

STRUCTURALLY CONTROLLED CARBON MATERIALS WITH HIGH PYRIDINIC-NITROGEN CONTENT

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Introduction

Structural control of nitrogen-containing functional groups of carbon materials is essential for improving various applications such as catalysts and electrodes. However, most carbon materials contain various nitrogen-containing functional groups and the reasons for the high performance of various applications are unclear. It is because of the instability of functional groups upon heat treatment and unclear reaction pathway of carbonization reaction^{1,2} and also because of the unclear analyses of nitrogen-containing carbon materials by X-ray photoelectron spectroscopy.³ In order to improve these properties, it is necessary to introduce one type of functional group, but structural control of the nitrogen-containing carbon material has just begun in recent years. In this study, nitrogen-containing aromatic compounds with different nitrogen positions were carbonized at 973 K and structural control of pyridinic nitrogen was attempted.

Materials and Methods

Eight aromatic compounds were used as precursors of carbon materials without further purification (**Figure 1**). These compounds were placed in quartz tubes. After drying the compounds at 50 K lower than melting points of each compound, those tubes were sealed and ampoule tubes were prepared. These ampoule tubes were heated mainly at 973 K for 1 h. After cooling, samples were collected from the ampoule tube, and those collected samples were placed in glass tube and further heated at temperature above 50 K higher than melting points for 1 h to remove precursors and other reacted materials with low molecular weight. The nitrogen-containing carbon materials were analyzed by XPS, elemental analyses, diffuse reflectance infrared Fourier transform (DRIFT), and Raman spectroscopy.

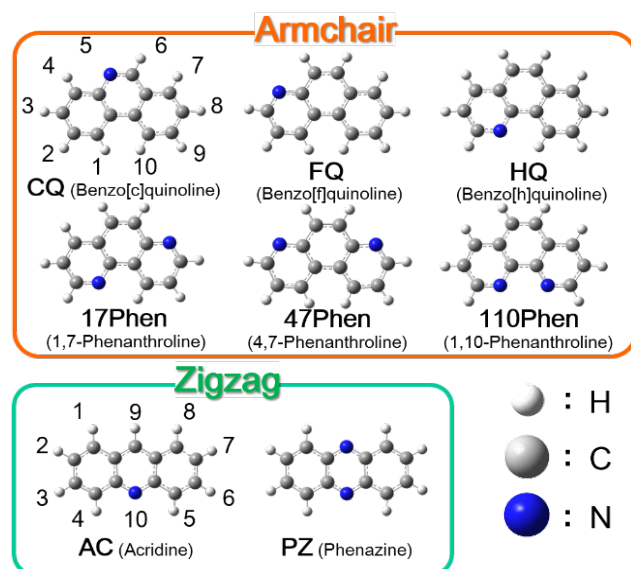


Figure 1. Structures of precursors used for preparation of carbon materials. White sphere: hydrogen atom. Gray sphere: carbon atom. Blue sphere: nitrogen atom.

Results and Discussion

As results of elemental analysis, the order of the degree of gasified nitrogen at 973 K was 37% (CQ) > 19% (110Phen) > 11% (PZ) > 10% (47Phen) > 9 % (HQ) > 8% (FQ, 17Phen) > 0% (AC). The order of percentages of pyridinic nitrogen remained at 973 K was 92% (17Phen) > 84% (HQ) > 81% (FQ) > 59% (47Phen) > 55% (CQ) > 39% (110Phen) for armchair edges (**Figure 2**). That of percentages of structural control of pyridinic nitrogen at 973 K was 50% (AC) > 38% (PZ) for zigzag edges. The reasons for the order of the percentage of pyridinic nitrogen can be explained from the results of density functional theory calculation from the point of views of 1) Scission of C-H bonding, 2) Hydrogenation (Formation of either C-H or N-H bonding), and 3) Scission of C-N bonding. The reasons are mainly because of the low possibility to be hydrogenated on nitrogen atom in pyridinic nitrogen and high possibility of intramolecular scission of C-N bonding after hydrogenation of pyridinic nitrogen (**Figure 3**).

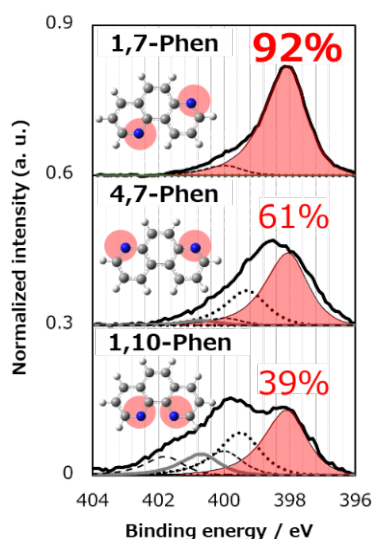


Figure 2. N1s XPS spectra of aromatic compounds carbonized at 973 K.

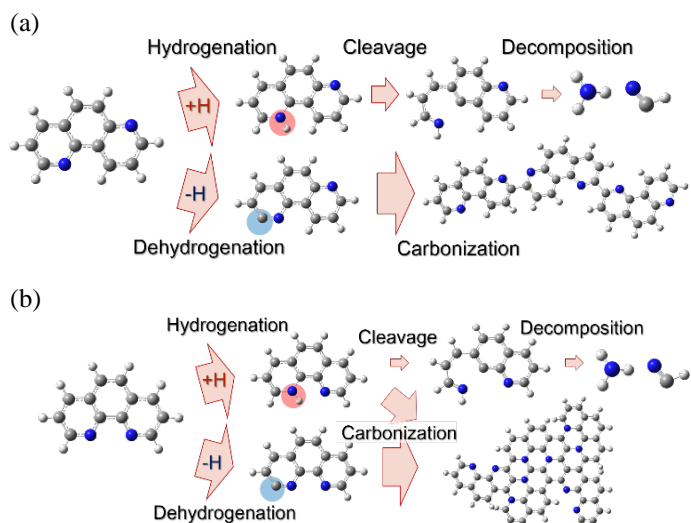


Figure 3. Plausible reaction routes of carbonization of 17Phen and 110Phen. (a) Carbonization of 17Phen. (b) Carbonization of 110Phen.

Conclusions

This work discovered the precursor molecules that form carbon materials with 92 % of pyridinic nitrogen prepared at 973 K. The reasons for the high percentage of remaining pyridinic nitrogen were explained by density functional theory calculation for reaction pathway of radical formation and simulated spectra combined with experimental spectra.

Acknowledgment

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References

1. Yamada Y., Gohda S., et al. (2017) Carbon materials with controlled edge structures. *Carbon* 122, 694-701
2. Tanabe T., Yamada Y., et al. (2016) Knoevenagel condensation using nitrogen-doped carbon catalysts. *Carbon* 109, 208-220
3. Yamada Y., Kim J., et al. (2014) Nitrogen-containing graphene analyzed by X-ray photoelectron spectroscopy. *Carbon* 70, 59-74.