THE EFFECT OF PITCH COMPOSITION ON THE ADSORPTION BEHAVIOR OF Pd-DOPED ACF

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Recent studies indicate that metal-containing activated carbon fibers (ACF) are promising adsorbents for hydrogen storage applications. In these studies, Pd compounds were added to a petroleum precursor and formed into ACFs. Results showed that the molecular composition of the pitch had a significant affect on critical characteristics of the ACFs, such as pore size and Pd particle size. In an ongoing Department of Energy project, we are testing pitch precursors with carefully controlled chemical compositions in order to develop an optimum precursor for hydrogen storage applications. A low softening point pitch made by Marathon Oil is being separated into narrow molecular weight fractions using a dense gas extraction (DGE) process. In the current series of tests the heavier portion of the extracted pitch was used to prepare both undoped and Pd-doped carbon fibers. These fibers were activated over a range of temperatures to determine the effect of temperature and pitch composition on ACF properties. Lower activation temperatures resulted in increased microporosity (desirable for hydrogen adsorption) for all Pd-doped pitch precursors. Comparing ACFs produced from various DGE-extracted pitches showed that even small quantities of mesophase-forming components inhibited activation and significantly reduced microporosity. Additional DGE pitch fractions are now being tested to further refine the optimum composition for hydrogen storage applications.

Introduction

Recent studies suggested that hydrogen spillover in metal-containing activated carbon fibers leads to enhanced hydrogen adsorption compared to non-promoted activated carbons, thus opening a route for preparation of promising adsorbents for hydrogen storage applications (Gallego et al. (2005)). They also show that the chemical composition of both the metal and the pitch precursors used to prepare the activated carbon fibers can significantly affect the final pore structure of the fibers and, therefore, the hydrogen adsorption behavior (Basova et al. (2004), Basova and Edie (2004), Basova et al. 2005)). In the current study pitch precursors with controlled chemical compositions are being produced by dense gas extraction. These precursors are then being formed into both pure and metal-containing activated fibers in order to determine the pitch composition that optimizes hydrogen adsorption.

Experimental

Several pitch precursors were used to prepare the activated carbon fibers for this study. A set of control fibers was produced from K-230, a precursor pitch supplied by Professor Seung Kon Ryu of Chungnam National University, in Daejon, Korea, and used in prior studies. A low softening point commercial M-50 pitch, supplied by Marathon Oil, was used to produce the other pitch samples. This pitch was fed to a dense gas extraction (DGE) column. By adjusting the temperature and pressure of the column, overhead and bottoms products can be obtained with controlled chemical compositions. In this initial series of tests, DGE was used to prepare two different pitch samples. DGE-71 was obtained by collecting the bottom product of DGE operating at 350ºC and 800 psi. DGE-82 was obtained by collecting the bottom product of DGE operating at 350ºC and 750 psi.

Two of the three pitch precursors (K-230 and DGE-82) were divided into two equal portions. A metal-containing salt (palladium acetylacetonate) was added to one portion of each yielding two pitch mixtures that were 1% Pd by weight. Each of these Pd-doped samples was then placed in a Rheomix Intensive Batch Mixer, heated to 225°C and mixed to evenly disperse the Pd throughout the precursor. Then these two samples, along with the three pure pitch samples were melt-spun into fibers. Following the

batch melt spinning process, the fibers were stabilized by gradually heating them in air using Fisher convection oven to 264°C. Next, one portion of the stabilized fibers was carbonized under nitrogen flow in Lindberg tubular furnace and then activated in the same furnace under carbon dioxide flow. For comparison the other portion of the stabilized fibers was directly activated skipping the carbonization step. Finally, the samples were degassed and the surface structure analyzed using a Micromeritics ASAP 2020 at Clemson University and a Quantachrome Autosorb 1C at Oak Ridge National Laboratory (ORNL).

Results and Discussion

Table 1 lists the conditions used to melt spin the fibers from the three pure pitch samples and the two Pd-doped samples. The spinning temperature difference between the pure and Pd-doped fibers is most likely due to a slight oxidation of the precursor during mixing, even though mixing was performed under nitrogen flow. In these trials our goal was to obtain fibers with similar diameters. Thus, the spinning pressure varied for each trial depending on the viscosity of the sample at its optimum spinning temperature. The optimum spinning temperature for a given pitch is related to its softening point and, therefore, to its molecular composition.

**Table 1**: Spinning conditions of the carbon fibers

	K-230	K-230 +1%Pd	DGE-71	DGE-82	DGE-82 +1%Pd
Temperature (°C)	245	263	330	240	252
Pressure (psi)	2100	345	1950	1550	380
Takeup Speed (m/min)	375	375	300	350	400
Avg. Diameter (µm)	20	24	31	26	25

Fig. 1 shows the weight change of the fibers during the oxidative stabilization process. The maximum weight gains are between 7-16%, indicating that the fibers are fully stabilized (Lin (1991)).
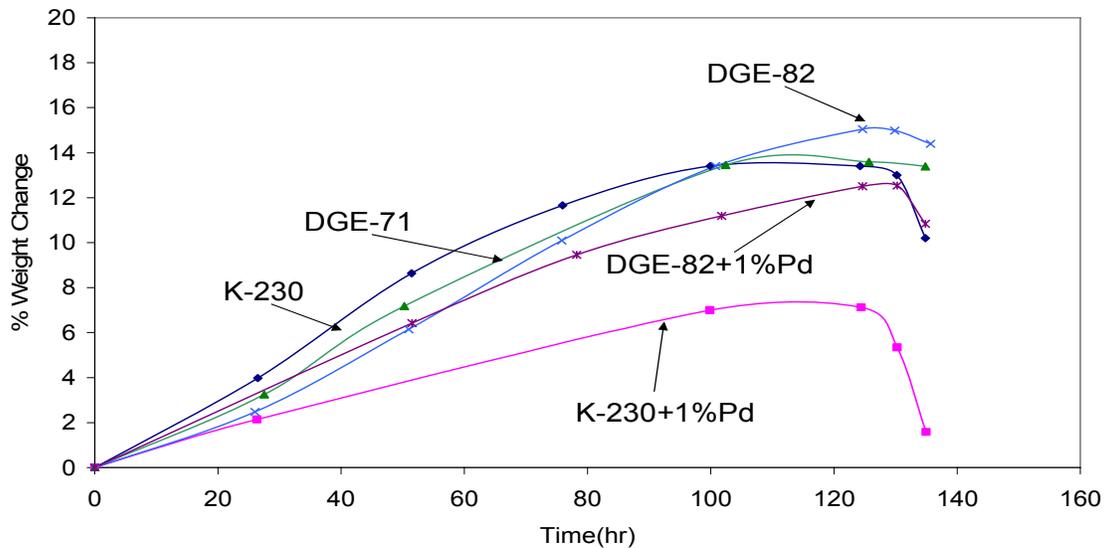
Figure 1: Fiber weight change during oxidative stabilization

When pure and Pd-doped fibers of the same precursor are compared, it is seen that the Pd-doped fibers gained less weight. This indicates that the Pd particles interact with the pitch precursor during stabilization. This interaction is also observed during activation resulting in a higher activation rate for the Pd-doped fibers. As **Fig. 1** also shows, the interaction between the Pd particles and pitch precursor during stabilization is less for DGE-82 than it is for K-230. This implies that the degree of interaction depends on the chemical composition of the pitch precursor.
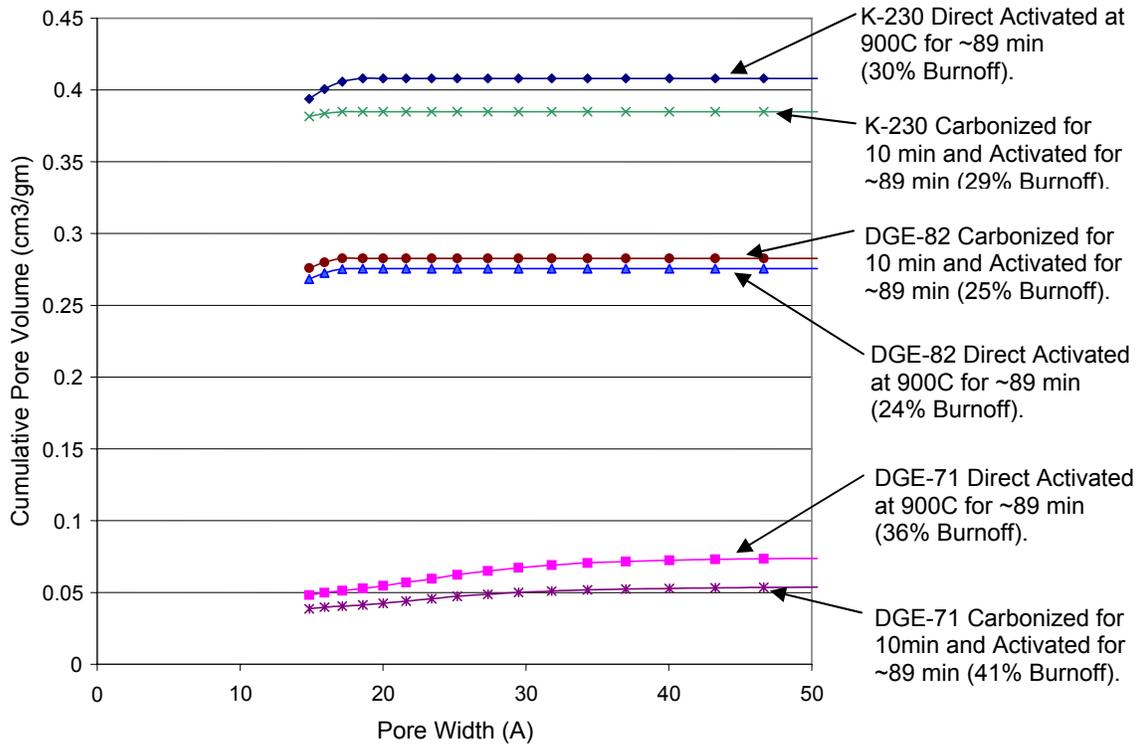
Figure 2: Pore size distribution for activated fibers. Cumulative pore volume distribution was estimated from nitrogen adsorption isotherms using density functional theory (DFT). (Micromeritics ASAP 2020)

Prior studies indicated that at high temperatures Pd particles tend to sinter and agglomerate. Prior research has also proven that carbonization is extremely rapid. When stabilized fibers produced from K-230 and K-230+1%Pd were carbonized for periods of from 1 to 10 min there was no substantial weight loss with time. In fact, the total weight loss during these rapid carbonizations was nearly identical to that obtained by the conventional method (heating the fibers to 1000°C at a rate 10°C /min and holding at this temperature for one hour). Thus, the stabilized fibers were carbonized and activated by two different techniques. One portion of the stabilized K-230, DGE-71 and DGE-82 fibers was carbonized in a tubular furnace at 900°C under N_2 flow for only 10 minutes. Then these carbonized fibers were activated in the same tubular furnace at 900°C under CO_2 flow for approximately 89 minutes. While STEM analyses showed that this more rapid carbonization did appear to reduce sintering and agglomeration of the Pd particles, some still occurred. Therefore, it was decided to modify the two step procedure and simply carbonize and activate the stabilized fiber in a single step, in an attempt to minimize the length of time that samples were exposed to high temperature and further reduce sintering and/or agglomeration of the Pd particles. To evaluate the effectiveness of this technique, the remaining portion of the stabilized fibers were directly activated at 900°C for approximately 89 minutes under CO_2 flow. **Fig. 2** shows the comparison of the pore distributions of activated fibers produced by these two different methods (carbonization followed by activation versus direct activation). Surprisingly, as **Fig. 2** indicates, for a given pitch precursor, the surface structure produced by the two methods is quite similar. Also, as the **Fig. 2** shows, the surface area (141-190 m^2/g) and cumulative pore volume of the activated fibers produced from DGE-71 was much smaller than that of the activated fibers produced from K-230, even though they lost

much more weight during the activation process. By comparison, the activated fibers produced from DGE-82 had relatively a high surface area (705-793 m^2/g), much closer to that of the activated fibers produced from K-230 fibers (995-1048 m^2/g). A differential pore volume analysis of these same data (**Fig. 3**) indicates that the pores in the activated fibers produced from both K-230 and DGE-82 fibers are less than approximately 19Å. By comparison, the pores in the activated fibers produced from DGE-71 are much larger. In subsequent testing it was discovered that the DGE-71 precursor was anisotropic with some molecular ordering. This small degree of molecular orientation is apparently sufficient to inhibit the development of microporosity during activation. Although the results shown in **Figs. 2** and **3** compare the pore structures for activated fibers produced from only the pure pitch precursors using direct activation versus carbonization followed by activation, similar trends were observed for the Pd-doped fibers.
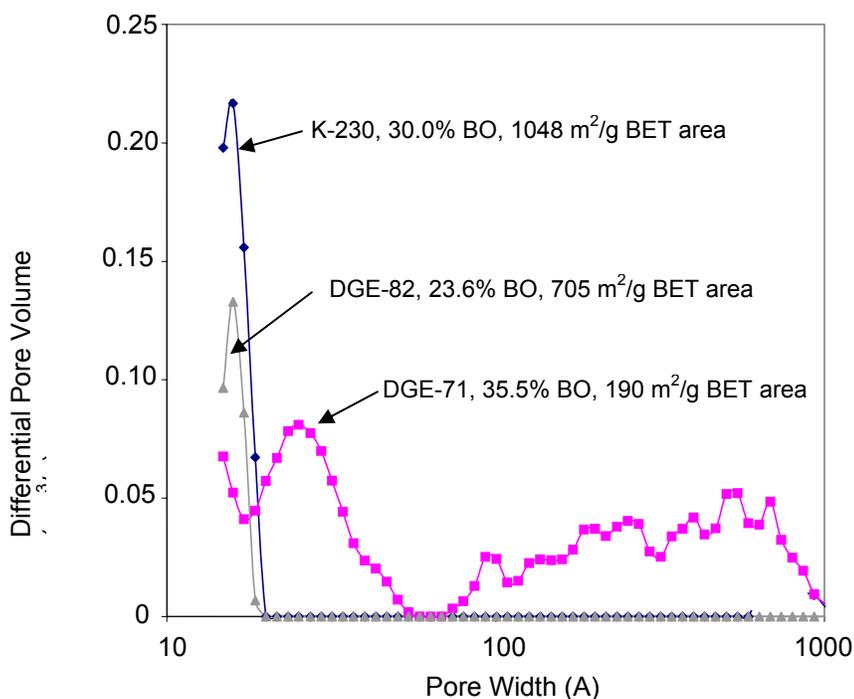

Figure 3: Pore size distributions for fibers that were directly activated at 900°C for ~89 min. The differential pore volume distribution was estimated from nitrogen isotherms using density functional theory.

These results indicated that, for a given pitch precursor, eliminating the carbonization step does not significantly affect the pore structure of the activated fibers. Thus, in a third series of tests stabilized fibers were directly activated at a slightly lower temperature, in order to further reduce Pd sintering and agglomeration. The rate of activation, like other chemical reactions, is an exponential function of temperature. Thus, although a lower activation temperature should reduce sintering, if it is too low, the time needed for activation may be excessively long. Based on the approximate energy of activation of carbon with carbon dioxide (55 kJ/mol), a temperature of 840°C was chosen for these trials (a compromise between low enough temperatures to totally eliminate sintering and the extremely long activation times needed for activation at these temperatures).

Fig. 4 shows the cumulative pore volume of pure and Pd-doped fibers formed from the K-230 and DGE-82 precursors that were directly activated at 840°C to approximately 40% burn-off. This degree of burn-off was selected based on experiments at Oak Ridge that indicated a 40% burn-off gives the highest micropore ratio (desirable for hydrogen adsorption). The DFT analyses of both N$_2$ and CO$_2$ isotherms indicate that the fibers formed from DGE-82, both pure and Pd-doped, and directly activated at 840ºC have

a pore structure that is very similar to that of those formed from K-230 at the same % burnoff. The results also indicate that at these activation conditions, the Pd particles do not significantly influence the pore size structure during activation. This is important since past studies had indicated that Pd and other metal particles tended to create macropores during activation, and these larger pores are not desirable for hydrogen adsorption applications. Theoretical calculations indicate that the optimal pore size for hydrogen adsorption in idealized carbon slit-shaped pores is 6 – 8 Å (Wang and Johnson (1999)).
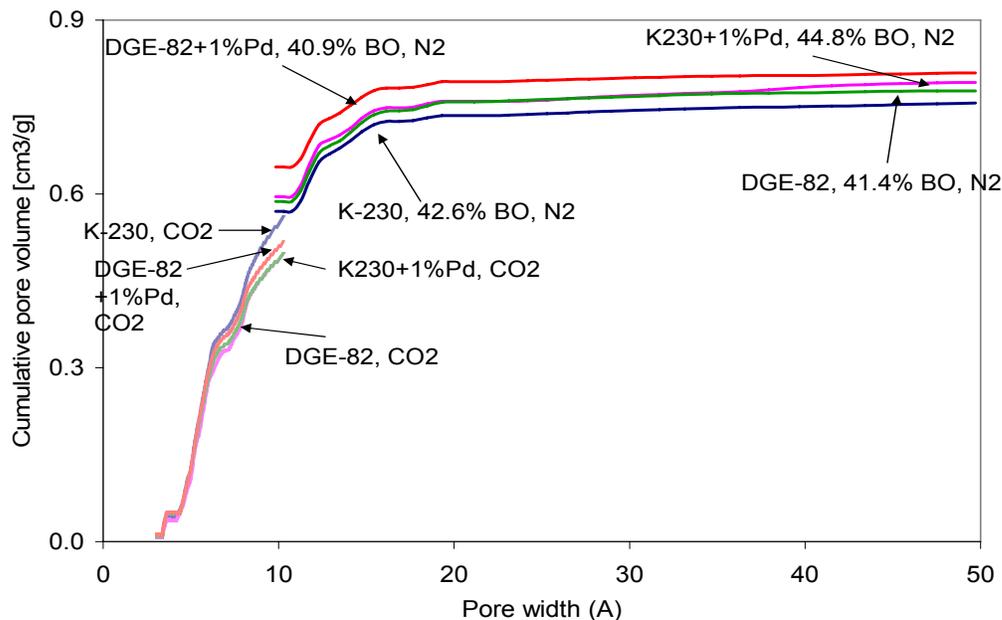
Figure 4: Pore size distribution for direct activated samples (at ~40% BO) at 840°C. Cumulative pore volume distributions were estimated from nitrogen and carbon dioxide isotherms using the density functional theory (Quantachrome Autosorb 1C)

Conclusions

Dense gas extraction was used to fractionate a low softening point, commercial M-50 pitch. The heaver cut was successfully used to produce activated carbon fibers with surface characteristics similar to those previously produced from K-230, an experimental pitch produced by Professor Ryu of Chungnam National University. When a slightly higher pressure was employed during dense gas extraction of M-50, the heavier cut yielded activated fibers with dramatically different pore structures. This indicates that the composition of the precursor pitch can have a dramatic impact on the development of pore structure during activation. In fact, even small quantities of mesophase-forming components inhibited activation and significantly reduced microporosity. The average pore size and distribution of activated fibers produced by direct activation of stabilized fibers was similar to that produced by the more conventional two-step method (carbonization followed by activation).

Acknowledgements

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