



Phenol Resin-Based Activated Carbon Fibre Catalytically Gasified by Potassium Hydroxide†

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Phenol resin-based activated carbon fibre could be prepared at 973 K by catalytic activation using potassium hydroxide. Phenol resin fibre was impregnated with ethanolic solution of potassium hydroxide, 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.

Key Words: Phenol resin, Activated carbon fiber, Potassium hydroxide, Catalysis, Activation, Narrow micropore.

INTRODUCTION

The use of activated carbon fibre (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. The manufacture of activated carbon fibre involves two main steps, *i.e.*, carbonization and activation. Carbonization involves thermal decomposition of the carbonaceous fibre, 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 above 1173 K. Carbon dioxide and water vapour are usually used as a gasification agent.

It would be of interest to operate at lower temperature in order to maintain a higher strength of the fibre and also to reduce the processing cost. Some attempts have already been done with rayon fibres as precursors^{1,2}. The rayon fibres 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^{3,4}.

The aim and objective of this work is to activate thermo-setting phenol resin fibres in presence of potassium hydroxide.

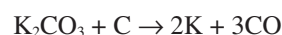
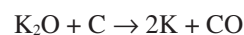
Phenol resin fibre was doped with potassium hydroxide which are known to act as catalysts during gasification. Then, activation at lower temperature-1073 K or less - may be expected. It is reported that chemical reactions take place during the chemical activation process as follows. Ehrburger *et al.*⁵ suggested three steps of reaction during the activation process with potassium hydroxide.

(a) Formation of potassium carbonate⁶:



(b) Reaction of potassium carbonate with the char close to 750 K, resulting in the formation of carbon dioxide and complex salt (C-O-K)⁷.

(c) Reaction of potassium carbonate and potassium oxide with carbon above 920 K, leading to the formation of carbon monoxide.



EXPERIMENTAL

Sample preparation: Reagent grade potassium hydroxide was used as the catalyst for carbon activation. Potassium hydroxide was dissolved in ethanol and then commercial phenol resin fibre (Kynol fibre KF-0270, Nippon Kynol Co.) was soaked in that solution at boiling point for 3 h. After soaking, the solvent ethanol was removed from the fibre by filtration, followed by drying at 393 K for 1 h. The resulting fibre was

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heated up to 973-1173 K at a rate of 10 K/min in argon atmosphere and kept for 0.25-2.00 h to produce carbon fibre (CF). Two carbon fibres with potassium contents of 6.6 wt. % (CF1) and 0.2 wt. % (CF2) were prepared together with the carbon fibre without potassium (CF0) as a reference (Table-1). Carbon fibre was 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 were performed in a tubular furnace.

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

*Potassium free basis.

The potassium content in the fibre was measured by using atomic absorption spectroscopy. The adsorption of nitrogen (77 K) and carbon dioxide (273 K) was performed in a volumetric adsorption apparatus in order to characterize the pore structure. Specific surface areas (BET equation), total pore volumes (Gurvitsch rule) and total micropore volumes (as 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.

RESULTS AND DISCUSSION

Effect of potassium hydroxide on carbonization: Table-1 shows the potassium content in carbon fibre and carbonization yield. Potassium did not contribute considerably for the carbonization yield. The potassium hydroxide-phenol resin fibre reaction is accompanied by some vapourization of potassium metal into the gas stream. It is known that potassium can enter into all forms of carbon except graphitizable carbon of low heat treatment temperature⁸. Most of the prepared activated carbon fibre were black in colour, 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} compounds⁹. It is thought that potassium forms several types of intercalation compounds in the microcrystalline graphite fraction of activated carbon fibre.

Some samples activated at 1173 K was weak in mechanical strength and was transformed to ashes partly. Potassium was responsible for the breakup of the carbon structure as reported earlier¹⁰.

Relationship between activation time and burn-off:

Fig. 1 shows the relationship between burn-off and activation time of carbon fibres. The activation rate of CF0 was very slow at 973 K, but those of CF1 and CF2 were relatively 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.

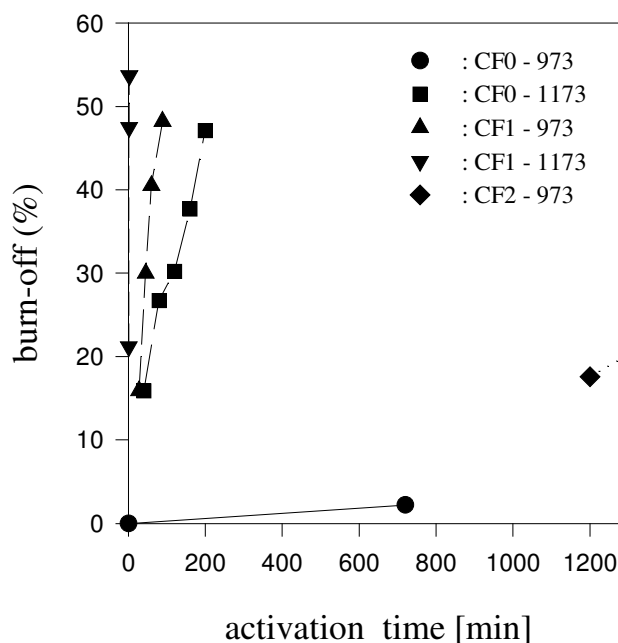


Fig. 1. Effect of activation time on burn-off

The potassium made activation temperature lower and the activation rate increased according to the increase of potassium contents. The reaction of carbon fibre with CO_2 is endothermic and potassium take part in carbon gasification at temperature below 1173 K.

Pore structure characterization: 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 Figs. 2-7. 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 behaviour was in contrast to the mild total pore development found for CF2. These observations indicate that potassium plays an important role in the activation rate and in controlling the porous texture development of the phenol resin based activated carbon fibres. The potassium influenced favorably narrow micropore formation as also found by coal activation¹¹.

Fig. 3 shows the α_s plot of CF1-973. The standard isotherm used was what Rodriguez-Reinoso *et al.*¹² proposed. 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 the slope 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

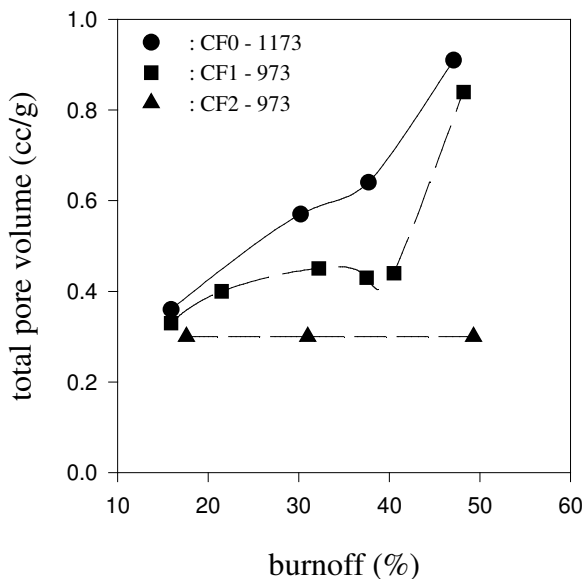


Fig. 2. Effect of burn-off on total pore volume

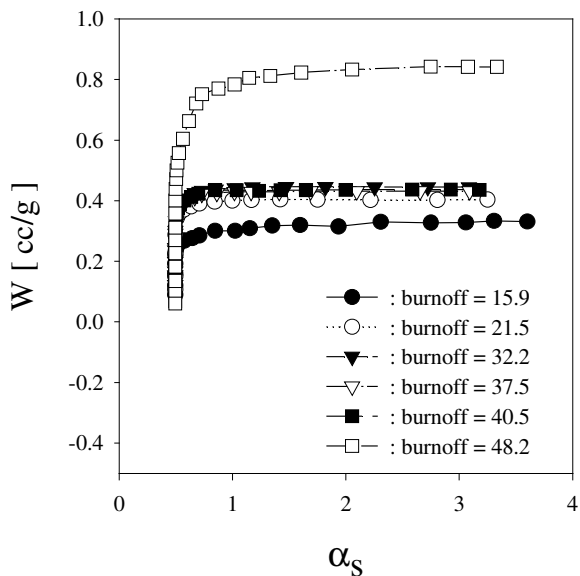


Fig. 3. A representative α_s plot (CF1-973)

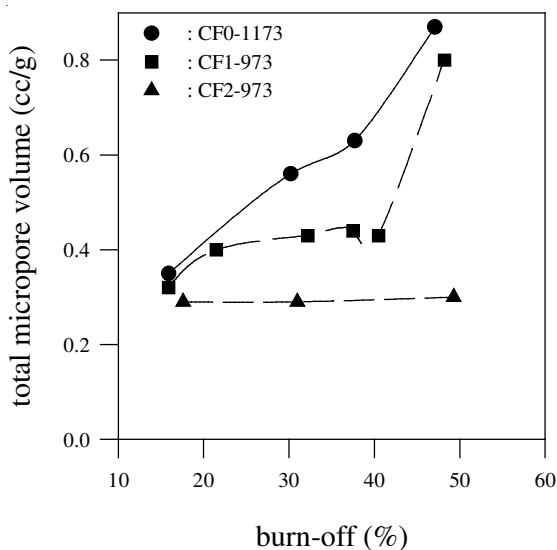


Fig. 4. Effect of burn-off on total micropore volume

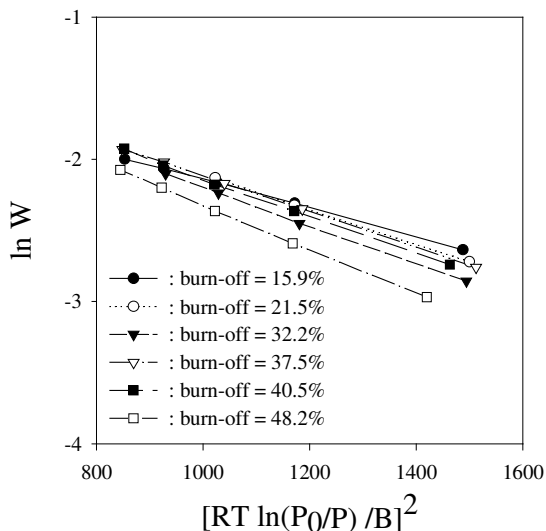


Fig. 5. A representative Dubinin-Radushkevitch plot (CF1-973)

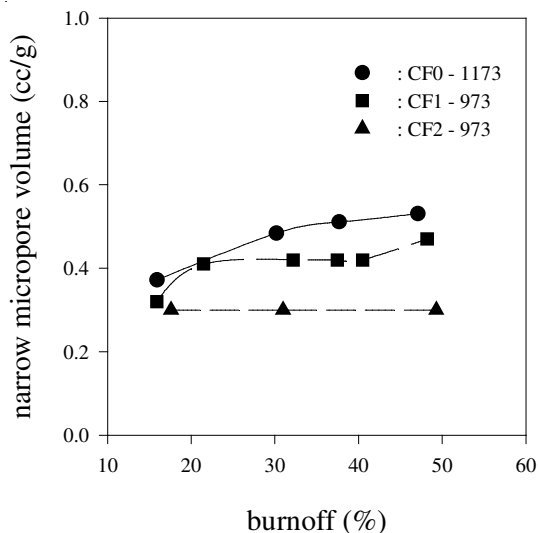


Fig. 6. Effect of burn-off on narrow micropore volume

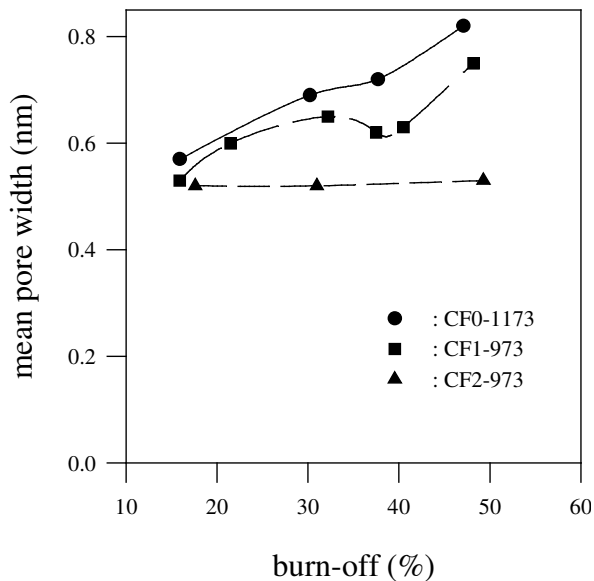


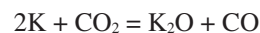
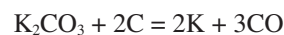
Fig. 7. Effect of burn-off on mean pore width

the micropores reform. No change in the size and volume of micropores means an equilibrium state is reached between both processes.

Fig. 5 shows the Dubinin-Radushkevich plot of CF1-973. According to Dubinin-Radushkevich equation, narrow micropore volume was calculated from the Y-axis intercept. Fig. 6 shows the 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 the 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 carbon fibre when compared with unimpregnated carbon fibre. Some papers discussed pore formation mechanism by the use of catalytic activation. Marsh and Rand¹³ carbonized and activated phenolic resin dispersing the finely divided nickel and iron. 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.*¹⁴ prepared mesoporous activated carbon fibre by catalytic activation using cobalt. 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 carbon fibre 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 vapourization of potassium metal has often been observed to accompany the C-CO₂ reaction when catalyzed by potassium carbonate, 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 steps¹¹:



Conclusion

Activated carbon fibre 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 fibre catalytically to form narrow micropore preferentially.

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