CHANGES IN PORE CHARACTERISTICS, SURFACE MORPHOLOGIES, AND FUNCTIONALITIES OF PHENOL FORMALDEHYDE-BASED POROUS CARBONS WITH CARBONIZATION ATMOSPHERES AND ACID OXIDATION

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Introduction

Porous carbons have been widely used as adsorbents in technologies related to pollution control due to their well-developed porous texture and excellent adsorption capacity toward pollutants. Recent global problems related to environment, energy, and resource issues demand higher performance for adsorbent materials, including porous carbons. Controlled pore size and surface characteristics are necessary for the application of those materials in specific end use because the performance of porous carbons depends strongly on pore structure as well as surface characteristics. So, it is no exaggeration to say that the pore structure as well as the surface characteristics of porous carbons must be controlled by certain methods in order to improve their adsorption capacity toward highly hazard pollutants. Thus, in this study we investigated effects of the environmental atmospheres during carbonization, and the subsequent oxidation by a acid on the porosity evolution and structure changes of phenol-formaldehyde resin.

Experimental

Phenol-formaldehyde beads (PFB) (50 \textmu m in diameter) were carbonized at 700°C and 1000°C under N\textsubscript{2} (NN-series) or CO\textsubscript{2} (CO-series) atmospheres. The carbonized spheres were subsequently oxidized with boiling nitric acid solution (13vol.\%) for 3hrs (ANN- and ACO-series). Thermal degradation behavior of samples was examined by Hi-Res TGA (Dupont, Hi-Res TGA 2950, USA) and the pore structure was obtained on BET sorptometer (Micromeritics, ASAP 2010, USA) by adsorption of N\textsubscript{2} at 77K. The structure change and the evolution of functional groups were monitored using various techniques such as X-ray diffractometer (Mac Science Co., MXP 18XMF22-SRA, Japan), FT-IR (Perkin Elmer, FT-IR Spectrometer Spectrum 2000, USA), and Boehm’s method [1]. The surface morphology change was monitored by an FE-SEM (JEOL, JSM-6330F, Japan).

Results and Discussion

The effect of carbonization atmospheres on thermal degradation behavior of PFB was examined on TGA and the resulting thermograms of PFB were shown in Figure 1. Thermal degradation behaviors under N\textsubscript{2} and CO\textsubscript{2} are almost similar to each other up to 800°C. However, above 800°C drastic weight loss occurs under CO\textsubscript{2}, indicating that since CO\textsubscript{2} has enough thermal energy to give rise to gasification reaction on PFB at this temperature, PFB are decomposed severely. Indeed, it can be seen from Figure 2 that CO-series samples show relatively deeper and larger surface pits in comparison with NN-series samples.

On acid oxidation (Figure 3), CO-series samples show more drastically corroded surface morphology than NN-series samples. It is well established that during carbonization, the active sites such as dislocation and heteroatoms disappear by thermal annealing and devolatilization of non-carbon atoms, resulting in more stable carbon structure [2-3]. On the other hand, in the case of CO\textsubscript{2} atmosphere, not only non-carbon atoms are eliminated, but surface oxide groups could be introduced on carbon surface in the way of reaction of carbon substrate with CO\textsubscript{2} [4]. These surface oxide groups can be easily attacked by acid solution, resulting in more corroded surface morphology. BET surface areas of both CO- and NN-series samples tend to increase with increasing carbonization temperature, however CO-series samples show higher BET surface area (700°C:610 /g, 1000°C:780 /g) in comparison with those of NN-series samples (700°C:380 /g, 1000°C:580 /g). After acid oxidation, BET surface area of NN100 increased from 580 /g to 650 /g, whereas that of CO100 decreased from 780 /g to 600 /g. This result is due to the different physical and chemical structure derived from the effect of different carbonization atmospheres. Indeed, from Table 1 which shows microstructural parameters calculated from XRD patterns, CO100 has higher amount of zig-zag type edge-carbon-atoms, being
known as more reactive sites than arm-chair type edge-
carbon-atoms, in comparison with NN100.

Figure 4 shows acidic surface functionality of carbon
spheres. CO-series has higher amount of carboxyl type
surface functional groups than NN-series samples. On
subsequent acid oxidation, acidic surface functional
groups increase in both ACO- and ANN-series samples,
however when compared the amount of surface oxide
groups in both series of carbon spheres, ACO-series
samples tend to have much higher amount of acidic
surface functional groups.

From the above-mentioned results, it was found that
pore structure as well as surface characteristics can be
controlled by combining the atmospheres and
subsequent acid oxidation. It was expected that these
carbon spheres might be used for removal of polar and
non-polar pollutants.

References

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Table 1. Microstructural parameters of carbon spheres.

<table>
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<tr>
<th></th>
<th>d(002)</th>
<th>I(002)/I(10)</th>
<th>Iz(10)</th>
<th>Zig-zag cars*</th>
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<tbody>
<tr>
<td>NN100</td>
<td>4.0</td>
<td>9.7</td>
<td>40.3</td>
<td>110</td>
</tr>
<tr>
<td>CO100</td>
<td>4.0</td>
<td>10.1</td>
<td>44.7</td>
<td>124</td>
</tr>
<tr>
<td>ANN100</td>
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<td>9.2</td>
<td>18.3</td>
<td>86</td>
</tr>
<tr>
<td>ACO100</td>
<td>4.0</td>
<td>9.6</td>
<td>17.5</td>
<td>87</td>
</tr>
</tbody>
</table>

* counted from the simulated graphene layer with the
observed value of Iz(10)

Figure 1. TG thermograms of phenol-formaldehyde
beads.

Figure 2. Surface morphologies of carbon spheres;(a)
NN70, (b) NN100, (c) CO70, and (d) CO100.

Figure 3. Surface morphologies of acid oxidized carbon
spheres;(a) ANN100 and (b) ACO100.

Figure 4. Acidic functional groups of (a) carbonized
and (b) acid oxidized carbon spheres.