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ISOTROPIC PITCH-BASED CARBON FIBER ANALYZED BY SPECTROSCOPIES AND COMPUTATIONS

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Introduction

Isotropic pitch-based carbon fiber has been utilized for various applications such as thermal insulation materials for high-temperature furnace and additives for slide member, but the structure of the carbon fiber is still under debate. One of the reasons is that the precursor pitch contains various aromatic compounds in addition to oxidation and carbonization reactions, generating various defects in the carbon fiber. Another reason is that conventional analytical techniques using reported assignments of spectroscopies such as Raman, infrared-ray (IR), and X-ray photoelectron spectroscopy (XPS) are insufficient to understand complicated structures of the carbon materials.[1-3] In this work, oxidation processes of model compounds of pitch such as pyrene (sp^2CH with zigzag-like edges), triphenylene (sp^2CH with armchair edges), fluorene (pentagon with sp^3CH_2), and 9-methylanthracene (hexagon with sp^3CH_3) in addition to pitch were analyzed in detailed.

Materials and Methods

Model compounds of pitch such as pyrene (sp^2CH with zigzag-like edge), triphenylene (sp^2CH with armchair edges), fluorene (pentagon with sp^3CH_2), and 9-methylanthracene (hexagon with sp^3CH_3 (zigzag edges) (**Figure 1**) were placed in glass ampoule tubes and the glass tubes were filled with 0.9 atm of oxygen and sealed to prepare ampoule tubes and heated at 330 degree C for 4 h. Similarly, oxidation of the pitch was conducted in a conventional open reactor under air flow conditions. Oxidized pitch was further heated at 800, 1600, and 2500 degree C. These compounds were analyzed using mass spectrometry, elemental analysis, infrared (IR), Raman, and X-ray photoelectron spectroscopy (XPS) in addition to calculation such as molecular dynamic simulation with a reactive force field (ReaxFF) and simulation of IR, Raman, and XPS spectra (Gaussian09).

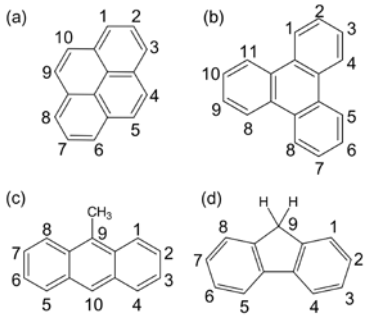

Figure 1. Four precursors selected in this work. (a) Pyrene. (b) Triphenylene. (c) Fluorene. (d) 9-Methylanthracene.

Results and Discussion

As results of analyzing oxidized structures of those four kinds of model compounds, crosslinking of all of compounds formed mainly because of the formation of quinone, which further formed ether bonding. As results of additional MD simulation, oxidation reaction of 9 compounds, such

as pyrene, triphenylene, fluorene, 9-methylanthracene, fluoranthene, benzopyrene, perylene, dibenzo[a,e]pyrene, dibenzo[a,h]py rene, revealed that OH and C=O groups were formed by oxidation reaction, and further oxidation generated cyclic ether, lactone, and acid anhydride. Further heat treatment of oxidized compounds in the absence of oxygen gas revealed that crosslinking reactions proceeded because of the presence of C=O and OH groups. Combination of calculations and experiments revealed that oxidation proceeded in the order of zigzag-like edges > sp^3CH_3 > sp^2CH_2 > armchair edges. The high reactivities of zigzag-like edges and sp^3CH_3 compared to armchair edges and sp^3CH_2 were explained from the difference in electron density, because the higher the electron density of carbon atoms is, the higher the reactivity with oxygen tends to be. Experimental and simulated results suggested that various defects with pentagon, heptagon, and oxygen-containing groups are present in pitch carbonized at 800 degree C. Further heat treatment above 800 degree C reduced oxygen-containing functional groups and remained defects such as non-hexagonal rings (**Figure 2** and **Table 1.**) and edges such as non-TRIO and -QUATRO. At 800 degree C, FWHM of C1s spectra of carbon fiber was 1.46 eV. As the temperature increased to 2500 degree C, the FWHM decreased to 1.18 eV. The decrement of FWHM indicates that the percentage of non-hexagonal ring is low and FWHM of carbon fiber at 2500 degree C was close to the that of graphite. Similar tendency of decrement of FWHM was also observed in case of Raman spectra.

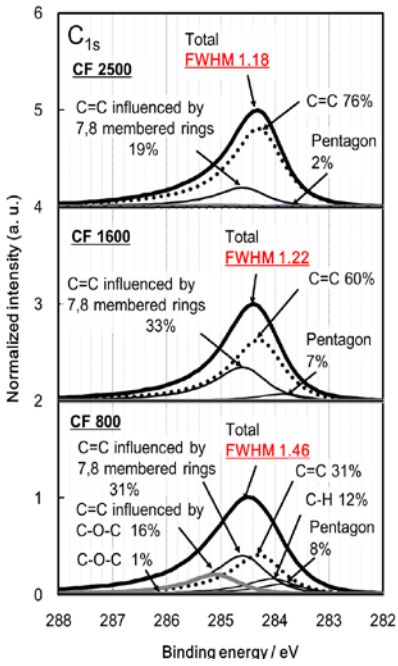

Figure 2. C1s XPS spectra of pitch-based carbon fiber prepared at various temperatures.

Table 1. Results of elemental analysis.

Name	Composition / at.%		
	C	H	O
CF2500	99.9	0.0	0.1
CF1600	99.8	0.0	0.2
CF800	86.9	11.9	1.2

Conclusions

This work clarified the reaction processes of oxidation and crosslinking of PAHs using basically four PAHs with representative edge structures, which are one of the most difficult problems in analysis of pitch-based carbon fiber. Summed DRIFT spectrum of oxidized model compounds showed similar DRIFT spectrum to oxidized pitch, indicating that this work explained the basics of the infusibilization reaction of pitch in detail. FWHMs of C1s spectra and Raman spectra revealed that the carbon fiber heated at 2500 degree C contained non-hexagonal rings, although the percentage decreased significantly as temperature increased.

References

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