



Changes in pore properties of phenol formaldehyde-based carbon with carbonization and oxidation conditions

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Abstract

Porous carbon beads were prepared by carbonizing at 700 and 1000 °C under N₂ (NN-series) or CO₂ atmospheres (CO-series) and a subsequent oxidization with boiling nitric acid solution (13%, v/v) for 3 h (ANN- and ACO-series). BET surface area of both CO- and NN-series samples tends to increase with increasing carbonization temperature, but CO-series samples show higher BET surface areas (700 °C: 610 m²/g, 1000 °C: 780 m²/g) compared with those of NN-series samples (700 °C: 380 m²/g, 1000 °C: 580 m²/g). After acid oxidation, BET surface areas of NN-series samples increased from 580 to 650 m²/g, whereas those of CO-series samples decreased from 780 to 600 m²/g. On subsequent acid oxidation, acidic surface functional groups increased in both CO- and NN-series samples, but the CO-series samples tend to have much more acidic surface functional groups. Adsorption of halogenated methanes, such as tetra-, tri- and dichloromethanes, onto the samples of CO-, NN-, ACO- and ANN-series was thought to be driven initially by the basicity, but the acidic functional groups that could attract adsorbates via dipole–dipole interaction might hinder the adsorption of subsequently incoming adsorbates.

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1. 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 of various forms [1,2]. 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.

Recently it has been reported that porous carbons with

high surface area and high adsorption capacities can be prepared from phenol–formaldehyde resins [3,4]. For example, one of the authors (M.I.) has reported that porous carbon beads can be prepared by carbonization at 1000 °C of phenol–formaldehyde beads under nitrogen or carbon dioxide atmosphere, followed by oxidation with boiling nitric acid [5–8]. For the prepared carbon beads it was found that environmental atmosphere seemed to influence the evolution of pore characteristics, such as specific surface area, pore size, etc. and carbon dioxide was irreversibly adsorbed [5]. These findings are interesting in that there has been little study of the effect of the carbonization atmosphere on the porosity evolution and adsorption of a specific gas molecule onto a porous carbon material, although it has been comparatively well understood that the activation conditions such as activation method, activation temperature and time, etc. play an important role in creating pore characteristics of the

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resulting porous carbons. Recently, the authors (C.H.Y. and C.R.P.) [9,10] have reported that the pore characteristics, particularly the pore size distribution and the surface chemistry of porous carbons can also be controlled to some extent by adequately selecting the atmospheres during carbonization process.

However, there has been little investigation into the details of the influences of the carbonization atmospheres on the physicochemical structural changes and the porosity evolution and adsorption characteristics of porous carbons. It is thus the aim of this study to scrutinize the effects of the environmental atmosphere during carbonization and the subsequent oxidation by an acid on the development and changes in the porosity, surface morphology and functionalities of phenol–formaldehyde resin based porous carbon beads. Based on the thermal degradation behavior under nitrogen and carbon dioxide, respectively, two different temperatures, 700 and 1000 °C, were chosen as heat treatment temperatures. Then, the above-mentioned issues were examined using various techniques such as XRD, FT-IR, elemental analysis, and Boehm's method.

2. Experimental

2.1. Materials

Commercially available phenol–formaldehyde beads (PFB) that are 50 μm in diameter, and said to be resol-type, were used after oven-drying at 50 °C for 5 h. The proximate and ultimate analyses of the PFB are shown in Table 1.

2.2. Preparation of porous carbons

Porous carbon spheres were prepared by heat-treating the PFB to 700 and 1000 °C with a fixed rate of 10 °C/min under N₂ (denoted NN100 when the temperature was 1000 °C) and CO₂ (denoted CO100) atmospheres, respectively, followed by a prompt cooling to room temperature under nitrogen atmosphere. The carbon spheres of both the NN- and CO-series were subsequently oxidized with a boiling nitric acid of 13% (v/v) for 3 h to modify the pore structure of ANN- and ACO-series, respectively. After oxidation, all the samples obtained were washed thoroughly with distilled water and vacuum-dried at 80 °C overnight.

2.3. Characterizations

Thermal gravimetric analysis (TGA) was carried out using a Hi-Res TGA 2950 (Dupont, USA) with a heating rate of 10 °C/min under N₂ and CO₂, respectively, from 50 to 1000 °C to investigate the thermal degradation behavior of PFB under different environmental atmospheres.

The surface morphological changes of the samples were examined with a field emission scanning electron microscopy (JSM-6330F, Jeol, Japan) operating at 10 kV. The samples were gold-sputter-coated for 300 s using a sputter coater (JFC-1100, Jeol), and then examined under various magnifications.

The physical structure changes of the samples were monitored using Ni-filtered CuKα radiation (λ=1.5405 Å) on a wide angle X-ray diffractometer (MXP 18X-MF22-SRA, MAC/Science, Japan) operating at 50 kV and 100 mA. After the peak-deconvolution of the obtained X-ray diffractograms, various structural parameters were determined with a conventional method [11]. Interlayer spacing d_{002} , stacking height along the *c* axis L_c , and stacking width $L_{a\perp}$, being determined from (10) reflection on the equator, were calculated using an inner standard of Si. The degree of carbonization (Dc) of each sample was calculated using following equation:

$$Dc (\%) = \frac{I_{c,26^\circ}}{I_{c,26^\circ} + I_{p,16^\circ}} \cdot 100$$

where $I_{c,26^\circ}$ and $I_{p,16^\circ}$ are the peak intensities at $2\theta=26^\circ$ and 16° , respectively. The number of edge-carbon atoms of zig-zag type, N_{zz} , was calculated from the model structure of carbon layer that has the same $L_{a\perp}$ value with the experimentally determined one.

The chemical structure changes induced by thermal treatment and/or acid oxidation were monitored with KBr-pelleted samples on an FT-IR spectrometer (Spectrum 2000, Perkin-Elmer, USA) with the scan number of 32 and the resolution of 4 cm⁻¹.

In order to determine the characteristic parameters of pores, such as BET surface area, pore size, pore size distribution, and total pore volume, nitrogen adsorption–desorption isotherms were recorded at 77 K on an automatic adsorption instrument (ASAP 2010, Micromeritics, USA) in the relative pressure ranging from 10⁻³ to 1. Prior to the measurement, all the samples were degassed at

Table 1
Ultimate and proximate analysis of PFB

Ultimate (wt.%, dry-ash-free basis)		Proximate (wt.%, as-received)	
Carbon	64.7	Moisture	2.0
Nitrogen	2.8	Volatile matter	36.3
Hydrogen	4.8	Fixed carbon	61.7
Oxygen	27.7	Ash	0.0

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