A COMPARATIVE STUDY OF TRANSITION METAL-
CONTAINING ACTIVATED CARBON FIBERS

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Introduction

Carbonaceous porous carbon fibers are attractive for a variety of filtration applications. Past studies have shown that the performance of metal or metal-containing particles in the formation of pore structures strongly depends on the chemical nature of the metal or metal-containing particle and the carbon precursor [1-4]. The objective of this work is to compare the effect of different metal precursors and production processes on the final properties of pitch-based activated carbon fibers. These include surface area, specific pore sizes and distribution, properties which can be useful in adsorbing specific chemicals.

In this project optimum processing parameters were determined for Ag-, Co- and Pd-containing ACFs. The procedure used to prepare the Ag-containing ACFs and some initial results were reported previous publications [1,5]. Additional properties of the Co- and Pd-containing ACFs are presented in reference [2].

Experimental

The isotropic pitch precursors (S.P. 230°C) used in this study were supplied by Professor S. K. Ryu of Chungnam National University in Daejeon, Korea. Three salts (AgNO₃, Co(acac)₂ and Pd(acac)₂) were ground into powders and the smallest particles (≤38µm) were mixed into an isotropic pitch, yielding precursors that contained 1.0 wt% of a metal or a mixture of metals. The mixed precursors were melt spun into round and trilobal fibers, thermally stabilized in air, carbonized, and finally activated in a CO₂ atmosphere at 900°C [1, 5]. Stabilization temperatures and times were estimated by TGA analyses performed in an air atmosphere (heating rate 0.5 deg/min, 50-500°C). According to TGA analysis, at lower temperatures the fiber weight increases as oxygen is incorporated into the structure and then at higher temperatures the weight decreases as the fibers begin to decompose. Thus, the temperature/time profile used to stabilize the fibers must encompass the region where the mass of the fiber increases and avoid, as much as possible, the region where mass begins to decrease. As might be expected these regions vary with precursor composition. Because of this, the optimum stabilization temperature/time profile must be determined for each type of fiber.
The notations in all tables and plots (KU, KA, KC and KP) indicate that Korean isotropic pitch (K) was either unmixed (U) or mixed with AgNO$_3$ (A), Co(acac)$_2$ (C) or Pd(acac)$_2$ (P), respectively. Notation KAC indicates that Korean isotropic pitch (K) was mixed with mixture of Ag and Co salts with Ag/Co ratio 1:1.

The surface morphology of the fibers as well as the size and dispersity of the metal/metal containing particles at each step of preparation were determined by inspecting a number of fibers using an Hitachi FE SEM 4700. The surface properties of the ACFs were determined by measuring nitrogen adsorption isotherms obtained at -196°C with a Micromeritics ASAP 2020 instrument. Details of the procedure are described in [5]. A Scintag 2000 XDS $\theta/\theta$ powder diffractometer was used to analyze the pitch mixtures prior to melt spinning and the fibers after each process step. This allowed the crystalline structure of Ag, Co and Pd compounds to be monitored after each step preparation.

**Results and Discussion**

The optimum spinning temperature varied with pitch composition and fiber shape. The melt spinning temperature for round fibers from the pure Korean pitch samples was found to be 246±1°C. By comparison, the melt-spinning temperature for round fibers from the Korean pitch containing 1 weight % Ag, Co, Pd or their mixtures was 253±1, 234±1 and 249±2°C, respectively. Spinning temperatures for the mixtures were intermediate between those for individual metals, i.e. 248 and 242±1°C for 1:1 Ag/Co and 1:1 Co/Pd-containing mixtures, respectively. The spinning temperatures for trilobal fibers were about 2 - 13°C lower than those for round fibers spun from the same pitch.

Over 500 SEM images of the surfaces and cross sections of the CFs and ACFs produced in this study were obtained. The images and data presented in Figs. 1 and 2 are representative of this large body of data. These SEM images give important information concerning the particle size and distribution in CFs before and after activation, as well as the surface morphology and the initiation of porosity in ACFs. The images also allow fiber quality and size to be carefully monitored at each step in the process. SEM inspection of the carbonized fibers (Fig.1) showed that the silver and palladium particles were smaller than the cobalt particles, even though the size of the initial particles and the mixing procedure were identical [2].

Figs. 3 and 4 show the pore size distributions for the ACFs produced in this study. In the case of the unmixed fibers, porosity (mainly microporosity) can only be created by degradation and/or volatilization processes. Micropores are observed in the Ag- and Pd-containing fibers, but these also contain larger pores. Activation created smaller micropores and larger mesopores in the Pd-containing fibers than in the pure or silver-containing fibers. By comparison, the porosity of the cobalt-containing ACFs was larger and similar to that observed in meso-/macroporous materials. The trends observed for trilobal CFs and ACFs produced from the pure and metal-containing pitches were similar to those observed for the round fibers, when equivalent cross-sections are compared.
The X-ray analyses shown that the Ag ion is reduced and the Pd ion is partially reduced either prior to or during carbonization. However, this was not observed for the Co-containing fibers. The metal peak in the X-ray pattern increases with activation time for Pd-containing fibers and decreases for Ag-containing fibers, indicating a corresponding change in relative concentration during activation. By analyzing these results we can begin to understand how pores form during the activation process, but many questions still remain.

One complicating factor often overlooked is that formation of porosity during activation is highly dependent on the heat-treatment conditions employed to form the CF. For example, the conditions used to stabilize the as spun fiber, affect the particle size and activation behavior of the fiber. To demonstrate this point, one set of Pd-containing fibers was incompletely stabilized. This caused the particles to agglomerate during carbonization. These larger particles, combined with the incomplete stabilization of the carbon, resulted in the formation of a non-uniform pore structure and large macropores in the fiber surface during activation.
Interestingly, the results for ACFs formed from isotropic pitches containing two metal salts differed from those reported earlier for ACFs prepared from phenolic resins [6]. Fig. 3 and Table 1 show activation and surface analysis results for Ag/Co-containing ACFs. The activation rates for these fibers appear to be intermediate between those for the Ag- and Co-containing ACFs. The Ag/Co-containing ACFs do not appear to form micropores at lower burn off values. However, micropores as well as meso-/macropores develop with increasing of activation time. At high degrees of burn off the Ag/Co-containing ACFs show properties that are characteristic of both Ag-containing and Co-containing ACFs. At high degrees of burnoff the Ag/Co-containing ACFs have high specific and mesopore surface areas and significantly higher micropore and meso-/macropore volumes.

Figure 3. Pore size distribution for Ag-, Co- and Pd-containing ACFs: a - Horvath-Kawazoe differential pore volume plot, b - BJH desorption dV/dw pore volume plot.

Figure 4. Pore size distribution of Ag-, Co- and Ag/Co-containing ACFs
Table 1. Activation conditions and physical properties of ACFs

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Act. time</th>
<th>BO %</th>
<th>BET SSA</th>
<th>( V_{total} )</th>
<th>Mesopore ratio</th>
<th>Average pore size^2</th>
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<tr>
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</table>

1 Calculated using BET model
2 Calculated using BJH model
3 Calculated as a ratio of surface area of mesopores to BET SSA

Conclusions

The optimum procedure needed to melt spin and stabilize transition metal-containing fibers depends on the metal additive and the cross section of spinneret capillary. The particle size and distribution, the formation of pore structure and the pore size distribution in transition metal-containing CFs and ACFs is strongly dependent on the chemical nature of the metal additive. Silver nitrate yielded an enlargement in micropores and the formation of small mesopores over a narrow range. The addition of cobalt (II) acetylacetonate catalyzed the activation process, creating large mesopores and macropores in the resulting ACFs. Adding palladium (II) acetylacetonate led to the formation of both small micropores and larger mesopores. However, the average pore size was found to be greater than that for the silver-containing ACFs. Heat-treatment conditions for the fibers during the production process (i.e. stabilization and activation) affect both the particle size and the pore structure in the final activated fibers. The activation mechanism seems to be different for all three metals resulting in different pore size distribution.

Acknowledgements

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References