

# Continuous Removal of SO<sub>2</sub> in Flue Gas over Hairy Pitch Based Activated Carbon Fibers

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## INTRODUCTION

Activated carbon fiber (ACF) is a unique adsorbent with superhigh surface area of 800 ~ 3000 m<sup>2</sup>/g, which basically stems from the microporous structure.[1] An application specific to carbon fibers is removal of SO<sub>x</sub> and NO<sub>x</sub> from the atmosphere as well as from flue gas.[2, 3] The basic principle of SO<sub>x</sub> removal is capture of SO<sub>2</sub> in the form of aqueous H<sub>2</sub>SO<sub>4</sub>. Continuous recovery of concentrated aqueous H<sub>2</sub>SO<sub>4</sub> is now being pursued.[4]

Recently, carbon nanofiber (CNF) has been greatly studied under recognition as a unique carbon material. [5, 6] CNF is characterized by the graphite-like structure in a nano scale, where variable alignments of laminated c-plane layers along the fiber axis provide typically three types of CNFs such as platelet (alignment perpendicularly against the fiber axis), tubular (alignment parallel along the axis), and herringbone (alignment angled to the axis) CNF.[7]

CNF also showed a high surface area from 50 to 800 m<sup>2</sup>/g as catalytically prepared or after chemically activated.[8] CNFs expose a free surface with little heteroatoms, differing from a negatively concaved surface of ACF based on micropore-developing structure. Although such surface of CNF appears to be advantageous to continuous H<sub>2</sub>SO<sub>4</sub> recovery in DeSO<sub>x</sub> and hydrophobicity for DeNO<sub>x</sub>, the nano-scaled size is not proper to fixed-bed reactors due to difficulty in handling and pressure reduction in process. In surface-relating application of carbon materials, it is important what surface morphology or structure and chemistry is effective and how much they have effective sites on their surface.

CNF/carbon fiber composites have been investigated (1) to improve adhesion properties at the interface between the fiber and matrix in carbon-fiber reinforced composites [9] and (2) to give a macroscopic frame or support to be anchored by CNFs to solve handling difficulty and pressure drop problem [10].

In this work, CNF/ACF composites were designed in order to realize a multi-catalytic surface using both externally protruded surfaces of CNF and micropores of ACF. The surface properties of products were expected to be controlled through (1) open/close of ACF micropores and (2) formation of new surface and pores via catalytic growth of CNF on ACF. Well-controlled multi-surface composites of CNF/ACF were expected to be very useful adsorbents, which may improve the ability of ACFs in such applications as DeSO<sub>x</sub> and DeNO<sub>x</sub>.

## EXPERIMENTALS

### Chemicals and materials

Reagent grade iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), and nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were obtained from Wako Inc. (Japan). Hydrogen (>99.9999%), ethylene (99.9%), and helium (>99.9999%) were obtained from Nihon Sanso Inc. (Japan) and used without further purification. Activated carbon fiber (ACF) in this study was OG-15A, which involves in OG series of pitch-based ACFs supplied by Osaka Gas Co.

### Impregnation of catalyst into ACF

Prescribed amounts of nickel and iron nitrates were dissolved in ethanol, and then ACF dried in an oven at  $65^\circ\text{C}$  was soaked in the solution. After evaporating ethanol, the wet ACF was dried in a vacuum oven at  $105^\circ\text{C}$  overnight and stored. In this study, 5% w/w of Ni-Fe (8:2 w/w) was impregnated into the ACF, which was named as NF82-ACF.

### Partial oxidation of NF82-ACF

The oxidation condition of NF82-ACF in air was determined by TG-DTA analysis (SEIKO SSO/5200, SEIKO Co., Japan). NF82-ACF was partially combusted in the furnace before being introduced into the furnace of CNF synthesis as described in the next section. The oxidation degree was controlled by the oxidation time at prescribed temperature. The partially oxidized NF82-ACF was named as PO-NF82-ACF.

### Synthesis of CNF over NF82-ACF

CNFs on the ACF were prepared in a quartz flow reactor (10 cm  $\times$  45 cm) heated by a conventional horizontal tube furnace. Prescribed amount of NF82-ACF or PO-NF82-ACF (250 ~ 300 mg) was placed in an alumina boat at the center of the reactor tube in the furnace. After reduction in a 20%  $\text{H}_2/\text{He}$  mixture for 2 h at prescribed temperature, helium was flushed for 30 min before introduction of  $\text{C}_2\text{H}_4/\text{H}_2$  (1:1 v/v) mixture (total flow rate = 200  $\text{cm}^3/\text{min}$ ) over the catalyst. All of the gas flows to 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.

### $\text{SO}_2$ removal

$\text{SO}_2$  removal was carried out in a fixed bed flow reactor as described elsewhere [11, 12]. ACF was packed in a tubular glass reactor of 8 mm diameter and the packing height was about 0.1 g/10 mm. The concentrations of  $\text{SO}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$  in model flue gas were 1000 ppm, 5 vol% and 20 vol%, respectively, under the balance of  $\text{N}_2$ . The weight of ACF, the total flow rate and reaction temperature were 0.05~0.25 g, 100 ml/min and  $50^\circ\text{C}$ , respectively. The  $\text{SO}_2$  concentration was detected with a flame photometric detector.

### Characterization

Multi-point Brunauer, Emmett, and Teller (BET) surface area was obtained using a surface area analyzer (Sorptomatic 1990, FISONS Instruments). Prior to this measurement, the samples were degassed at  $150^\circ\text{C}$  for 8 h. The pore distribution was calculated by the method of Barrett, Joyner and Halenda. [13]

The nanostructure and morphology of the nanofibers were observed under both scanning electron microscope (SEM) (JSM-6320F, JEOL) and transmission electron microscope (TEM) (JEM-2010F, JEOL).

## **RESULTS**

### **Growth of CNF on ACF**

The carbon yield in the activated carbon fiber-supported catalyst (NF82-ACF) was examined according to the synthetic temperature, summarized in Table 1. Critical factors such as the nature of the catalyst, the hydrocarbon reactant, and the growth conditions were based on the preliminary work with Ni-Fe (8:2) supported on carbon black, which produced fish bone-type CNFs with 5~40 nm diameter in high catalytic activity of 100 ~ 150 g CNFs per 1 g catalyst from ethylene at 480 ~ 600°C [14]. After synthesis of CNF on the ACF, the CNF content in the product was gravimetrically measured from 10 wt% at 480°C to 50% at 600°C for 1 h reaction time.

PO-NF82-ACF was prepared through oxidation of NF82-ACF in air at 350°C for 1 h, where the weight loss of the NF82-ACF ranged 20~30 wt%. The partial oxidation appears to affect hardly the catalytic activity of Ni-Fe catalyst on the ACF, since the amount of carbon deposition on the PO-NF82-ACF showed little difference from that on the NF82-ACF (Table 1).

### **Surface area and pore distribution of CNF/ACF composites**

The ACF in this study had a high surface area over 1000 m<sup>2</sup>/g, and CNFs from ethylene on Ni-Fe catalyst showed the surface area of 150 ~ 220 m<sup>2</sup>/g.

The BET specific surface area and the pore specific volume were summarized in Table 1. After impregnation of Ni-Fe catalyst into the original ACF, the surface area greatly fell down to 118 m<sup>2</sup>/g. The results of pore volume indicate most of ACF micropores were blocked by the catalyst deposition.

Growth of carbon nanofiber on NF82-ACF exerted little influence on increase of the active surface sites, irrespective of the amount of the produced CNF according to synthetic temperature and time. The micropores which contributed to the large surface area had not a chance to be opened during CNF growth after closed by catalyst particles.

After partial oxidation of the NF82-ACF in air, the surface area increased dramatically up to 1625 m<sup>2</sup>/g, where the pore volume increased remarkably over that of the original ACF. Catalytic growing the nanofiber on the PO-NF82-ACF resulted in stepwise decrease of the surface area depending on the amount of the nanofiber as shown Figure 1.

In Figure 2, pore size distributions of products were obtained from N<sub>2</sub> adsorption/desorption isotherm. In ACF, the micropores with radii of 0.6 ~ 1.0 nm appears to contribute to its large surface area. After impregnation of catalyst, most of the micropores were blocked, which means the catalyst particles were selectively deposited on the pores of the ACF. After partial oxidation, the surface area was recovered by regeneration of micropores with the radii of 0.9 ~ 1.8 nm, which are larger than those of the original ACF. Formation of CNF regenerated new pores with

the radii of 0.6 ~ 0.9 nm but blocked partially the pores probably originated from the surface of the ACF.

#### **Activities of hairy for SO<sub>2</sub> removal**

The SO<sub>2</sub> breakthrough profiles for the as-prepared and hairy ACFs are illustrated in Figure. 3. The as-prepared ACF showed very poor activity, SO<sub>2</sub> started to break through after about 20 min, as the C/Co quickly increased to about 75% of C<sub>0</sub>. Calcination in N<sub>2</sub> at 1100°C enhanced its activity. SO<sub>2</sub> started to break through after 16 h and C/Co gradually increased to 18% of C<sub>0</sub>. CNF/ACF (OG15A-CNF5min-H1100) showed the highest activity. SO<sub>2</sub> started to break through after 28 h and C/Co gradually increased to 15% of C<sub>0</sub>. Compared to OG15A-CNF5min-H1100, CNF/ACF (OG15A-CNF20min-H1100) CNF/ACF (OG15A-CNF5min-H1100) showed relatively lower activity than CNF/ACF (OG15A-CNF5min-H1100). SO<sub>2</sub> started to break through after 8 h and C/Co gradually increased to 18% of C<sub>0</sub>.

#### **CONCLUSION**

In this article, we have described a series of preparation of CNF/ACF composites on the purpose of introduction of a new catalytic surface (CNF) on ACF surface with the active sites of ACF left during the procedure. Partial oxidation prior to growing CNF was necessary for exposing ACF surface in CNF/ACF composites. The conclusion is summarized as following.

(1) CNF/ACF composites in this work provide a free surface of CNF as well as microporous surface of ACF. Such protruded free surface is likely to be advantageous to continuous H<sub>2</sub>SO<sub>4</sub> recovery in DeSO<sub>x</sub> process. Fixation of CNFs on macroscopic frames may release handling and pressure drop problem in practical processes.

(2) Hairy ACF (CNF/ACF (OG15A-CNF5min-H1100)) showed the highest activity. SO<sub>2</sub> started to break through after 28 h and C/Co gradually increased to 15% of C<sub>0</sub>.

(3) The pore size was found to be controlled through growth of CNF on ACF through partial oxidation.

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#### **REFERENCES**

[1] Yoon S-H, Korai Y, Mochida I. Carbon Fibers and Active Carbon Fibers. In Marsh H, Rodriguez-Reinoso F, editors, Sciences of Carbon Materials, Alicante : Universidad de Alicante, 2000: 287-325.

[2] Kisamori S, Kuroda K, Kawano S, Mochida I, Matsumura Y, Yoshikawa M. Energy & Fuels 1994; 8: 1337-1340.

- [3] Mochida I, Kisamori S, Hironaka M, Kawano S, Matsumura Y, Yoshikawa M. *Energy & Fuels* 1994; 8: 1341-1344.
- [4] Kisamori S, Mochida I, Fujitsu H. *Langmuir* 1994; 10 (4): 1241-1245.
- [5] Iijima S. *Nature* 1991; 354: 56-58.
- [6] Rodriguez NM. *J Mater Res* 1993; 8: 3233-3250.
- [7] Rodriguez NM, Chambers A, Baker RTK. *Langmuir* 1995; 11(10): 3862-3866.
- [8] Baker RTK, Rodriguez NM. High performance carbon filament structures. US Patent No. 5618875, April 8, 1997.
- [9] Downs WB, Baker RTK. Novel carbon fiber-carbon filament structures. *Carbon* 1991;29(8):1173-1179.
- [10] Nhut JM, Vieira R, Keller N, Pham-Huu C, Boll W, Ledoux MJ. *Stud Surf Sci Catal* 2002; 143: 983-991.
- [11] Kuroda K. Removal of SO<sub>2</sub> in the form of aq. H<sub>2</sub>SO<sub>4</sub> from flue gas over active carbon fiber. Master thesis 1996; Kyushu University, Fukuoka, Japan.
- [12] Mochida I, Kuroda K, Kawano S, Matsumura Y, Yoshikawa M. Kinetic study of the continuous removal of SO<sub>x</sub> on polyacrylonitrile-based activated carbon fibers: 1. Catalytic activity of PAN-ACF heat-treated at 800°C. *Fuel* 1997; 76 (6): 533-536.
- [13] Barrett EP, Joyner LG, Halenda PP. *J Amer Chem Soc* 1951; 73: 373-380.
- [14] Lim S, Yoon S-H, Korai Y, Mochida I. Selective Synthesis of Thin Carbon Nanofibers: I. Over Nickel-Iron Alloys Supported on Carbon Black. *Carbon* 2004, in press.

Table 1. Carbon yield and surface area according to the synthetic condition.

Sample No.	Reaction		Product/ Starting (g/g)	CNF/ Product (wt/wt %)	Surface Area (m <sup>2</sup> /g)	Pore specific volume (cm <sup>3</sup> /g)
	Temp. (°C)	Time (min)				
ACF A-15	-	-	-	-	1014	0.73
NF82-ACF <sub>F</sub>	-	0	-	-	118	0.08
	480	60	1.11	10	114	0.08
	530	60	1.27	21	-	-
	600	60	2.05	51	131	0.09
	600	20	1.08	7	-	-
PO-NF82-ACF	-	0	-	-	1625	0.92
	600	20	1.12	10	1099	0.61
	600	40	1.44	31	582	0.38
	600	60	1.79	44	479	0.35

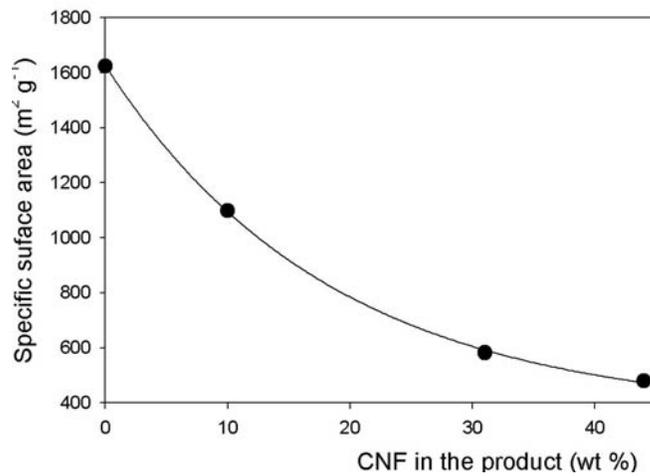


Figure 1. Dependence of the specific surface area on CNF growth from ethylene/H<sub>2</sub> (1:1) on PO-NF82-ACF at 600°C.

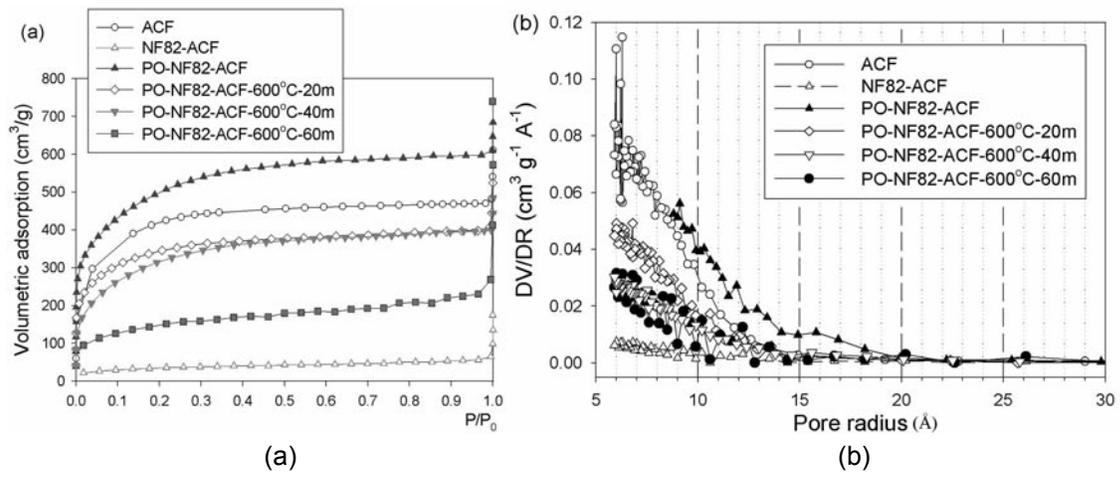


Figure 2. Surface properties of ACF, NF82-ACF, PO-NF82-ACF, and CNF/ACF composites: (a) N<sub>2</sub> adsorption isotherms (b) pore size distributions calculated by BJH procedure

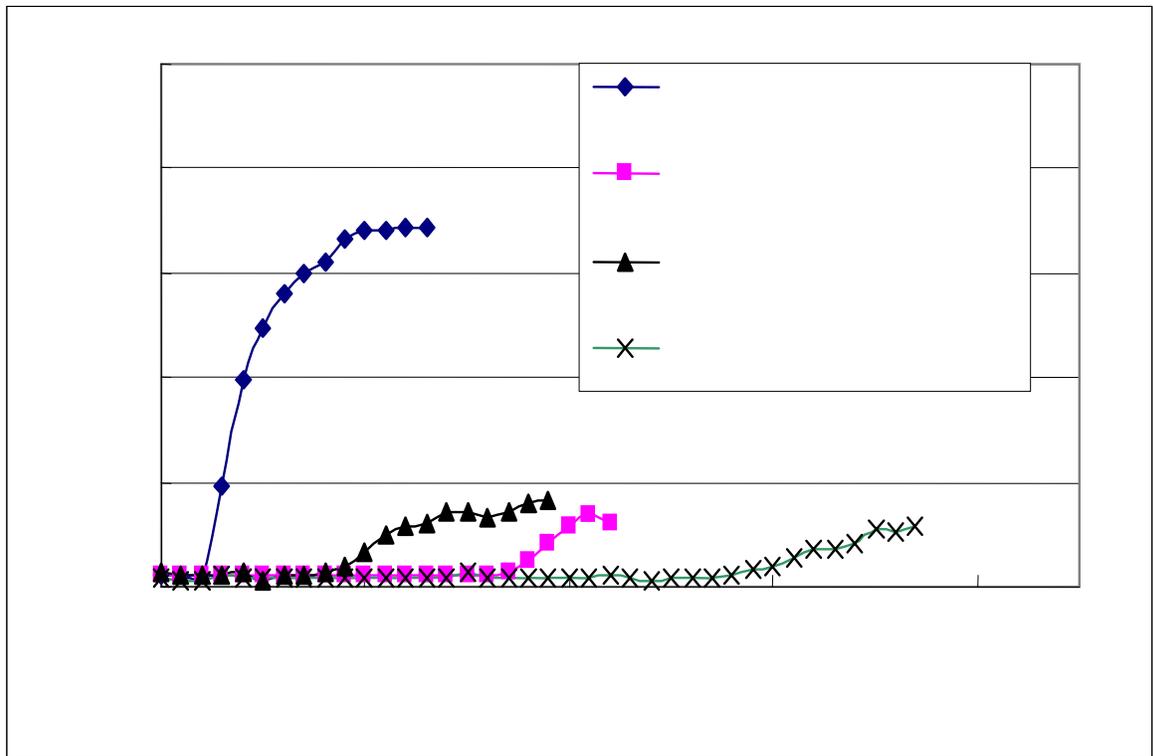


Fig.3 OG15A-AS: Pitch based as-prepared ACF from Osaka Gas OG15A-H1100: Heat treated OG15A-AS at 1100°C for 0h, OG15A-CNF5min-H1100: Heat treated CNF-OG15A-AS composites