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Steam activation of a phosphorous-containing phenolic resin-based carbon fiber

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A chemical filter is a device to purify air by the action of active reagents loaded on supports, and is now popularly used in clean rooms where ultra large scale integrated circuits (ULSI) are manufactured [1]. Activated carbon fibers are the commonly used supports for such purposes, as they have significantly large surface areas. The present authors have been interested in developing suitable chemical filters for removing alkaline gases such as ammonia based on activated carbon fibers. Impregnation is a popular method for loading active reagents, which includes dipping the fibers into solutions of the reagents followed by drying. However, this method has been pointed out as having the following shortcomings: one is the insufficient penetration of the reagent's solution inside the pores and another is the blockage of pores by deposits of the reagents, both of which lead to a decrease in the effective surface areas of the fibers. The authors believe that these shortcomings may be overcome by preparing a phosphorus-loaded activated carbon fiber by carbonizing and activating the phenolic resin that contains atomically dispersed phosphorus atoms in the network structure of the resin.

A phosphorus-containing phenolic resin has been developed by the present authors and has been found to show an anomalous graphitizing behavior, i.e. promotion of graphitization by phosphorus was observed when heat treated at 2800°C [2], while phosphorus had earlier been recognized as an inhibitor for graphitization [3, 4]. This unusual behavior probably resulted from the atomically dispersed states of phosphorus in our resin, however we have not clarified the uniqueness of the introduced phosphorus yet. Apart from the graphitization, our phosphorus-containing resin gives us an expectation of finding unusual behavior in the activation of the carbon. In this letter, we report the activation behavior of the phosphorus-containing phenolic resin-based carbon fiber under steam.

Heating a mixture of tetrakis (hydroxymethyl) phosphonium sulfate (THSPS, 80% aq. soln.), formaldehyde and phenol, in the molar ratio 0.1:0.75:1.0 at 85°C for 1h gave the starting resin for the phosphorus-containing carbon studied in this study.

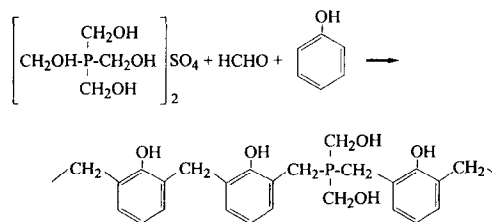


Fig. 1 Reaction scheme for preparing the P-containing phenolic resin.

An expected chemical structure of the resin is presented in Figure 1. Details are described elsewhere [2]. The resin was spun and then cured by keeping the raw fibers in the hardener solution, mainly consisting of formaldehyde, at 95°C for 8h. The carbonized sample was prepared by heating the resin at a heating rate of 5°C/min to 800°C in a nitrogen flow and then keeping it at this temperature for 30 min. Activation was successively performed in the same furnace without cooling after carbonization, by switching the gas from nitrogen to steam in a nitrogen carrier for predetermined periods. The resulting fibers are called as P-ACF. The reference samples (ref-ACF) were obtained by applying the same procedures to a novolac-type phenolic resin fiber.

Figure 2 shows the variation in burn-off with activation time. The phosphorus-containing carbon fiber prepared here is more reactive for activation than the reference carbon fiber, and the difference is particularly obvious during the initial stages of activation. Regarding the fact that phosphorus had been revealed to be an inhibitor for activation or oxidation [5], the promoting effect observed here is a quite interesting finding. We do not yet understand these differences in the behavior of phosphorus and consider this to be an interesting aspect of the present material.

Nitrogen adsorption and desorption isotherms measured at 77K are presented in Figure 3. The isotherms were classified as type I, which is commonly seen for microporous adsorbents. With increasing burn-off (B.O.) level of ref-ACF sample, as shown in

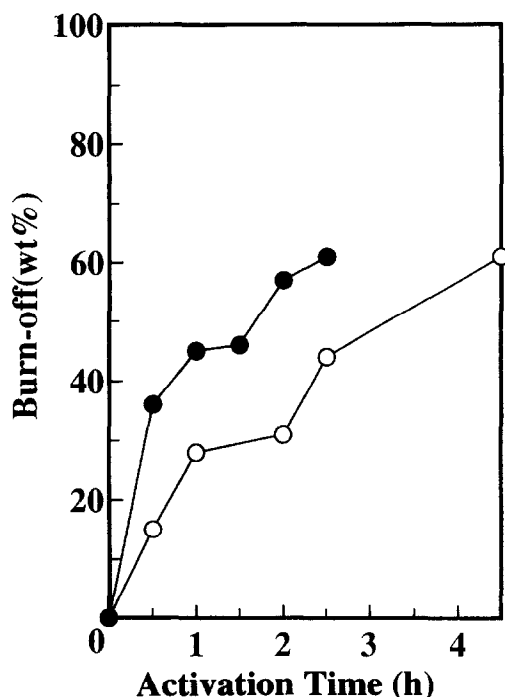


Fig. 2 A plot of the burn-off level of reference (O) and P-containing carbon fibers (●) as functions of activation time.

Fig. 3a, the amount of adsorbed nitrogen at lower P/P_0 increased and the onset of multilayer condensation in mid- to higher P/P_0 ranges was observed.

In the case of P-ACF, shown in Fig. 3b, the

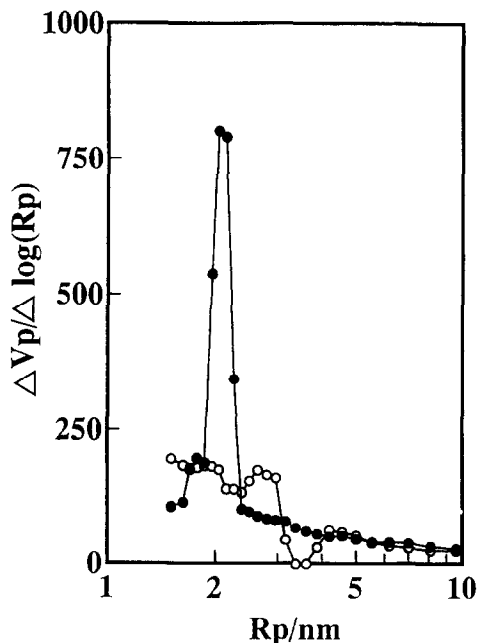


Fig. 4 Pore radius distribution functions calculated with DH theory. O: ref-ACF with the burn-off level of 61 wt %; ●: P-ACF with burn-off level of 57 wt %.

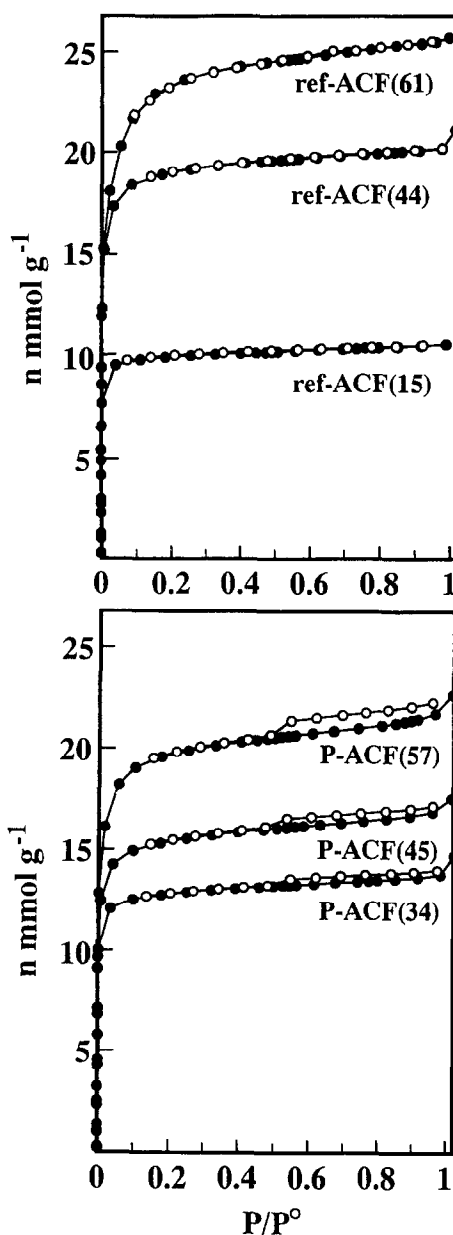


Fig. 3 Nitrogen adsorption and desorption isotherms of the activated carbon fibers. The figures in parentheses indicate the burn-off level.

increase in the micropore volume with activation was not so large as for ref-ACF, however the hysteresis loop became larger with activation. These are characteristic features of mesoporous media.

Figure 4 compares the pore radius distribution curves in the mesopore region analyzed by the Dollimore-Heal method. The PACF (57 wt % B.O.) had a narrow pore size distribution at a radius of 2 nm, while the ref-ACF (61 wt % B.O.) showed a simply decreasing curve toward the larger pore size region. A few authors have commented on the formation of mesopores by the activation of carbons loaded with

phosphorus compounds, however no papers illustrated the mesopore distribution curves of these materials [6,7]. Possible explanations for the formation of mesopores in our case are due to catalytic action of the introduced phosphorus, or to changes in the structure of the phenolic resin introduced by phosphorus. We are undertaking investigations to clarify the effect of phosphorus on the formation of mesopores.

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