

Preparation of Mesoporous Activated Carbon Fibers by Catalytic Gasification

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Abstract—A commercial activated carbon fiber with micropores, CH700-20 (Kuraray), was reformed to a mesoporous one by catalytic gasification. The catalytic gasification was composed of two steps: CO₂ pretreatment and air oxidation. Cobalt was used as the catalyst and gasification was performed in the temperature range of 500-700 °C. BET surface area and pore volume of catalytically modified carbon fiber were analyzed by N₂ adsorption. BET surface area of the original CH700-20 was 1,711 m²/g, and the mesopore volume percentage was 11.9%. After catalytic gasification, BET surface area was similar to the original CH700-20, while mesopore volume percentage increased up to 56%. The average pore size of mesopores was 3-4 nm in diameter. The average size of mesopores could be controlled with nanometer resolution by varying the temperature and time of activation.

Key words: Activated Carbon Fiber (ACF), Mesopore, Catalytic Gasification

INTRODUCTION

Hybrid electric vehicles have been drawing continuous attention for many years because of their potential for preventing air pollution and increasing fuel efficiency. A secondary battery or fuel cell is used as the energy source of a hybrid electric vehicle, and an electrochemical capacitor is used as the power source [Sperling 1996; Burke et al., 1995]. Ultracapacitors store the electric energy in the electric double layer that forms at the interface between the electrode and the electrolyte [Bard et al., 1980; Nishino, 1996]. High-surface-area carbon is used as the electrode of the ultracapacitors. This material has several merits such as high surface area, good stability, good conductivity and low cost. However, high-surface-area carbons mostly consist of micropores smaller than 20 Å, and there is a question about the origin of capacitance of porous carbon electrodes since micropores are too small to harness the electric double-layer. It is expected that porous carbons with mesopores are superior as electrodes of ultracapacitors because mesopores are favorable to the formation of an electrical double layer. It has been reported that mesoporous carbon fiber was better than microporous in view of the cyclic voltammetry and capacitance [Kastening et al., 1986; Mayer et al., 1993; Shi, 1996; Tanahashi et al., 1990]. Many efforts to make mesoporous carbon fiber have been made: polymer additives or catalyst was added to the carbon source and carbonized to make mesoporous carbon fiber. Among them, mesoporous carbon fibers containing catalyst have limitations due to the difficulty in elimination of catalyst [Oya et al., 1995; Freeman et al., 1988; Tamai et al., 1996; Mckee et al., 1978].

In this work, catalytic gasification with cobalt catalyst is suggested as a method for making mesopores and controlling pore size distribution of the activated carbon fiber. We studied the catalytic gasification of activated carbon fibers, where microporous

activated carbon fibers can be modified to mesoporous ones by enlarging pores, and the catalyst loaded on the activated carbon fibers, not added into carbon source, could be easily removed. In this study, the optimum conditions for catalytic gasification, composed of CO₂ pretreatment and air oxidation, and the role of each step were investigated.

EXPERIMENTAL

Commercial activated carbon fiber, CH700-20 (Kuraray), was used as a starting material and cobalt (Co) was used as a catalyst. CoCl₂ was impregnated as Co catalyst precursor. Then 1 g of activated carbon fiber was soaked into 100 ml of 0.05 M CoCl₂ aqueous solution at 80 °C for 24 hrs, and the content of Co loading was changed with the concentration of aqueous CoCl₂ solution. The immersed activated carbon fiber was dried at 110 °C for overnight and gasified. Catalytic gasification was composed of two steps, CO₂ pretreatment and air oxidation. Pretreatment temperature was increased to 500-800 °C at a rate of 10 °C/min and maintained for 30 minutes in CO₂ atmosphere. Air oxidation was followed for several tens of minutes. The flow rates of CO₂ and air were fixed as 200 ml/min/g. Prior to the gasification experiment, TGA analysis of Co catalyst-loaded carbon fiber was carried out to determine the temperature range of catalytic gasification. BET surface area and the pore volume of the gasified activated carbon fiber were analyzed by using N₂ adsorption (Micromeritics, ASAP2010). The content of Co catalyst was measured by atomic absorption.

RESULTS AND DISCUSSION

The BET surface area of the original CH700-20 was 1,711 m²/g. It mainly consisted of micropores smaller than 20 Å, where mesopore volume percentage was only 11.9%. Catalytic gasification was performed to make mesopores and cobalt, which has been known as one of the active transition metals for gasification

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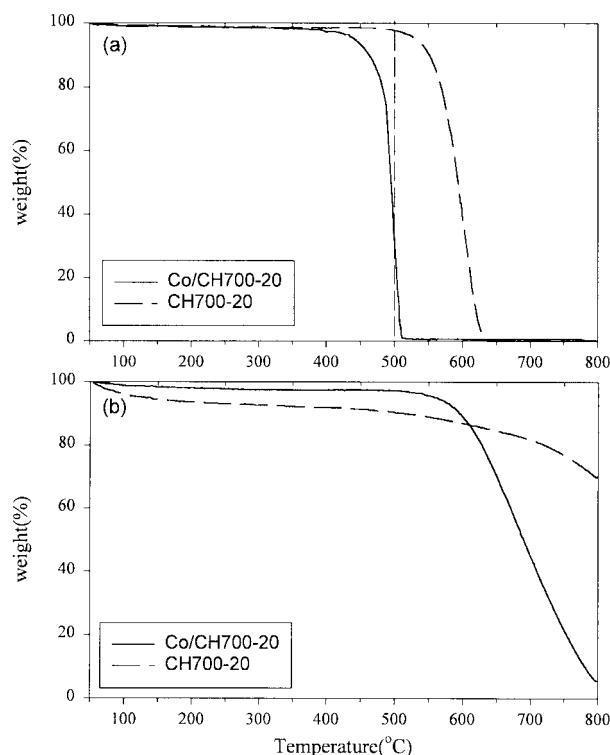


Fig. 1. TGA patterns of CH700-20 and Co-loaded CH700-20. (a) in air, (b) in CO₂

of carbon, was used as the catalyst [McKee, 1978]. And the content of Co loaded on CH700-20 was about 1 wt%.

To predict the temperature range of catalytic gasification, TGA analysis of Co catalyst-loaded activated carbon fiber was carried out in air and CO₂. Fig. 1 shows the TGA patterns of the CH700-20 and Co-loaded CH700-20 (CH700-20-Co, hereafter). In the case of air, it was observed that the weight of the CH700-20-Co began to decrease sharply around 450 °C while the CH700-20 started to burn over 550 °C. In CO₂ atmosphere, however, the weight of CH700-20-Co decreased over 600 °C at a much slower rate, while no significant reaction was observed with the CH700-20 below 700 °C. Considering the TGA patterns in air and CO₂, catalytic gasification was carried out at a temperature over 600 °C for CO₂ pretreatment and 500 °C for air oxidation.

Table 1 shows the effect of CO₂ pretreatment temperature on the formation of mesopores. CO₂ pretreatment temperature was varied from 500 to 900 °C and maintained for 30 min, fixing air oxidation temperature at 500 °C for 10 min. Later, CO₂ pretreatment time was varied from 0 to 60 min at the optimum CO₂ pretreatment temperature. Table 1 shows that mesopore volume percentage generally increases with the CO₂ pretreatment temperature, and the quantitative mesopore volume has a peak at 700 °C, while the CH700-20-Co could not retain its shape at a temperature over 700 °C. Fig. 2 shows the effect of CO₂ pretreatment time on the formation of specific-sized pores. The development of mesopores in the diameter of 3–4 nm is outstanding in this figure. So we knew that the pretreatment time had some effect on the increase of mesopores, and CO₂ pretreatment time at 650 °C had a noticeable effect on the distribution of pore size in the nanometer range.

Table 1. The effect of CO₂ pretreatment temperature and time on BET surface area and the formation of mesopores

CO ₂ pretreatment: 30 min; air oxidation: 500 °C, 10 min				
CO ₂ pretreatment temperature (°C)	Burn-off (%)	BET area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore volume %
500	22.82	1622.60	0.7823	11.00
550	26.35	1602.68	0.7749	10.93
600	17.89	1754.80	0.8540	11.96
650	22.83	1780.56	0.8808	22.83
700	37.01	1855.75	0.9452	22.03
800	33.75	1729.72	0.8614	16.60
900	93.59	-	-	-

CO ₂ pretreatment: 650 °C; air oxidation: 500 °C, 10 min				
CO ₂ pretreatment time (min)	Burn-off (%)	BET area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore volume %
0	21.57	1856.70	0.9012	25.18
30	22.83	1780.56	0.8808	22.83
60	29.53	1643.23	0.8234	27.25

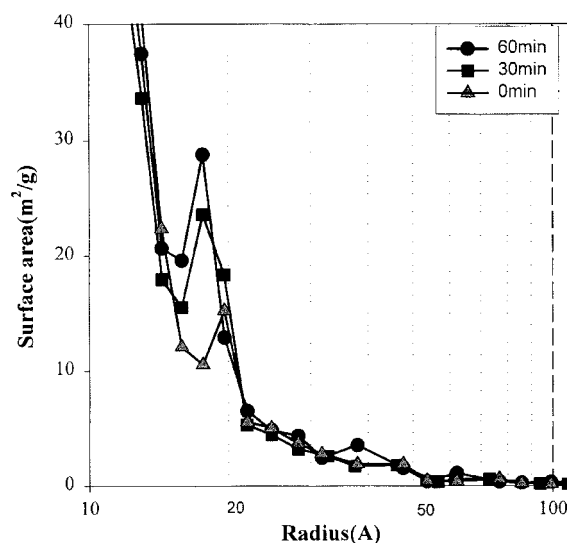


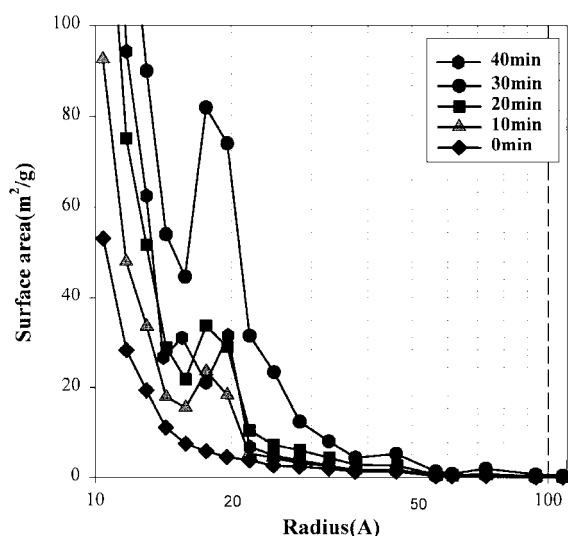
Fig. 2. Effect of CO₂ pretreatment time on PSD.

Reaction condition: ramp=10 °C/min, flow=200 ml/min/g. Pretreatment : gas : CO₂; temp.=650 °C, time=0–60 min. Oxidation : gas : air; temp.=500 °C, time=10 min

We arbitrarily set the condition for CO₂ pretreatment temperature and time as 650 °C and 30 min, hereafter. With this condition, we investigated the effect of air oxidation. As shown in Table 2, mesopore volume increases with air oxidation and has a peak for 30 minutes of oxidation where mesopore volume percentage is 56%. Mesopore volume begins to decrease after 30 minutes of oxidation due to the severe burn-off, and Fig. 3 clearly shows the development of mesopores with air oxidation. There is an obvious trade-off between burn-off and mesopore volume. Therefore, it was observed that pretreatment with CO₂ at 650 °C for 30 minutes and the following air oxidation at 500 °C for

Table 2. The effect of air oxidation time on the formation of mesoporesCO₂ pretreatment: 650 °C, 30 min; air oxidation: 500 °C

Air oxidation time (min)	Burn-off (%)	BET area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore volume %
0	5.06	1623.39	0.78127	13.81
10	22.83	1780.56	0.88080	22.83
20	40.38	1915.08	0.97699	32.25
30	33.05	1984.71	1.12350	56.42
40	77.18	1699.12	0.85816	38.08

**Fig. 3. Effect of air oxidation time on PSD.**

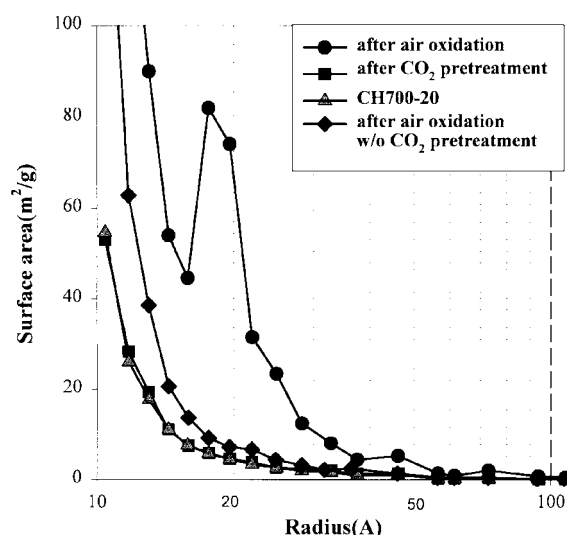
Reaction condition: ramp=10 °C/min, flow=200 ml/min/g. Pre-treatment : gas : CO₂; temp.=650 °C, time=30 min. Oxidation : gas : air; temp.=500 °C, time=0-40 min

30 minutes was suitable for catalytic gasification of CH700-20-Co. It was reported that the catalytic gasified carbon fiber became fragile [Oya et al., 1995]. The activated CH700-20-Co, however, had no damage under these conditions.

To know which step is mainly responsible for making mesopores, we investigated the two-step catalytic gasification step by step. Mesopore volume percentage and PSD after each step of catalytic gasification are shown in Table 3 and Fig. 4. It was observed that mesopores and specific-size pores were formed dur-

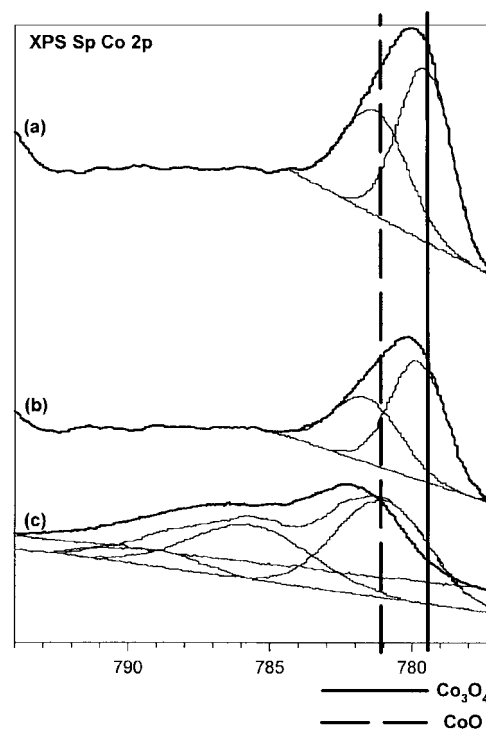
Table 3. The effect of each step on the formation of mesoporesCO₂ pretreatment: 650 °C, 30 min; air oxidation: 500 °C, 30 min

Gasification step	Burn-off (%)	BET area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore volume %
CH700-20	0.0	1711.40	0.82035	11.90
After CO ₂ pretreatment	5.06	1623.39	0.78127	13.81
After air oxidation (30 min)	33.05	1984.71	1.12350	56.42
After air oxidation for 10 min w/o CO ₂ pretreatment	39.19	1866.16	0.89984	24.30

**Fig. 4. Effect of catalytic gasification step on PSD.**

Reaction condition: ramp=10 °C/min, flow=200 ml/min/g. Pre-treatment : gas : CO₂; temp.=650 °C, time=30 min. Oxidation : gas : air; temp.=500 °C, time=30 min. Oxidation w/o CO₂ pretreatment : temp.=500 °C, time=10 min

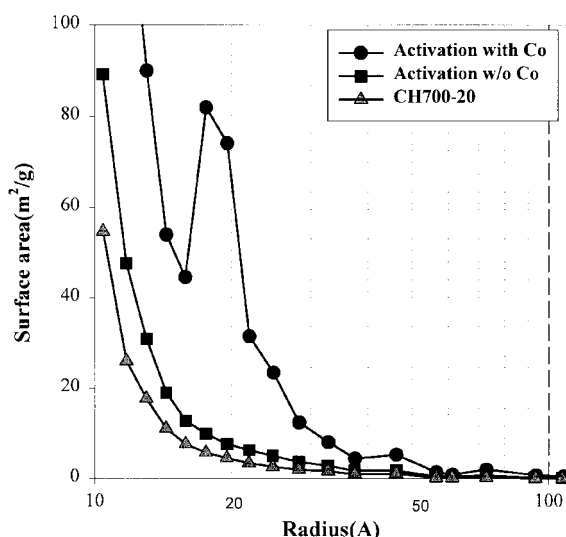
ing the air oxidation step. After CO₂ pretreatment, there was little difference in the mesopore volume percentage. On the contrary, catalytic gasification in air without CO₂ pretreatment resulted in a small increase of mesopore volume and no development of specific-size pores. Therefore, the pretreatment might have some positive effect on the formation of mesopores and it was related

**Fig. 5. Change of Co phase of CH700-20-Co after each catalytic gasification step.**

(a) After air oxidation, (b) After CO₂ pretreatment, (c) After heating step in flowing CO₂

Table 4. The effect of catalyst on the formation of mesopores

CO ₂ pretreatment: 650 °C, 30 min; air oxidation: 500 °C, 30 min				
Sample	Burn-off (%)	BET area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore volume %
CH700-20	0.0	1711.4	0.82035	11.90
Gasification w/o Co	6.50	1591.63	0.77911	22.62
Gasification with Co	33.05	1984.71	1.12350	56.42

**Fig. 6. Effect of catalyst on PSD.**

Reaction condition : Sample : CH700-20, Co (1 wt%)/CH700-20; ramp=10 °C/min, flow=200 ml/min/g. Pretreatment : gas : CO₂; temp.=650 °C, time=30 min. Oxidation : gas : air; temp.=500 °C, time=30 min

to the development of specific-size pores. Cobalt phase, which existed during the reaction, was identified from the XPS data after each step of the catalytic gasification of CH700-20-Co. It was reported that the binding energies for CoO, CoCl₂, and Co₃O₄ were 780.5 eV, 780.8 eV, and 779.6 eV, respectively, and the decrease of satellite intensity showed Co³⁺ formation [Gazzoli et al., 1996; Mekki et al., 1997]. As shown in Fig. 5, cobalt was loaded on CH700-20 as CoCl₂ and changed to Co₃O₄ through CoO during CO₂ pretreatment and existed as Co₃O₄ throughout air oxidation. From BET and XPS results, it is obvious that the formation of mesopore occurred during the air oxidation step and Co₃O₄ played an important role on making mesopores. CO₂ pretreatment step led to the decomposition of cobalt chloride and transformation to Co₃O₄. It is quite likely that the development of specific-sized pores was related to the interaction of cobalt catalyst and activated carbon fibers during CO₂ pretreatment. Therefore, the two-step catalytic gasification consisting of CO₂ pretreatment and air oxidation was appropriate for making mesopores of specific-size.

To verify the role of Co catalyst, gasification reactions of CH700-20 with and without Co catalyst were further investigated. It was reported that catalytic gasification was better than gasi-

fication without catalyst, and the catalyst accelerated the preferential formation of mesopores [Oya et al., 1995]. Table 4 and Fig. 6 show the volume percentage of mesopores and the pore size distribution. Under the same conditions, catalytic gasification results in the formation of 56% of mesopores and specific-sized pores of ca. 40 Å, while non-catalytic gasification only led to a small increase of mesopores volume without specific-sized pores. Therefore, Co catalyst was effective for making mesopores and the catalysts might participate in the formation of specific-size mesopores.

REFERENCES

- Burke, A. F. and Murphy, T. C., "Material Characteristics and the Performance of Electrochemical Capacitors for Electric/Hybrid Vehicle Applications," *Mat. Res. Soc. Symp. Proc.*, **393**, 375 (1995).
- Bard, A. J. and Faulkner, L. R., "Electrochemical Methods," John Wiley & Johns (1980).
- Freeman, J. J., Gimblett, F. G. R., Roberts, R. A. and Sing, K. S. W., "Studies of Activated Charcoal Cloth. III. Mesopore Development Induced by Phosphate Impregnants," *Carbon*, **26**, 7 (1988).
- Gazzoli, D., Occhiuzzi, M., Cimino, A., Cordischi, D., Minelli, G. and Pinzari, F., "XPS and EPR Study of High and Low Surface Area CoO-MgO Solid Solutions: Surface Composition and Co²⁺ Ion Dispersion," *J. Chem. Soc., Faraday Trans.*, **92**, 22, 4567 (1996).
- Kastening, B. and Sprinzig, S., "Electrochemical Polarization of Activated Carbon and Graphite Powder Suspensions," *J. Electroanal. Chem.*, **214**, 295 (1986).
- Mayer, S. T., Pekala, R. W. and Kaschmitter, J. L., "The Aerocapacitor: An Electrochemical Double-Layer Energy Storage Device," *J. Electrochem. Soc.*, **140**, 446 (1993).
- McKee, D. W., "The Catalyzed Gasification Reactions of Carbon," *Physics and Chemistry of Carbon*, edited by Thrower, P. A., McKee, D. W. and Chatterji, D., The Catalyzed Reaction of Graphite with Water Vapor, *Carbon*, **16**, 53 (1978).
- Mekki, A., Holland, D., Ziq, Kh. and McConville, C. F., "XPS and Magnetization Study of Cobalt Sodium Silicate Glasses," *J. Non-Cryst. Solids*, **220**, 267 (1997).
- Nishino, A., "Capacitors: Operating Principles, Current Market and Technical Trends," *J. Power Sources*, **60**, 137 (1996).
- Oya, A., Yoshida, S., Alcaniz-Monge, H. and Linares-Solano, A., "Formation of Mesopores in Phenolic Resin-Derived Carbon-Fiber by Catalytic Activation Using Cobalt," *Carbon*, **33**, 1085 (1995).
- Shi, H., "Activated Carbons and Double Layer Capacitance," *Electrochimica Acta*, **41**, 1633 (1996).
- Sperling, D., "The Case for Electric Vehicles," *Scientific American*, **11**, 54 (1996).
- Tanahashi, I., Yoshida, A. and Nishino, A., "Electrochemical Characterization of Activated Carbon Fiber Cloth Polarizable Electrodes for Electric Double-Layer Capacitors," *J. Electrochem. Soc.*, **137**, 3052 (1990).
- Tamai, H., Kojima, S., Ikeuchi, M., Mondori, J., Kanata, T. and Yasuda, H., "Preparation of Mesoporous Activated Carbon Fibers and Their Adsorption Properties," *Tanso*, **175**, 243 (1996).