

Preparation of carbon nanofiber / carbon fiber composites and their catalytic performance

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Introduction

Recently, carbon nanofiber (CNF) has been extensively studied under recognition as a unique nano-carbon material [1-4]. CNF is characterized by the graphite-like structure with variable alignments of laminated hexagon layers along the fiber axis [4]. In surface-relating applications of carbon materials, it is important what surface morphology, structure and chemistry is effective and how much they have effective sites on their surface. CNF can be of a high surface area from 50 to 800 m²/g as catalytically prepared or after chemically activated [5, 6]. Platelet and herring-bone CNFs expose free edges of hexagons with few heteroatoms, differing from the microporous surface of activated carbons. Such a surface of CNF appears to be advantageous to providing active sites of exposed hydrophobic hexagon edges for high activity in DeSO_x and DeNO_x. However, the nano-ordered size is not adequate to be packed in a fixed-bed reactor due to difficulty in handling and pressure drop at rapid gas flow in processes [7].

CNF/carbon fiber (CNF/CF) composites have been investigated to improve adhesive properties at the interface between the fiber and matrix in carbon-fiber reinforced composites [8-10] and to give a macroscopic frame or support to be anchored by CNFs to solve handling difficulty and pressure drop problem [7].

In this work, CNF/CF composites were attempted to be prepared in order to introduce multi functions to the catalytic surface of ACF by catalytic growth of CNF. Such products were expected to be very useful adsorbents and catalysts.

Experimental

Three types of CFs such as pitch-based carbon micro-fiber (MCF), FE300 (PAN-based, activated), and pitch-based spun-stabilized fiber (SSF) were used in this study. Table 1 shows some properties of support fibers.

Table 1. Some properties of support fibers

Support fibers	C	H	N	O(diff.)	Diameter μm	Surface area m ² /g
	weight %, dry					
SSF	62.0	4.1	22.0	11.9	11	< 50
FE300	81.5	1.0	3.8	9.6	10	669
MCF	99.5	0.4	0.0	0.1	1.2	< 50

Prescribed amounts of nickel and iron nitrates were dissolved in ethanol, and then CF dried in an oven at 65°C was soaked in the solution. After evaporating ethanol, the wet

CF was dried in a vacuum oven at 105°C overnight and stored. In this study, 5% w/w of Ni-Fe (8:2w/w) was impregnated onto the CF, which was named as NF82-CF (by the sample name).

CNFs was synthesized over CF in a quartz flow reactor (10 cm × 45 cm) heated by a conventional horizontal tube furnace. Prescribed amount of NF82-CF (250 ~ 300 mg) was placed in an alumina boat at the center of the reactor tube in the furnace. After reduction in a 20% H₂/He mixture for 2 h at prescribed temperature, helium was flushed for 30 min before introduction of C₂H₄/H₂ (1:1) (v/v) mixture (total flow rate = 200 cm³/min) over the catalyst. All of the gas flows in the reactor were precisely monitored and regulated by MKS mass flow controllers. The total amount of carbon deposited during the time on stream was determined gravimetrically after cooling the product to ambient temperature.

Multi-point Brunauer, Emmett, and Teller (BET) surface area was measured with nitrogen adsorption-desorption isotherm using a surface area analyzer (Sorptomatic 1990, FISONS Instruments). Prior to this measurement, the samples were degassed at 150°C for 8 h. The pore distribution was calculated by the method of Barrett, Joyner and Halenda [11].

The nanostructure and morphology of the nanofibers were observed under scanning electron microscope (SEM) (JSM-6320F, JEOL).

Results

Figure 1 shows the CNF yield and surface area depending on the synthesis temperature. The CNF yield was presented as the weight of CNF produced per the weight of NF82-support. The yield increased at higher temperature in the range of 480 ~

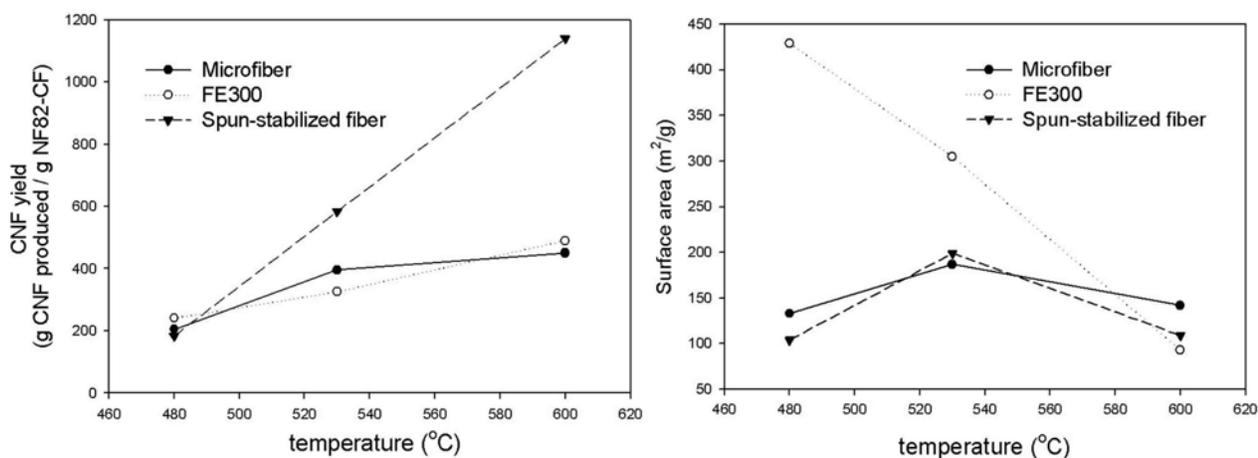


Figure 1. CNF yield and surface area dependant on the synthesis temperature.

600 °C. In the cases of FE300 and MCF, the increase of yield appeared to be saturated at and above 530°C, whereas CNF was highly produced on SSF at higher temperature than 530 °C.

The surface areas of products were higher than the original fibers of both MCF and SSF. The change of surface area showed a similar tendency on MCF and SSF, which

exhibited a maximum value around 530°C, whereas the products from NF82-FE300 had the surface area decreased as the temperature and yield increased.

The pore size distribution was calculated from desorption isotherms (BJH method) as shown in Figure 2. The samples from three supports showed development of particular pore size at 3 ~ 4 nm hydraulic radii. However, the change of micropores appeared to be dominant in the case of FE300 depending on the CNF growth, reflecting a progressive blockage of micropores on FE300 by the growth of CNF. Both of MCF and SSF basically have no porous surface. Small amount of CNF grown on both MCF and SSF resulted in development of a particular pores as well as very small micropores, whereas further growth of CNF appeared to block such pores progressively.

Figure 3 shows SEM images of the composites produced at 480°C from three kinds of fiber. CNFs appeared to be uniformly produced over all of the support fibers. However, CNFs produced over FE300 were more homogeneous in the diameter of around 20 nm, whereas CNFs produced over both MCF and SSF showed wide range of diameters from 10 ~ 120 nm. The diameter of CNF was found to be less homogeneous at a higher temperature (not shown).

Discussion

We described preparation of CNF on the micro-sized fibers with various surface properties and pore system. The yield of CNF appears to be affected by the pore system of surface of the support. SSF (spun-stabilized fiber) has basically non-porous surface with a large amount of functional groups containing nitrogen and oxygen (see Table 1). Catalyst particles dispersed on such a surface appeared to be more exposed to exhibit high activity for production of CNF than the supports with a pore system developed.

From Figure 3, development of new pores can be guessed on both MCF and SSF through reduction of catalyst in hydrogen and successive synthesis of CNF, probably by gasification of carbon around catalyst particles. More growth of CNF, however, appeared to block the pores newly developed, since much higher yield of CNF resulted in lower surface area. The maximum surface area at 530°C in MCF and SSF suggests that the formation of pores is so competitive to the blockage of such pores by the growth

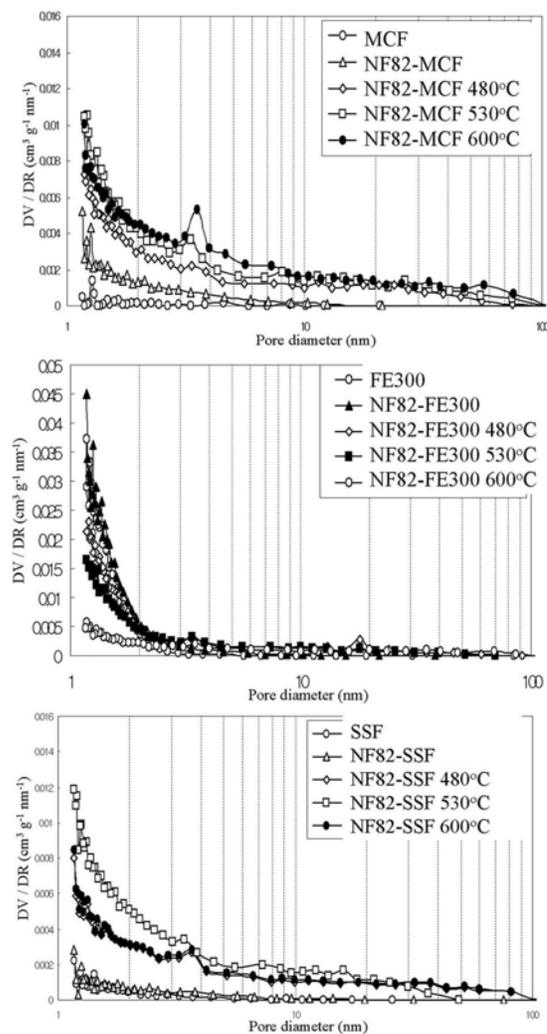


Figure 2. Pore size distribution of three original fibers and fiber/CNF samples at temperatures denoted.

of CNF that there are optimum temperatures to produce CNF/CF composites with high surface areas.

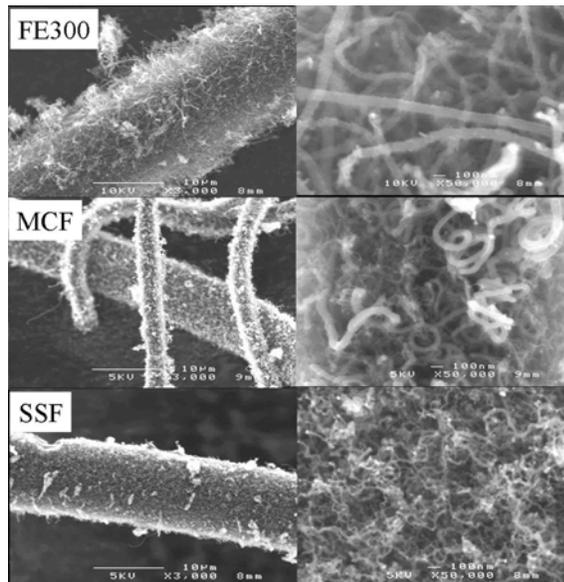


Figure 3. SEM images of three original fibers and fiber/CNF samples at 530°C.

Conclusion

Various CNF/CF composites with various surface properties were successfully prepared. The results of this study provided some information to control the surface properties for the best application. Activated CF generally has showed a good catalytic performance in several applications such as DeSOx due to its very high surface area with micropores. However, several steps such starting from carbon precursor, spinning, stabilizing, carbonization, and activation with purification cause the cost-up. CNF/SSF or CNF/MCF in this study showed new possibility to introduce new surface of CNF as well as to develop the micropores. Now some tests of these products as a catalytic surface donor are in progress.

References

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