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Characteristics and humidity control capacity of activated carbon from bamboo

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ABSTRACT

Activated carbons were prepared from bamboo by chemical activation with K_2CO_3 or physical activation with CO_2. The structural and surface chemical characteristics of the activated carbons were determined by N_2 adsorption–desorption and Boehm titration, respectively. The water vapor adsorption properties of the activated carbons with various pore structures (preparation conditions) were examined. The relationship between water vapor adsorption capacity and pore properties, and the humidity control capacity of the prepared activated carbons are also discussed. The water adsorption isotherms show a region of rapidly increasing uptake of water vapor, and the relative humidity corresponding to those regions was different according to the preparation conditions, especially activation temperature. Water vapor adsorption capacity was improved with larger pore volume and surface area, but the humidity control capacity in a certain specific humidity region differed greatly according to the relative humidity corresponding to the steeply rising regions of the isotherms. In the typical operating conditions of an adsorption heat pump, RH 10–35%, the bamboo-sourced activated carbon that was prepared at 873 K by potassium carbonate activation with impregnation ratio 1.0 had the highest humidity control capacity.

1. Introduction

Carbon materials such as activated carbons are well known as excellent adsorbents with high specific surface area and large pore volume, and are widely used in separation (Horikawa et al., 2002), purification (Caqueret et al., 2008), catalysis (Cabiac et al., 2008), and energy storage (Khomenko et al., 2008).

Carbon materials, such as charcoal, have been used as humidity conditioning adsorbents since ancient times. Researchers have investigated the use of carbon materials in adsorption heat pumps (AHPs) or desiccant humidity conditioners (DHCs) as an adsorbent (Kawano et al., 2008), because water vapor adsorption on carbon materials has a sharp adsorption uptake accompanied by a clear adsorption hysteresis for desorption at medium or high relative humidity.

AHP is a compressor-free machine that operates like an inverse Carnot cycle utilizing a low temperature energy source such as solar energy or waste heat. Consequently, AHP has been attracting much attention in recent years as an environmentally friendly technology for utilizing waste heat. The principle of AHP is to use the exothermic/endothermic changes associated with adsorption/desorption of vapors on adsorbents (Wang et al., 2005). The characteristic pore properties of the adsorbent used have a great influence on the performance of the AHP. The ideal heat output of AHP of the water vapor type depends directly on the equilibrium adsorption ability of the adsorbent in the operational relative pressure range of AHP, Δq. There is a need for development of an innovative adsorbent with high adsorption capability for water vapor, prepared from environmentally friendly source materials such as biomass.

Various agricultural sources of biomass have been investigated as source materials for preparing activated carbons, including nutshells (Hayashi et al., 2002a), chickpea husk (Hayashi et al., 2002b), cherry stones (Olivares-Marín et al., 2006), olive stones (Ubago-Pérez et al., 2006), coffee endocarp (Nabais et al., 2008), and pine cones (Duman et al., 2009). Natural materials, which must be available in large quantities, may have potential as inexpensive precursors for activated carbon production. Bamboo is an abundant and inexpensive natural resource in Japan. It is well known that bamboo grows rapidly, so that it is possible to ensure a stable supply of bamboo as a source material.

Activated carbon is commonly prepared by chemical activation (with $ZnCl_2$, KOH, K_2CO_3, etc.) or physical activation (with CO_2 or H_2O) under various conditions, to carefully control the development of pore structure. When a biomass is used as the source material to prepare activated carbon, the applicability of the activation conditions should be verified because the ash composition is different in biomass species, and it can be different even in the same biomass species grown in different locations.

In the present study, we have used bamboo to prepare activated carbon by chemical activation with K_2CO_3 and physical activation

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with CO_2. We have investigated the influence of preparation conditions on the pore structure, the surface chemical properties, and the water vapor adsorption properties of the activated carbons that were prepared. We have also investigated possible applications of the prepared activated carbons as water vapor adsorbents for AHP and DHC, and general humidity conditioning, in typical operating conditions.

2. Methods

2.1. Preparation of activated carbon from bamboo

We used Moso bamboo (*Phyllostachys pubescens*; from Tokushima, Japan, Ban Co. Ltd.) which had been crushed to fibroids by blasting treatment, as the raw material for preparing activated carbon. The raw material was milled to minced fiber. The elemental composition (C, N, H and O) of the raw bamboo was determined with simultaneous multielement analysis equipment (Microcorder JM10, J-Science), and the ash was analyzed using X-ray fluorescence (XRF; JSX-3202 M, JEOL). The oxygen content (%) was calculated as 100 − (sum of the amounts of C, N, and H) − (amount of ash), assuming that other elements were not present.

Activated carbon was prepared by chemical activation with K_2CO_3 (Hayashi et al., 2002a,b, 2005) or physical activation with CO_2. Milled raw bamboo was mixed with saturated K_2CO_3 solution and kneaded, and the mixture oven dried at 383 K for 24 h. The impregnation ratio was estimated as

$$(\text{impregnation ratio}) = \frac{(\text{weight of } K_2CO_3 \text{ in solution})}{(\text{weight of milled bamboo})} \quad (1)$$

The impregnation ratios used were 0.5, 1.0 and 2.0.

The impregnated bamboo was placed in a ceramic boat, heated in an electric furnace (KRO-13K, Isuzu) to the activation temperature at a programmed heating rate of 10 K min^{-1} in a N_2 flow (300 cm^3 min^{-1}), and maintained for 1 h at that temperature. The activation temperature was changed within the range 773–1173 K. The activated sample was washed several times with hot water to remove residual chemicals, then dried at 383 K to give the activated carbon product (AC–K_2CO_3).

Samples of the milled raw bamboo were placed in a ceramic boat, heated in the electric furnace to the carbonization temperature at 10 K min^{-1} in an N_2 flow (300 cm^3 min^{-1}) and maintained for 1 h at that temperature to give bamboo chars (BCs). The carbonization temperature was varied within the range 773–1173 K. The bamboo char that was carbonized at 1173 K was activated for a further 0.5 or 1 h by carbon dioxide at 1173 K to give another activated carbon (AC–CO_2).

2.2. Characterization of prepared samples

The weight loss behavior during activation or carbonization of the impregnated bamboo and raw bamboo were measured using a thermobalance (Exstar6000 TG/DTA, SII). Samples were heated at 10 K min^{-1} in flowing N_2 to 1273 K which considerably exceeded the activation temperature of 1173 K.

The surface morphologies of the prepared samples were observed by field emission scanning electron microscopy, FE-SEM (S-4700, Hitachi). The elements present in the ash from bamboo char were determined with an energy dispersive spectrometer, EDS (Apollo 40, EDAX).

The surface functional groups of carbon–oxygen complexes were measured by Boehm titration (Boehm, 1966). A ca. 0.1 g carbon sample was added to excess (100 cm^3) standard base (0.01 N NaOH, 0.001 N Na_2CO_3, and 0.001 N $NaHCO_3$) solution, and the acidic oxides on the carbon surface were determined by back-titration with HCl after standing for 48 h at 298 K to reach equilibrium.

The adsorption isotherms of N_2 on the prepared samples were measured at 77 K using a constant volume adsorption apparatus (BELSORP-mini, Bel Japan). Before measuring the adsorption isotherm, the samples were heated to 473 K for 2 h in an N_2 flow to clean their surfaces. We determined the BET surface area, the mesopore size distribution, and the pore volume of the prepared samples. The specific surface area was calculated by the BET method based on the N_2 adsorption isotherm data. The micropore volume was calculated from the amount of N_2 adsorbed at a relative pressure of 0.1, and the mesopore volume was calculated by subtracting the amount adsorbed at relative pressure 0.1 from the amount adsorbed at relative pressure 0.95 (Rodriguez-Reinoso et al., 1982). The pore radius distribution was estimated by applying the Dollimore–Heal method to the measured desorption isotherm (Dollimore and Heal, 1964).

In addition, the carbon dioxide and water vapor adsorption isotherms of some samples were measured at 298 K using a constant volume adsorption apparatus (BELSORP-28, or -18, Bel Japan). Before measuring the adsorption isotherms, the samples were degassed at 473 K for 2 h.

3. Results and discussion

3.1. Characterization of bamboo char and bamboo activated carbon

3.1.1. Influence of activation method on pore structure

N_2 adsorption isotherms of the bamboo char (BC) and bamboo activated carbons (AC–K_2CO_3 and AC–CO_2) that were prepared at 1173 K are shown in Fig. 1; the characteristic pore properties of the prepared samples are given in Table 1. All of the N_2 isotherms were close to Type I. The largest amount of N_2 was adsorbed by AC–K_2CO_3, which had the largest specific surface area (1946 m^2 g^{-1}).

By contrast, the amount of N_2 adsorbed by AC–CO_2 was smaller than for BC which was prepared by carbonization only. The specific surface area of AC–CO_2 was 391 m^2 g^{-1}, approximately half that of BC. We could observe there were many tens of nanometer sized

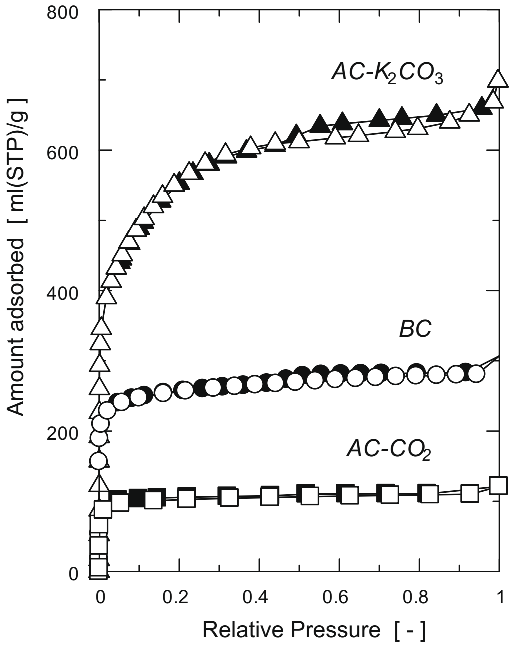

Fig. 1. The N_2 adsorption isotherms of BC, AC–K_2CO_3 and AC–CO_2.