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Activated carbon production by co-carbonization of feathers using water-soluble phenolic resin under controlled graphitization

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ABSTRACT

We attempted to use feathers for the production of activated carbon (AC). A water-soluble resol-type phenolic resin was hybridized to prevent the liquefaction of the feathers and to control the graphitization degree of charcoal. The hybridization could effectively increase the yield of charcoal over 30% and maintained the graphitization degree at approximately 0.1, suitable for the production of AC. The Brunauer–Emmett–Teller (BET) surface area and the iodine-adsorption capacity of hybrid charcoal-based AC were 706 m^2/g and 550 mg/g, respectively, which were 1.7-1.8 times greater than those of the feather-based AC at a similar activation level.

1. Introduction

Pitch and coke, the heavy fractions of petroleum and coal, respectively, are the two major starting materials for obtaining various carbons, such as carbon blacks, carbon fibers, and activated carbons (ACs). Their carbonization behavior and the properties of the resulting carbons have been extensively studied. However, such carbon resources are not sustainable because of their limited reserves and the rising price of oil. Instead of fossil fuels, we have proposed alternative starting materials, such as coffee lees [1], triacetylcellulose waste [2], and oak woods [3], to produce AC. As for the cost of the resources, bottom ash [4] and waste rubber tires [5] are attractive, and adsorbents applicable to the wastewater treatments have been developed.

To establish the mass production of AC from biomass, it is important to secure the resources from the viewpoint of supply chain costs. In the case of woody biomass, it is sometimes difficult to secure a healthy supply of waste wood chips from lumber mill factories because normally they are scattered in the mountain areas, which raises the costs for the development of transport networks in terms of the effective agglomeration of waste wood chips. In contrast, poultry industries have already established their transport networks. Therefore, we can expect a healthy supply of waste feathers, preventing the extra costs for transportation and agglomeration; for example, the American poultry industry deals with more than 4 billion lb of chicken feathers per year [6].

As for the application technologies for the waste feathers, the anaerobic (oxygen-free) digestion process producing biogas energy and manure for agricultural use has been developed and is used worldwide [6]. To develop more functional materials from waste feathers, several trials have been conducted, e.g., self-organizing oligopeptides for synthesizing new biopolymer [7], bioplastic [8], and regenerated fiber production [9]. However, these material recycling processes require the purification of waste feathers. In the case of AC, the contamination of chicken blood in the feather waste will not affect the quality of AC because both chicken feathers and chicken blood can be similarly converted into carbon. In addition, concerning the structure of feathers, it can be assumed as an assembly of short hollow fibers. Thereby, feathers have excellent strength-to-weight ratios as well as large surface areas. For the production of AC, the hollow structure of feathers would be advantageous if its structural features could be retained during the carbonization process. Concerning the hollow structure, carbon nanotubes (CNTs) with hollow and layered nano-sized structures

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are attractive to separate or remove the hazardous pollutants by functionalizing the hollow structure with acids or oxidizing agents [10,11]. However, it seems difficult to use CNTs for the daily wastewater system considering its running costs. Instead, if the feather can be carbonized while retaining its hollow structure, the carbon obtained will be functionalized to some extent, similarly as in the case of CNTs via chemical treatments, although their hollow structure is in a micrometer scale.

In this study, we have focused on the fundamental carbonization behavior of feathers. To prevent the feathers from undergoing liquefaction during the carbonization process and to control the graphitization properties of keratin molecules, we used a water-soluble phenolic resin as the feather modifier and investigated the potential of waste feathers as a starting material for the production of AC.

2. Experimental

2.1. Materials

Feathers were obtained from bedclothes waste that underwent dry-cleaning several times. Water-soluble phenolic resin (resol type IG-1002, nonvolatile: 50%) was supplied by DIC Co. (Tokyo, Japan). Other chemicals used in this study were all laboratory-grade from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

2.2. Carbonization and activation at the laboratory-scale

A newly designed electric furnace (TL1, Carbo-tec Co. Kyoto) with an internal volume of approximately 81 L was used. For carbonization, a 125–200 g sample was packed at the bottom of a reaction vessel (with an internal volume of ca. 10 L and diameter of ca. 20 cm) by placing a stainless drop-lid and filling the gap between the edge of the lid and the wall of the vessel with ceramic fibers. Then, the sample was heated to 800 °C at a heating rate of 3.4 °C/min, kept at 800 °C for 60 min, and left alone to cool to room temperature. For the production of the hybrid charcoal from feathers and phenolic resin, a certain amount of feathers was pretreated via dipping in an aqueous solution of the water-soluble phenolic resin, followed by drying at 70 °C for 60 min. In the case of the water-soluble phenolic resin alone, pre-heating was sufficient to produce a cast film at the bottom of the reaction vessel. The charcoal samples obtained are listed in Table 1 with the respective codes used throughout the text. The mass ratio in Table 1 was defined as the relative mass of the feathers versus the mass of the phenolic resin on a dry base.

To activate the charcoal, a rotary kiln (with an internal volume of ca. 0.75 L) was used. First, 30–60 g of charcoal was heated to 900 °C at a heating rate of 10 °C/min under N_2 gas flowing at 0.6 L/min; then, water vapor was added. The activation lasted for 5 min.

2.3. Heat treatment at 3000 °C

Samples heat-treated at 800 °C were further heated from room temperature to 3000 °C in 140 min, kept at 3000 °C for 30 min, and cooled to room temperature using the electric furnace (SCC-U-120/203/135, Kurata Giken Co., Konan Shiga, Japan) under argon gas flow.

Table 1
Sample codes of the starting materials.

Sample code	Starting material
F4Ph1	Feather waste (F) and phenolic resins (Ph), mass ratio = 4:1
F1Ph1	F and Ph, mass ratio = 1:1
TRY	L-Tryptophan
CEL	Cellulose (reed grass)
ACE	Acenaphthylene
Pr1S4	L-Proline (Pr) and Shellac (S), mass ratio = 1:4

2.4. Thermogravimetric analysis/differential thermal analysis (TG/DTA) measurement

TG/DTA was performed using an analyzer (WS-002, Bruker AXS K.K., Yokohama, Japan) on a 10 mg sample at a heating rate of 20 °C/min, up to 1000 °C, under N_2 gas flow at 50 mL/min. The sample was prepared as follows. In the case of the feather/phenolic resin mixture, the milled feathers were dispersed into 50% phenolic resin aqueous solution and then dried at 60 °C for 60 min. The obtained film was milled, and 10 mg was sampled. As for the phenolic resin, the cast film obtained from its solution was used.

2.5. X-ray diffraction

Wide-angle X-ray diffraction (WAXD) was performed on isotropic samples, which were obtained by grinding and mixing the carbons with high-purity silicon powder as the inner standard. The X-ray source was CuKα radiation.

The degree of graphitization (P1), defined as the probability for adjacent hexagonal carbon layers to have positional correlation in the graphite, was determined from the Fourier coefficients of both the 101 and 112 diffraction profiles [12,13], which were measured using step-scanning with a step of 0.01 and an accumulation time of 30 s. The average interlayer spacing was calculated using Bragg's equation from the peak diffraction angles of the carbons determined by referring to the diffraction of the silicon standard. The average interlayer spacings determined from the 002, 004, and 006 diffractions were denoted as $d_{002}(002)$, $d_{002}(004)$, and $d_{002}(006)$, respectively. The crystallite sizes parallel and perpendicular to the c-axis (Lc and La) were calculated from the full-width at half-maximum for the diffraction peaks of the carbons, which were corrected for the instrumental peak broadening by referring to the diffractions of the silicon standard. The size parameters determined from the 002, 004, 006, and 110 diffractions using Scherrer's equation were denoted as Lc(002), Lc(004), Lc(006), and La(110), respectively. The standard deviation of the distribution in the interlayer spacing (σ_c) and the true crystallite size (L_0) was determined using Hosemann's equation [14].

$$[1/\mathrm{Lc}(00\,l)]^2 = [1/L_0]^2 + \pi^4 \sigma_c{}^4 l^4 / \left[16\mathrm{d}_{002}(004)^6\right] \tag{1}$$

where l is the order of diffraction.

2.6. Surface characterization

The N_2 gas adsorption capacity was determined using an adsorption measurement instrument (BELSORP-18plus, BEL Inc. Jpn, Toyonaka, Japan). The surface area (S) was determined using the Brunauer–Emmett–Teller (BET) plot [15]. The volume (V) was determined from the amount of N_2 adsorbed at a relative pressure of 0.98. The mean pore diameter (D) was calculated as $D = 4\ V/S$ by assuming that the pores are uniform nonintersecting cylindrical capillaries.

The iodine adsorption capacity was determined with a titration method using 0.1 M sodium thiosulfate [16].

3. Results and discussion

3.1. Co-carbonization behavior of phenolic resin-modified feathers

For the production of carbonaceous adsorbents, the hollow structure of feathers would be advantageous if its structural features could be retained during the carbonization process. However, feathers tend to easily decompose hydrothermally and dissolve into water during hot pressurized water treatment over 180 °C [7]. Therefore, modifying the thermal properties of feathers from the viewpoint of thermosetting is