

# THE INFLUENCE OF PITCH CHEMISTRY ON PARTICLE SIZE AND DISTRIBUTION IN METAL-CONTAINING ACTIVATED CARBON FIBERS

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## **Introduction**

The preparation, characterization and application of activated carbons containing metal particles are topics of considerable interest [1-5]. Although transition-metal particles distributed within a carbon matrix have been recognized as effective catalytic agents for mesopore formation in activated carbon fibers (ACFs) for a number of years, the mechanisms that control this process have yet to be explained.

Recently we reported [6] a relationship between the chemical composition of the pitch precursor and the silver particle distribution in the carbonized fibers (CFs) and the activated carbon fibers (ACFs). The small size of the silver particles in the mixture formed from the pitch and metal salt was most likely the result of metal ion-aromatic complexes that form as the metal salt particles are mixed into the molten isotropic pitch. A plethora of polycyclic aromatic hydrocarbon (PAH) molecules are capable of forming metal-PAH complexes. The complex creates a protective shell which keeps the silver particles separated by more than their bonding distance, causing steric stabilization and preventing particle agglomeration. An analogous stabilization of the metal precursor also improves particle distribution. A number of transition metals, including Ag, Co, Ni, Fe, metals of the Pt group and others, are known to form metal ion-aromatic complexes of different compositions and architectures [7-11].

The objective of this extended abstract is to illustrate how metal species-pitch precursor interactions affect the size and distribution of the metal-containing particles formed during the preparation of pitch-based fibers. Special emphasis will be placed on chemical composition of the isotropic pitch and nature of the metal salt used to prepare the metal-containing ACFs, as it seems reasonable to suggest that both play a key role. Ultimately this may lead to a unifying perspective on the metal-containing ACFs formation problem.

## **Experimental**

The isotropic pitch precursor (S.P. 230°C) used in this study was supplied by Prof. S. K. Ryu of Chungnam National University, Daejeon, Korea. Three metal-containing salt

precursors commonly used for the generation of mesopores during carbon material preparation (i.e.  $\text{AgNO}_3$ ,  $\text{Co}(\text{acac})_2$  and  $\text{Pd}(\text{acac})_2$ ) were evaluated. Each salt was ground into a powder, and the smallest size fraction ( $\leq 38\mu\text{m}$ ) was mixed into a molten sample of the pure pitch. Then the mixtures were melt-spun into fiber form, stabilized, carbonized and activated. Details of the exact procedures used to produce and characterize the ACFs are described elsewhere [12].

## Results and Discussion

The results on Gas Chromatography-Mass Spectrometry (GC-MS) show that the concentration of major PAHs in all three metal-containing mixtures was lower than that in the pure pitch. In fact, the concentration of PAHs in the pitch- $\text{AgNO}_3$  mixture was significantly less (32%) than that in the pure pitch. This suggests that the silver species form complexes with certain PAHs present in the pitch. Surprisingly, the other two mixtures did not show this dramatic decrease. The concentration of PAHs in the Pd- and Co-containing mixtures was about 16 and 10% less, respectively, than that in the pure pitch. This difference of molecular composition was also detected by MALDI-TOF(matrix-assisted laser desorption/ionization time of flight) mass spectrometry.

As shown in the SEM images (Fig.1), Ag, Co and Pd-containing particles are uniformly distributed throughout all three types of metal-containing CFs. However, the average particle sizes in the CFs varies, with Ag being the smallest and Co the largest (Table 2).

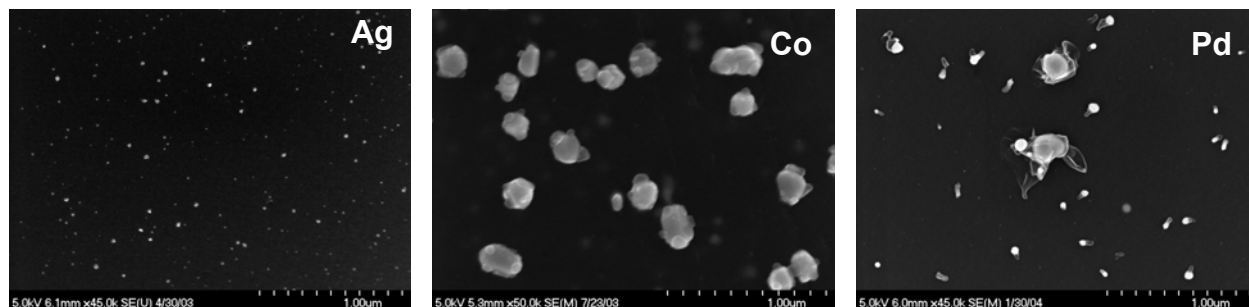


Figure 1. SEM images of carbonized metal-containing fibers

These differences can be explained by considering the effect of the chemical composition of the pitch precursor and the chemical nature of the metal precursor. It is highly probable that the silver salt dissociates during mixing and forms a sandwich complex with the PAHs in the pitch precursor. These aromatic compounds not only influence the coordination positions, but they also dictate the final structure of the product. In particular, symmetric ligands, such as the PAHs contained in the Korean pitch, enhance intramolecular and intermolecular interactions. This sterically stabilizes the silver-containing particles during the mixing stage and yields a uniform distribution of nearly perfect spheres of silver particles in the nanoscale range (5-50 nm) after the heat treatment.

Table 2. Average particle size distribution in metal-containing CFs.

Particle size	Ag-containing fibers (KAR)	Pd-containing fibers (KPR)	Co-containing fibers (KCR)
	Particle concentration, %		
< 20 nm	85 - 95	62 - 85	-
20-50 nm	5 - 15	10- 20	40 - 60
50-100 nm	0 - 1	6- 11	
100-200 nm	-	1 - 4	17 - 28
> 200nm	-	0 - 1	13 - 32

One might expect that salts of other transition metals such as Pd and Co would also interact with PAHs in the pitch precursor and produce a uniform particle dispersion. However, GC-MS results show that the presence of Pd and Co ions does not cause a dramatic decrease in the concentration of PAHs. The SEM analyses also showed that the average particle size was largest in the Co-containing fibers, next largest in the Pd-containing fibers and smallest in the Ag-containing fibers (Fig. 1, Table 2). The reason for the larger particles in the Co- and Pd-containing fibers may be explained by the nature of the counter ion in the cobalt and palladium salts. The acetylacetonates, or metal-diketonate compounds, as exemplified in reference [7], are classified by their ability to form "polymers" (oligomers), allowing coordinative saturation of metals. Thus, metals of the Pt group, including Pt, Pd, Ru, Ir etc, are known to form C-bonded  $\beta$ -diketonate complexes when the metal is bound to the central carbon atom. These C-bonded groups have two free C=O groups that can act as chelate donors for other metal atoms. The  $\text{Co}(\text{acac})_2$  salt is a tetrameric, a compound which contains bridging  $\beta$ -diketonate groups. The linking of  $\beta$ -diketonate groups by bridges allows the formation of "face-to-face" complexes similar to those of face-to-face porphyrins. Proof of this activity was clearly evidenced through TGA, which showed a two-step decomposition for  $\text{Pd}(\text{acac})_2$  and a four-step decomposition for  $\text{Co}(\text{acac})_2$ . Considering this evidence, one can surmise that Pd and Co ions are involved in the acac complexes mentioned above and thus inhibit interaction with PAHs.

The interactions between the pitch and the metal-containing compounds also affected the structure of metal-containing CFs (Fig. 2) and final activation process [13]. This suggests that final properties of ACFs and pore structure formation depend on both the particle size and the mechanism of gasification, which in turn depend on the chemical nature of the particle.

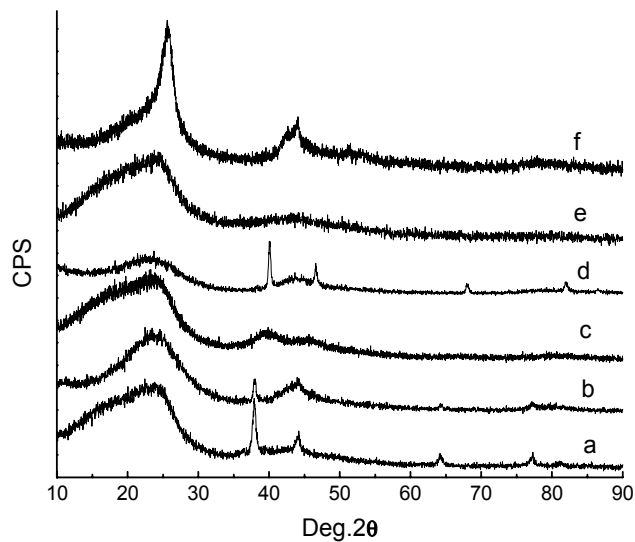


Figure 2. X-ray diffraction patterns of metal-containing as-spun and carbonized fibers: a - KAR as-spun, b - KAR carbonized, c - KPR as-spun, d - KPR carbonized, e - KCR as-spun, f - KCR carbonized.

## Conclusions

In summary, metal salt - pitch precursor interactions provide a powerful tool for creating and controlling metal-containing ACF architectures for a wide variety of applications in adsorption and catalysis. However, the chemical nature of the counter anions in the metal salt precursor must also be considered. These can act either as spacers or linkages between metal-interacting networks, and thus they play an important role defining the final structure of the mixture and the resulting ACF.

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