Noble Interactions between Ar and Carbons

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ABSTRACT

Noble interactions between Ar and carbons are observed for carbons, such as carbon nanotubes and carbon blacks by means of mass-analyzed thermal desorption. The absorption states exist at around 300 K as well as at around 100 K. X-ray photoelectron spectroscopy reveals that Ar2p shows the chemical shifts. These results suggest that Ar is in charge and it is in valence state, or gives the evidence of the chemical interaction.

Keywords: Ar; Interaction; Carbon; Valence States

1. Introduction

The compounds of rare gas elements such as Kr and Xe have been reported [1-5].

The examinations of compressibility for C60 using He, Ne and Ar as pressure media and the study of diffusion kinetics in solid C60 have been carried out under the conditions of high pressure at around several kbar [6-9]. In these, the chemical interactions have not been discussed.

We have reported the chemical interactions of rare gases [10], such as He, Ne and Ar, in solid carbon nanotubes. Closed carbon nanotubes (CNTs) show larger amounts of absorption for gases such as hydrogen, He, Ne and Ar than opened CNTs. From these results, we conclude that sites that are preferentially found in endcaps provide more active electronic states for the chemical interaction between rare gases and solid carbon nanotubes.

This paper presents results on the thermal desorption from carbon blacks and the X-ray photoelectron spectra of Ar2p.

2. Experimental

C60 (Hoechst, 99.98% purity) was used without further purification.

Endcaps and endcaps-opened multi wall carbon nanotubes (CMWCNT and OMWCNT, Bucky USA BU-200 and 201, 3 - 10 multi-layer with 2 - 10 nm diameter and 3 - 30 µm length), endcaps and endcaps-opened single wall carbon nanotubes (CSWCNT and OSWCNT, Bucky USA BU-202 and 203, 1.4 - 3 nm diameter and 10 - 50 µm length) were used without further purification. As for the single and multi-wall carbon nanotubes, there is the only difference in the both end structure, and the another structure is the same.

Carbon black (Seast 3HAF (S3)) and graphitized carbon blacks (3855, 3845 and 3800) were supplied from Tokai Carbon Co. Table 1 shows the characterizaion of samples.

After vacuum heating at 653 K or 1073 K, samples were exposed to Ar (Nippon Sanso, >99.99% purity) of 1 to 1.4 atm, at 473 K for 1 to 10 days. After the sample was cooled to liquid nitrogen temperature, the sample tube was evacuated to ultra-high vacuum. In-situ measurements of the thermal desorption with the temperature-rise rate of 5 K/min and X-ray photoelectron spectra by using MgKα were carried out.

3. Results and Discussion

Figures 1 and 2 show the thermal desorption of Ar from carbon blacks.

The Ar desorption peaks were observed at around 90 - 100 K in the lower temperature region for all carbon blacks. These peak temperatures were higher than that of boiling point of Ar such as 87 K. Therefore, these results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle radii/nm</th>
<th>N2 specific surface area/m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seast 3HAF (S3)</td>
<td>28</td>
<td>79</td>
</tr>
<tr>
<td>3855</td>
<td>25</td>
<td>90</td>
</tr>
<tr>
<td>3845</td>
<td>40</td>
<td>57</td>
</tr>
<tr>
<td>3800</td>
<td>70</td>
<td>27</td>
</tr>
</tbody>
</table>

Table 1. Characteristics of carbon blacks.
suggest the stronger interaction than van der Waals interaction.

In addition, the Ar desorption peaks were observed at around 350 K in the higher temperature region than room temperature. Therefore, these results suggest the chemical interaction between Ar and carbon blacks.

**Figure 3** shows the X-ray photoelectron spectra of Ar2p for C60, graphite and closed and open multiwall carbon nanotubes. Ar2p for C60 and closed and open multiwall carbon nanotubes exposed to Ar gas at around room temperature, and the Ar+-sputtered graphite.

The peaks appeared at around 275 eV are assigned to the peaks due to the X-ray impurities.

For Ar+-sputtered graphite, Ar2p1/2-Ar2p3/2 peaks were observed. This spin-orbit interaction indicates that Ar exists as the neutral molecule in the graphite. On the other hand, for C60, Ar2p peak was not observed at around 241 eV and the peak appears at around 269 eV, showing the large chemical shift to that for the Ar+-sputtered graphite at around 241 eV. The spin-orbit interaction was also not observed.

For the closed and open multiwall carbon nanotubes, although the signal intensities were weak, Ar2p peaks were observed at around 264 eV, showing also the large chemical shift to that for the Ar+-sputtered graphite at around 241 eV.

**Figure 4** shows the X-ray photoelectron spectra of Ar2p for the Ar+-sputtered carbon blacks. Although characteristics of the thermal desorption were different from amorphous-type carbon black and graphitized carbon blacks, the Ar2p peaks were observed at around 242 and 244 eV. The spin-orbit interaction was observed for all spectra.

For the Ar+-sputtered graphite, the difference between C1s and Ar2p3/2 was observed as 43.3 eV, and the splitting width of the spin-orbit interaction was 2.2 eV. For carbon blacks, the difference between C1s and Ar2p3/2
Figure 4. The X-ray photoelectron spectra of Ar2p for carbon blacks.

was observed as 42.6 ± 0.1 eV, and the splitting width of the spin-orbit interaction was 3.0 eV. By the comparison with the Ar⁺-sputtered graphite, the difference between C1s and Ar2p 3/2 became to be lower and the splitting width of the spin-orbit interaction increased for the carbon blacks. These results indicate that the ad-/ab-sorption states observed at around 90 - 100 K and 350 K are due to the weak and strong chemical interactions.

4. Conclusions

Carbons show the noble interaction with Ar due to the characteristic structures and those electronic states. The X-ray photoelectron spectroscopy results in the chemical interaction between Ar and carbons such as C₆₀, CNTs, and carbon blacks. Carbons have possibilities of the diversity of chemical interactions with designs of structure and those electronic states.

5. Acknowledgements

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REFERENCES