Hetero atom doping effect on thiophene adsorption on graphite

Iwao SHIMOYAMA* and Yuji BABA
Japan Atomic Energy Agency, Tokai-mura, Ibaraki 319-1195, Japan

1 Introduction
Recently, catalytic activity of carbon alloys prepared by hetero atom dopings like boron and/or nitrogen has been extensively studied [1]. However, the role of hetero atoms is still unclear and there are many untamed territories for functionalities of carbon alloys. With regard to phosphorus doping in carbon materials, there are many studies on semiconducting property, field emission, photoelectrical property, and catalytic activity. We focus desulfurization as a new functionality. Adsorptive desulfurization (ADS) with activated carbon attracts attention as an alternative method to conventional hydrodesulfurization (HDS) because of low cost, catalysts-free, and ambient-condition processing. So far, it has been indicated that pores less than 7 Å and oxygen functional groups in activated carbon are important for adsorption of sulfur compounds [2, 3]. However, hetero atom doping effect on desulfurization has not been sufficiently investigated. In this work, we chose thiophene as a model molecule of aromatic sulfur compounds that are extremely difficult to desulfurize by HDS. Highly oriented pyrolytic graphite (HOPG) was also chosen as a model system of π-conjugated carbon and adsorption property of thiophene was studied on HOPG doped with nitrogen and phosphorus atoms in order to study hetero-atom doping effect.

2 Experiment
Experiments were performed at the BL27A. PCl$_3$ and N$_2$ were used for P and N dopings, respectively. Fragment ions formed by a cold cathode ion gun were irradiated on HOPG with an acceleration energy of 3 keV. Three samples were compared. Sample A was prepared by phosphorus doping at room temperature. The fluences of the total fragment ions was $1 \times 10^{17}$ ions/cm$^2$. After doping, this sample was annealed at 800°C. Sample B was prepared by nitrogen doping at room temperature with the fluences of $1 \times 10^{17}$ ions/cm$^2$, and then annealed at 800°C. Sample C was prepared by Ar$^+$ ion irradiation with an acceleration energy of 3 keV to study the influence of radiation damage caused by ion beam. The fluence of Ar$^+$ ion was $2 \times 10^{17}$ ions/cm$^2$, and this sample was annealed at 800°C after irradiation. Contents of phosphorus and nitrogen were estimated by P1s/C1s and N1s/C1s photoelectron-peak intensity-ratios in XPS spectra measured with a monochromatic X-ray of 3keV.

3 Results and Discussion
Figure 1 shows S 1s XPS spectra of the samples A, B, and C after thiophene exposure. All spectra were normalized by the intensity of C 1s photoelectron peak. While, phosphorus-doped sample A showed clear peak, nitrogen-doped sample B and Ar$^+$ irradiated sample C showed only little peaks. From the data in Fig.1, we estimated thickness of thiophene layer. Table 1 summarizes the atomic density of dopant, thickness, and coverage of thiophene.

![Fig. 1: S 1s photoelectron spectra of phosphorus-doped, nitrogen doped, and Ar$^+$ ion irradiated HOPG after exposure of thiophene gas.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic composition ratio of dopant</th>
<th>Thiophene thickness (nm)</th>
<th>Thiophene coverage (ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.1% (P)</td>
<td>0.27</td>
<td>0.11</td>
</tr>
<tr>
<td>B</td>
<td>3.5% (N)</td>
<td>0.02</td>
<td>0.008</td>
</tr>
<tr>
<td>C</td>
<td>–</td>
<td>0.03</td>
<td>0.012</td>
</tr>
</tbody>
</table>
We obtained normalized coverage $\theta$ dividing thiophene coverage by atomic composition ratio of dopant. The values of $\theta$ were 0.052 and 0.0023 for samples A and B, respectively. This means that phosphorus doping had about twenty times larger adsorption ability on thiophene than nitrogen doping.

It has been reported that phosphorus and nitrogen dopings can introduce curved structures in $\pi$-conjugated carbon, which are called fullerene-like structures [4, 5]. Then, we simulated thiophene adsorption on a phosphorus site doped in planar and curved structures of $\pi$-conjugated carbon clusters using semi-empirical PM5 molecular orbital calculation with WinMOPAC ver. 3.9. Fig. 2 shows the model clusters calculated. In the figure, purple, brown, yellow, and pink balls correspond to phosphorus, carbon, sulfur, and hydrogen atoms, respectively. Minimum energy path (MEP) analysis was performed calculating total energy as a function of phosphorus-sulfur distance.

Fig.3 shows results of MEP analysis of thiophene adsorption on phosphorus-doped carbons. Red and blue circles represents results for planar and curved structures, respectively. Planar structure shows an energy-minimum around 2.6 Å, and adsorption energy was calculated to be 0.14 eV. Curved structure shows an energy-minimum around 2.4 Å with an adsorption energy of 0.47 eV. These calculations means that phosphorus-doped $\pi$-conjugated carbon can form stable adsorption structures for thiophene.

Furthermore, similar analysis was performed for nitrogen-doped carbon systems as shown in Fig.4. In this case, total energy decreases with distance between sulfur and nitrogen atoms indicating both planar and curved structures didn’t show stable adsorption structure. We also performed similar analysis for non-doped carbon clusters and thiophene didn’t have stable adsorption structure. These calculations explain our experimental results in Fig.1.

Fig.4: MEP analysis results of thiophene adsorption on planar (red) and curved (blue) structures of N-doped $\pi$-conjugated carbon clusters.

We consider that the better doping effect of phosphorus than nitrogen is attributed to net charge. In $\pi$-conjugated carbon matrix, nitrogen atom has negative net charge and phosphorus atom has positive net charge. Because of the negative net charge of sulfur in thiophene, thiophene is prone to approach a positively charged site. Our results suggest hetero atom doping is one way to control desulfurization property of activated carbon.

Acknowledgement

The authors thank Dr. Sekiguchi for his experimental support.

References


* shimoyama.iwao@jaea.go.jp