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Role of nitrogen in pore development in activated carbon prepared by potassium carbonate activation of lignin

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ABSTRACT

The present work focuses on the role of nitrogen in the development of pores in activated carbon produced from lignin by K_2CO_3 activation, employing a fixed bed reactor under a high-purity He stream at temperatures of 500–900 °C. The specific surface area and pore volume obtained by activation of lignin alone are 230 m^2/g and 0.13 cm^3/g at 800 °C, and 540 m^2/g and 0.31 cm^3/g at 900 °C, respectively. Activation of a mixture of lignin and urea provides a significant increase in the surface area and volume, respectively reaching 3300–3400 m^2/g and 2.0–2.3 cm^3/g after holding at 800–900 °C for 1 h. Heating a lignin/urea/K_2CO_3 mixture leads to a significant decrease in the yield of released N-containing gases compared to the results for urea alone and a lignin/urea mixture, and most of the nitrogen in the urea is retained in the solid phase. X-ray photoelectron spectroscopy and X-ray diffraction analyses clearly show that part of the remaining nitrogen is present in heterocyclic structures (for example, pyridinic and pyrrolic nitrogen), and the rest is contained as KOCN at $\leq$600 °C and as KCN at $\geq$700 °C, such that the latter two compounds can be almost completely removed by water washing. The fate of nitrogen during heating of lignin/urea/K_2CO_3 and role of nitrogen in pore development in activated carbon are discussed on the basis of the results mentioned above.

1. Introduction

The high surface area and large pore volume of activated carbon (AC) are well known. AC is consequently widely used as an adsorbent and catalyst support. Its production continues to be the subject of a considerable amount of research [1–20], with methods being mainly classified into physical activation and chemical activation. The physical methods are well-proven technologies and involve treatment with H_2O, CO_2 or O_2 of carbonaceous materials formed by the carbonization of organic resources. As drawbacks, however, high-temperature treatment at 900–1100 °C is required, and the yield of AC is low. In the chemical methods, on the other hand, activation agents such as zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4) and potassium hydroxide (KOH) are mixed with organic resources, allowing activation and carbonization to advance simultaneously at temperatures lower than those used for the physical methods. However, a washing process is required to remove the added activation agents. Moreover, KOH employed in the activation of coal and/or petcoke causes corrosion problems in AC manufacturing facilities, while the K-species recovered by washing is in the form of potassium carbonate (K_2CO_3), which is difficult to reuse. Therefore, AC production methods that employ K_2CO_3 as an activation agent have been studied. [3,4,9–12,14–16,18–20]. According previous works, [15,16,18–20] it has been reported that nitrogen in organic resources as the carbon source might influence to increase of AC surface area. Consequently, it may be important that clarification of the role of nitrogen on AC pore development from the viewpoint of investigation about nitrogen release and retention including the state of nitrogen in the solid phase during AC production process.

In the present study, AC is prepared by activation and carbonization of a mixture of nitrogen-free lignin, urea (CH_4N_2O) and K_2CO_3 based on prior literature reports. The N-containing compounds formed in the process and the change in chemical form of nitrogen in the solid phase are investigated in detail, with the ultimate goal of elucidating the influence of nitrogen on AC porosity.

2. Experimental

2.1. Samples

In this research, commercially available lignin, urea and K_2CO_3 were respectively used as the carbon source, N-containing compound and activation agent. The chemical composition of the lignin was as follows: C, 53; H, 4.6; N, 0.26; S, 4.3; ash, 16 mass% -dry, with the purity of the latter two compounds being greater than 99%.

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Urea and K_2CO_3 were added to the lignin in a N_2 atmosphere at room temperature, corresponding to the physical mixing method. The lignin/urea, lignin/K_2CO_3 and lignin/urea/K_2CO_3 mixing ratios were respectively 1/1, 1/1 and 1/1/2 by weight, in accordance with prior literature [15,16].

2.2. Preparation of activated carbon and analysis of nitrogen-containing gases

The AC was prepared using a horizontal cylindrical quartz reactor (4.5 cm i.d., 64 cm long) installed in a transparent glass electric furnace, while streaming high-purity He (greater than 99.99995%). About 2.0 g of the sample described above was first loaded into a mullite boat (10 mm wide, 75 mm long, 9 mm deep) and held in the center of the reactor. After leak checks, the reactor was heated at 10 °C/min up to the predetermined temperature (500–900 °C), and then rapidly cooled to room temperature. The resulting sample was repeatedly washed with deionized water to remove the remaining K-species and finally dried in an oven maintained at 110 °C. In this paper, AC obtained from lignin/K_2CO_3 or lignin/urea/K_2CO_3 is denoted as $AC_{K_2CO_3}$ or AC_{urea/K_2CO_3}, respectively.

To analyze the gas formed during the activation/carbonization process, a flow-type fixed-bed quartz reactor equipped with an infrared image furnace was employed. This apparatus has been previously described in detail [21]. In a typical experiment, approximately 0.25 g of the sample was heated to 1000 °C at 10 °C/min under a high-purity He stream and held for 1 h. The NH_3 and HCN formed during this process were analyzed at 2 min intervals using a photoacoustic multi-gas monitor, while N_2 was quantitatively analyzed at 2 min intervals using high-speed micro gas chromatography. The yields of NH_3, HCN and N_2 were expressed as percentages of the nitrogen content in the feed sample, these yields were calculated by Eq. (1). The reproducibility of NH_3 and HCN evaluation was within ±3%, and for N_2 within ±2%.

$$NH_3,\ HCN\ or\ N_2,\ N-\% = \frac{\text{Amount of } NH_3,\ HCN \text{ or } N_2 \text{ desorption, mol/g}}{\text{Amount of N in feed samples, mol/g}} \times 100 \qquad (1)$$

2.3. Characterization

N_2 adsorption analysis of the AC samples was performed at −196 °C. The specific surface area was estimated using the BET method, and the pore volume was calculated using the αs plot method. [12,22] X-ray diffraction (XRD) measurement was carried out before and after water washing, using a conventional powder-diffraction apparatus employing Cu-Kα radiation monochromatized by Ni filtering. A sample selected for analysis using X-ray photoemission spectroscopy (XPS) was held on an In plate, and the N 1s spectrum was recorded under a high vacuum of $1–5 \times 10^{-7}$ Pa using an Mg-Kα X-ray source [23–25]. The binding energy of the spectrum obtained was referred to an In $3d_{5/2}$ peak of In_2O_3 at 444.9 eV [26].

3. Results and discussion

3.1. Influence of nitrogen on development of pore structure of activated carbon

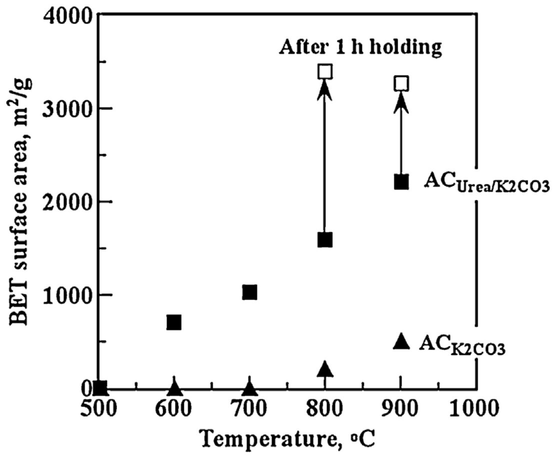

Fig. 1. Dependence of BET surface area of AC samples prepared from lignin/K_2CO_3 and lignin/urea/K_2CO_3 on activation/carbonization temperature and holding time.

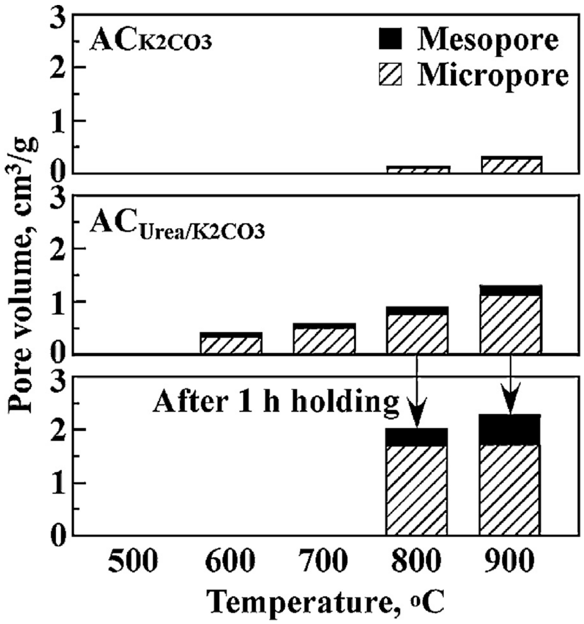

Fig. 2. Micropore and mesopore volumes for AC samples shown in Fig. 1.

The BET surface areas (denoted as S_{BET}) for $AC_{K_2CO_3}$ and AC_{urea/K_2CO_3} samples prepared at 500–900 °C are shown in Fig. 1. These values were calculated based on the N_2 adsorption isothermal as shown in Fig. S1 in Supplementary material. The carbonized products from lignin alone and lignin/urea had S_{BET} values small enough to be negligible, regardless of the temperature. The value for $AC_{K_2CO_3}$ increased somewhat with temperature, yet remained at about 500 m^2/g at 900 °C (Fig. 1). In contrast, the value surpassed 500 m^2/g at 600 °C when urea was added to lignin/K_2CO_3, and became approximately 2200 m^2/g at 900 °C (Fig. 1). Moreover, the S_{BET} value increased further to 3300–3400 m^2/g when AC_{urea/K_2CO_3} was retained for 1 h at 800–900 °C (Fig. 1). This tendency has also been observed for a mixture of lignin/K_2CO_3 and melamine ($C_3H_6N_6$) [16]. It is thus evident that N-containing compounds play an extremely important role in increasing the specific surface area of AC produced from lignin/K_2CO_3.

The micropore and mesopore volumes for the AC samples in Fig. 1 are given in Fig. 2. As expected from the results shown in Fig. 1, $AC_{K_2CO_3}$ exhibited little porosity, regardless of the temperature. The micropore and mesopore volumes for AC_{urea/K_2CO_3} both increased with temperature, however, with the greatest increase being seen for micropores. For the latter samples, holding for 1 h at 800–900 °C resulted in further pore development, with a combined increase for both types of pores of almost two times (2.0–2.3 cm^3/g) compared to the case for no holding time (1.0–1.2 cm^3/g). Other researchers have published similar results [16], and the effect has also been observed for AC derived from lignin/melamine/K_2CO_3 [16]. Thus,