nitrogen at the temperature of softening point plus 20-30 ℃.

The fiber spun was stabilized in the electronic oven by circulating air at a heating rate of 5 ℃ /min up to 300 ℃ and followed by carbonization 600 and 1000 ℃ for one hour in Ar atmosphere. The identification of FeCF-600 represents that the fiber prepared from the addition of the 3wt.% $FeCl_3$ was carbonized at 600 ℃.

The carbon fibers were activated at 900 ℃ through supplying steam (H_2O/N_2=0.4) for 30 min.

The identification of FeACF-1000 represents that the $FeCl_3$ containing carbon fiber carbonized at 1000 ℃ was activated at the conditions mentioned.

3. Results and Discussion

Tetrahydrofuran(THF) soluble coal tar pitch was oligomerized in presence of bromine and Lewis acid catalyst ($FeCl_3$) to be precursors of fiber spinning (Table 2). The product yield of the precursor in the presence of $FeCl_3$ showed 67 %. The precursor containing metal components were spun into fibers, stabilized under air atmosphere and carbonized to be carbon fibers at 600 and 1000 ℃. The behaviors of metal in the fibers were chased by using TEM and SEM. The remaining metal Fe during carbonization showed peculiar behaviors; Fe introduced graphitic layers around the metals at 1000 ℃ (Fig. 1).

Table 2. Softening temperatures and yields of the samples

		TSP/Br_2	TSP/Br_2-$FeCl_3$
Softening temp. (℃)		261	268
Yield (%)	precursor pitch	59	67
	carbonized fiber at 600 ℃	78	82.4
	carbonized fiber at 1000 ℃	72	66

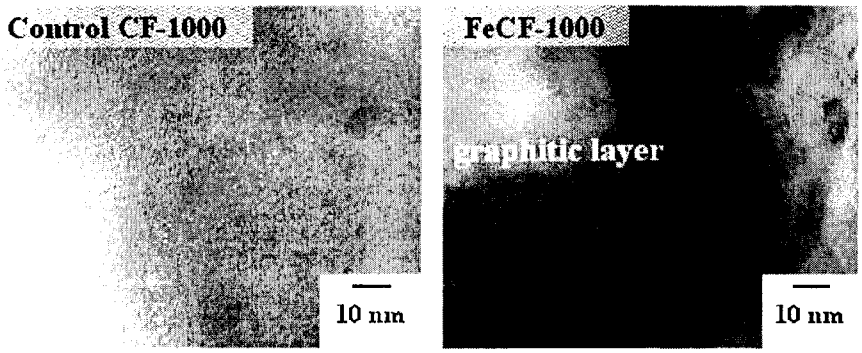

Fig. 1. TEM microphotographs of fibers carbonized at 1000℃: (a) Control CF-1000; (b) FeCF-1000.

The carbon fibers with the graphitic layers enhanced the oxidative stability up to 600 ℃ and the oxidation was accelerated above the temperature.

The metal containing carbon fibers carbonized at 600 ℃ and activated exhibited specific surface area of 2,910 m^2/g and the surface area from mesopores were characterized of 43 % by BET (Table 3). The Fe fine particles dispersed on the surface of FeCF-600 would activate the oxidative combustion to create ultra-high surface area (Fig. 2). The ACF from the FeCF-600 shows bilateral structure, i.e., compact along the surface and porous inside of the fiber (Fig. 3).

Table 3. Some properties of activated carbon fibers from CF-600 and CF-1000

Samples	Burn-off (%)	Surface area (m^2/g)	Mesopore area (m^2/g)	Micropore area (m^2/g)	Mesopore fraction (%)	Average pore radius (Å)
Control ACF-600	60	1,149	207	941	18	12.0
FeACF-600	65	2,910	1,243	1,667	43	14.8
Control ACF-1000	34	683	50	633	7.3	13.08
FeACF-1000	57	1,268	130	1,138	10.3	13.64

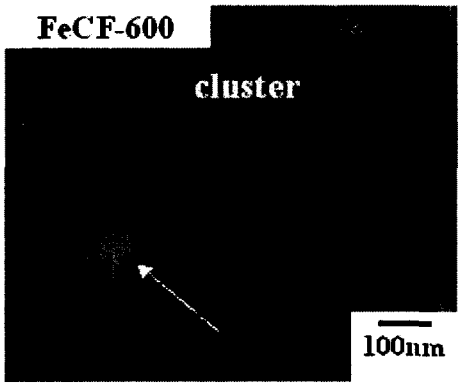

Fig. 2. TEM microphotograph of FeCF-600.

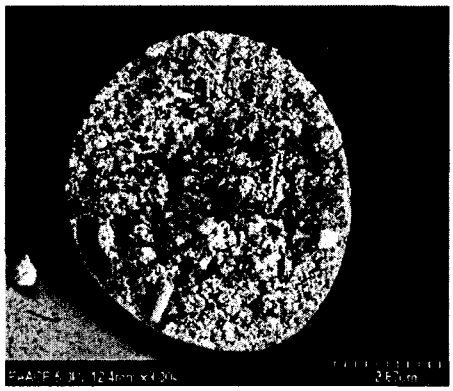

Fig. 3. SEM microphotograph of FeACF-600.

4. Conclusions

The Lewis acid of $FeCl_3$ showed catalytic effects not only on condensation reaction but also on the activation creating the high surface area. The metal dispersed in the carbon fibers diffused out, finely clustered, and crystallized with an increase in carbonization temperature. Fe showed no indication of puffing but formation of fine particles on the surface of carbon fibers at 600 ℃, which gives effects in generating high surface area majorly from mesopores. Consequently, the addition of Fe catalyst is believed to be useful not only in raising the production yield of the procedures and but also in accelerating the activation reaction resulting developing the mesopores.

References

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