

The Effect of Potassium Hydroxide on the Porosity of Phenol Resin-based Activated Carbon Fiber

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Abstract

Activated carbon fiber could be prepared at 973 K by catalytic activation using potassium hydroxide. Phenol resin fiber (Kynol) was impregnated with potassium hydroxide ethanol solution, carbonized and activated at 973 K, resulting in activated carbon fibers with different porosities. The potassium hydroxide accelerated the activation of the fiber catalytically to form narrow micropore preferentially in carbon dioxide atmosphere. The narrow micropore volume of 0.3~0.4 cc/g, total pore volume of 0.3~0.8 cc/g, mean pore width of 0.5~0.7 nm was obtained in the range of 20~50% burnoff.

Keywords : Activated carbon fiber, potassium hydroxide, catalysis, activation, narrow micropore

1. Introduction

The manufacture of activated carbon fiber (ACF) involves two main steps; carbonization and activation. Carbonization involves thermal decomposition of the carbonaceous fiber, eliminating noncarbon species and resulting in an elementary pore structure. The process is usually performed below 1273 K in the absence of any oxidizing gas. The function of activation is to enlarge the radius of the pores, which were created during the carbonization process, and to create some new porosity. The properties of raw materials and the procedure adopted for its carbonization essentially predetermine the porosity and pore size distribution. The gas activation is carried out by the gasification of the char in the temperature range 1123~1373 K. Carbon dioxide and water vapor are usually used as a gasification agent.

The use of ACF as an adsorbent is now well recognized. Although their adsorbent properties are quite satisfactory, their use is often limited due to weak mechanical properties and processing cost. Generally, the activation process is carried out above 1173 K. It would be of interest to operate at lower temperature in order to maintain a higher strength of the fiber and also to reduce the processing cost. Some attempts have already been done with rayon fibers as precursors [1-3]. The rayon fibers are impregnated with different salts (Zn, Al, etc...), carbonized and activated by carbon dioxide. This combination of chemical and gas activation leads to interesting results [4, 5].

The aim and objective of this work is to activate thermo-setting phenol resin fibers in presence of potassium hydroxide. Phenol resin fiber was doped with potassium hydroxide which are known to act as catalysts during gasifi-

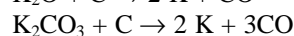
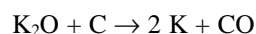
cation. Then, activation at lower temperature – 1073 K or less – may be expected. It is reported that chemical reactions take place during the chemical activation process as follows. Ehrburger et al. suggested three steps of reaction during the activation process with potassium hydroxide [6].

1) Formation of potassium carbonate [7]:



2) Reaction of potassium carbonate with the char close to 750 K, resulting in the formation of carbon dioxide and complex salt (C-O-K) [8].

3) Reaction of potassium carbonate and potassium oxide with carbon above 920 K, leading to the formation of carbon monoxide [7].



2. Experimental

2.1. Sample preparation

The catalyst for carbon activation was the reagent grade potassium hydroxide. Potassium hydroxide was dissolved in ethanol and then commercial phenol resin fiber (Kynol fiber KF-0270, Nippon Kynol Co.) was soaked in that solution at boiling point for 3 hrs. After soaking, the solvent ethanol was removed from the fiber by filtration, followed by drying at 393 K for 1 hr. The resulting fiber was heated up to 973~1173 K at a rate of 10 K/min in argon atmosphere and kept for 0.25~2 hrs to produce carbon fiber (CF). Two CFs

Table 1. Carbonization yield.

Sample	Carbonization temp. [K]	K contents in CF [wt.%]	Carbonization yield* [wt.%]
CF0	973	—	58.8
CF0	1173	—	57.0
CF1	973	6.6	61.1
CF1	1173	5.7	58.3
CF2	973	0.2	58.1
CF2	1173	0.1	57.8

*potassium free basis

with potassium contents of 6.6 wt.% (CF1) and 0.2 wt.% (CF2) were prepared together with the CF without potassium (CF0) as a reference (Table 1). CFs carbonized at 973 K were activated by carbon dioxide at 973~1173 K. The number following these symbols, such as 973 and 1173, means the activation temperature. Carbonization and activation was performed in a tubular furnace.

2.2. Property analysis

The potassium content in the fiber was measured by using atomic absorption spectroscopy. The adsorption of nitrogen (77 K) and carbon dioxide (273 K) was performed in a volumetric apparatus in order to characterize the pore structure. Specific surface areas (BET equation), total pore volumes (Gurvitsch rule), and total micropore volumes (α_s plot) were calculated from the nitrogen adsorption isotherms. Narrow micropore volumes (Dubinin-Radushkevich equation) and mean pore width (Dubinin equation) was obtained from the adsorption isotherm of carbon dioxide.

3. Results and Discussion

3.1. The effect of potassium hydroxide on carbon

Table 1 shows potassium content of CF and carbonization yield. Potassium did not contribute considerably for the carbon yield. The potassium hydroxide-phenol resin fiber reactions was accompanied by some vaporization of potassium metal into the gas stream. It is known that potassium can enter into all carbon forms except graphitizable carbon of low heat treatment temperature [9]. Most of the prepared ACF were black in color, but some parts were bronze-copper red or steel-blue. According to Fredenhagen and Cadenbach, bronze-copper red part is KC_8 compounds and steel-blue part is KC_{24} compounds [10]. It is thought that potassium forms several types of intercalation compounds in the micro-crystalline graphite fraction of ACF. Some samples activated at 1173 K was weak in mechanical strength and was reduced to ashes partly. Potassium was responsible for the breakup of

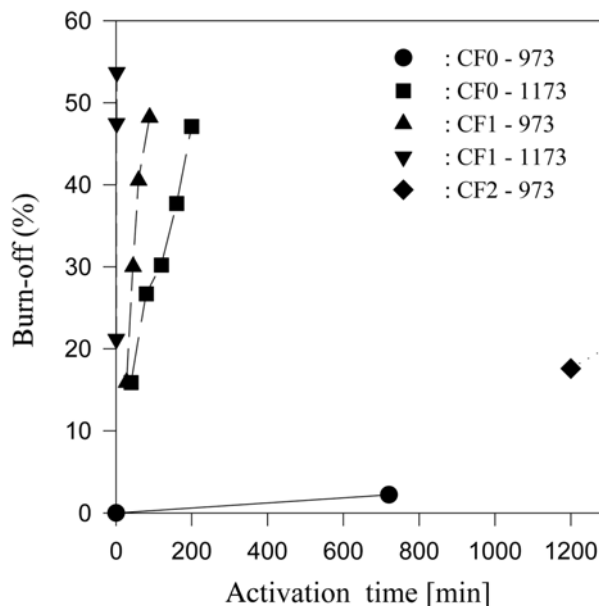


Fig. 1. The effect of activation time on burn-off.

the carbon structure as described previously [11].

3.2. Relationship between activation time and burn-off

Fig. 1 shows the relationship between burn-off and activation time of carbon fibers. The activation rate of CF0 was very slow at 973 K, but those of CF1 and CF2 were high. The activation rates of CF1 and CF2 at 1173 K were too high to activate all of the sample homogeneously. These results show that potassium accelerates the activation process remarkably. The potassium made lower activation temperature and the activation rate increased according to the increase of potassium contents. The reaction of carbon fiber with CO_2 is endothermic and potassium helps to produce substantial gasification rates at temperature below 1173 K.

3.3. Pore structure

As CF1-1173 and CF2-1173 were not activated homogeneously, it is not proper to discuss on pore structure of those samples. CF0-973 was not activated at 973 K. As a result, discussion will be focused on the pore structure of CF0-1173, CF1-973 and CF2-973.

The pore characteristics are shown in Fig. 2~Fig. 7. Fig. 2 shows the relationship between total pore volume and burn-off. The density of liquid nitrogen at 77 K was considered as 0.808 g/cc for a calculation basis to get the values of total pore volume. The total pore volume of CF0 increased remarkably with the extent of the activation. Such activation behavior was in contrast to the mild total pore development found for CF2. These observations indicate that potassium

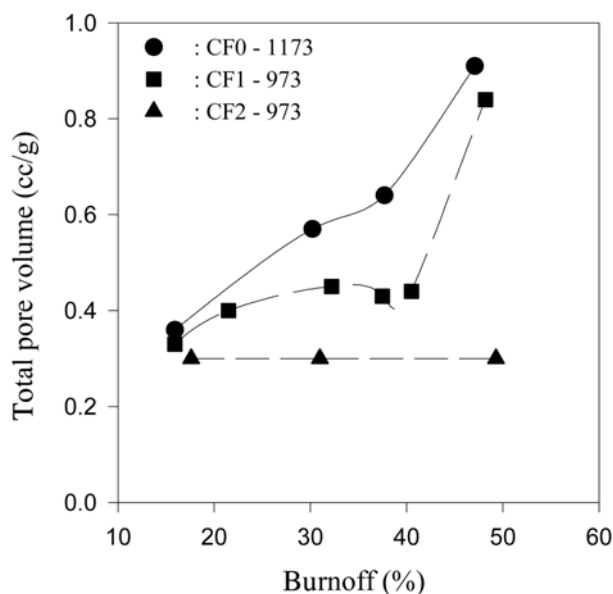


Fig. 2. The effect of burn-off on total pore volume.

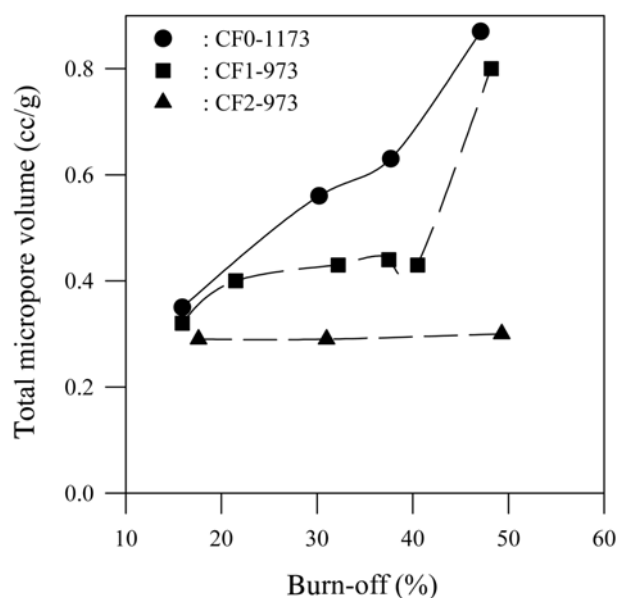


Fig. 4. The effect of burn-off on total micropore volume.

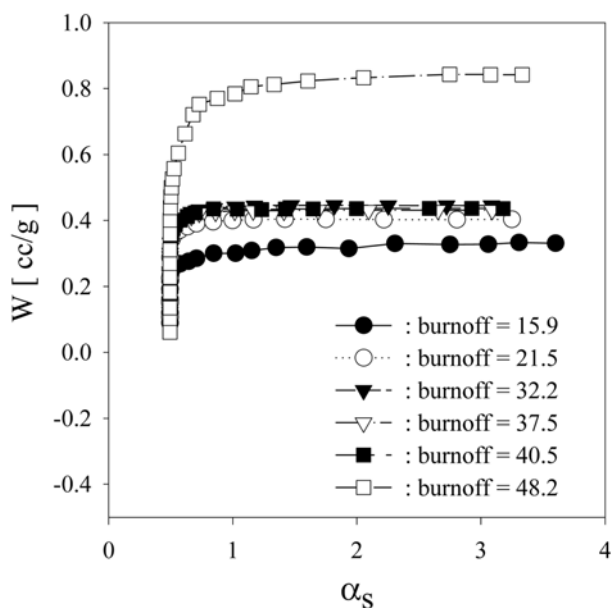


Fig. 3. A representative α_s plot (CF1-973).

plays an important role in the activation rate and in controlling the porous texture development of the phenol resin based activated carbon fibers. The potassium influenced favorably narrow micropore formation as also found by coal activation [12].

Fig. 3 shows the α_s plot of CF1-973. The standard isotherm used was what Rodriguez-Reinoso *et al.* proposed [13]. The α_s plot can provide the information about the micropore and external surface containing the mesopore and macropore. As the data corresponding to α_s in the range of 1.5~3.5 have shown good linearity, they were fitted to get

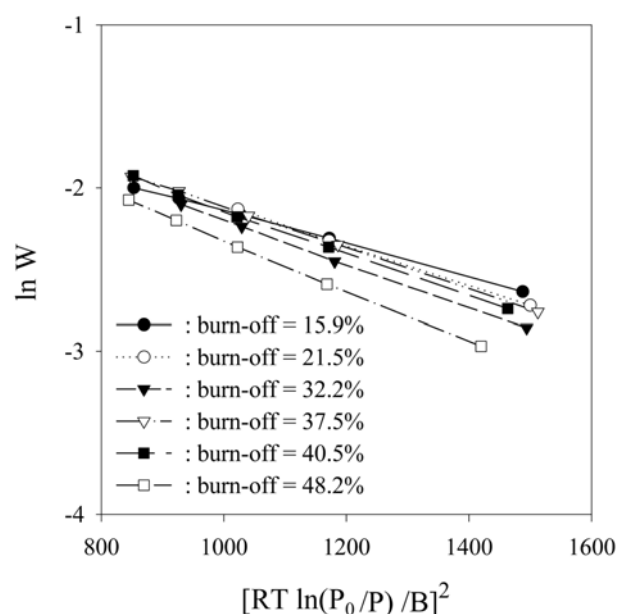


Fig. 5. A representative Dubinin-Radushkevitch plot (CF1-973).

the slop of linear regression line and the intercept of Y-axis, resulting in total micropore volume.

Fig. 4 shows the change of total micropore volume with the proceeding of activation. The total micropore volume in CF2 was remained unchanged in spite of proceeding of activation in contrast to the increase in CF0. This extraordinary phenomenon is thought to take place as follows: the formed micropores are removed by the burn-off, but simultaneously the micropores reform. No change in the size and volume of micropores means an equilibrium state is

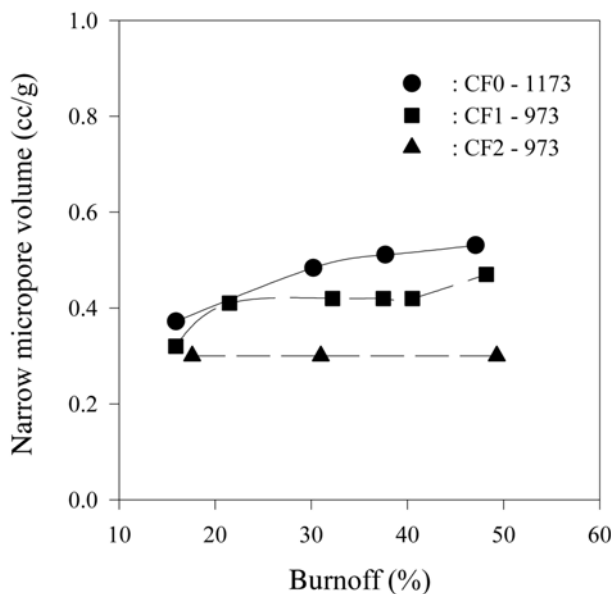


Fig. 6. The effect of burn-off on narrow micropore volume.

reached between both processes.

Fig. 5 shows Dubinin-Radushkevich plot of CF1-973. According to Dubinin-Radushkevich equation, narrow micropore volume was calculated from the intercept. Fig. 6 shows change of narrow micropore volume with the proceeding of activation. The increase of narrow micropore volume according to burn-off increase is less than that of total pore volume.

Fig. 7 shows change of mean pore width with the proceeding of activation. The activation in CF0 increased the radius of micropores. A narrower micropore is formed in potassium impregnated CF when compared with unimpreg-

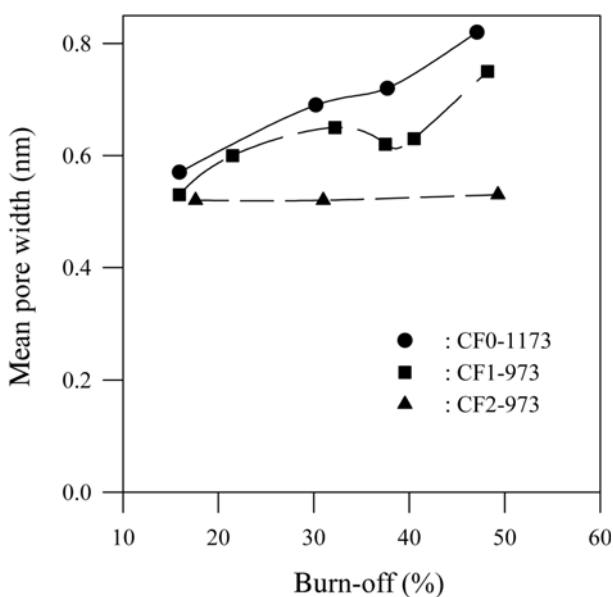
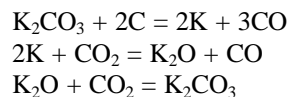


Fig. 7. The effect of burn-off on mean pore width.

nated CF. Some papers discussed pore formation mechanism by the use of catalytic activation. Marsh *et al.* carbonized and activated phenolic resin dispersing the finely divided nickel and iron [14]. They suggested a formation mechanism of the porous structure as follows: The finely dispersed metal particles coalesce to larger particle at carbonization and activation stages. The activation is carried out preferentially nearby the vicinity of the resulting particles, leading to formation of meso- and macropores. As a result, micropore volume in the catalytically activated carbon is smaller than that in a conventionally activated one without catalyst. Oya *et al.* prepared mesoporous ACF by catalytic activation using cobalt [15]. The present work gave dissimilar results. The potassium hydroxide tends to produce narrow micropore preferentially at a low amount of potassium hydroxide content such as 0.2 wt.%. Fine potassium particles tend to coalesce more easily in the CF containing a larger amount of potassium, and thus leading to more larger pore width.

The catalysis mechanism is thought as follows. The potassium hydroxide reacts with carbon dioxide resulting in potassium carbonate. The fact that vaporization of potassium metal has often been observed to accompany the C-CO₂ reaction when catalyzed by potassium metal carbonates, suggests that an oxidation-reduction cycle involving the intermediate formation of free potassium metal might be occurring. A possible cycle might consist of the following sequential steps [12]:



4. Conclusion

Activated carbon fiber could be produced at lower temperature such as 973 K by potassium catalytic activation in carbon dioxide atmosphere. Potassium hydroxide don't help considerably on the carbonization yield, but it accelerates the activation of the phenol resin based carbon fiber catalytically to form narrow micropore preferentially.

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