Preparation of microporous activated carbon from coconut shells without activating agents

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1. Introduction

Activated carbon is one of the widely applied adsorbents, and can be produced from a variety of raw materials [1–4]. Coconut shell is suitable for preparing microporous activated carbon due to its excellent natural structure and low ash content [5]. There are two methods for the manufacture of activated carbon: physical and chemical activation. The difference is whether the activation agent is solid or gaseous. In chemical activation, the activation agent functions as a dehydrating agent inhibiting the formation of tar [6–9]. However, the product needs washing to remove residual inorganic, which causes a serious pollution problem. Physical activation uses gaseous activation agents [10,11], and does not produce waste water, therefore, is considered to be an environmentally benign technology. However, it takes a long time and much energy for producing microporous activated carbon. Recently, we tried a new method of preparing microporous activated carbon without using any activating agents and with little time and energy.

2. Experimental

Coconut shells produced in Hainan Island of China were chosen for precursors. Dry shells were crushed to pieces of 2–5 mm. The thermal degradation equipment used is schematically shown in Fig. 1. About 30 g of coconut shell pieces was placed in a vertical airtight reactor (R), which could be heated externally by an electric furnace (EF). Nitrogen was introduced into the reactor until 1.0 MPa of pressure was reached before raising the temperature. The reactor was then heated at a rate of $3\,^{\circ}C\,min^{-1}$ until a prescribed temperature in the range 250–350 °C was reached. A pressure gauge monitors the pressure change in the reactor. Constant temperature and pressure were maintained for a definite period of time and then valve 3 was opened suddenly leading to adiabatic expansion and sudden cooling. The sample was moved to another horizontal oven for carbonization. The temperature of the oven was raised at $5\,^{\circ}C\,min^{-1}$ to 850 °C in nitrogen atmosphere, and maintained for 1 h at the temperature. The carbonized sample was then cooled down to room temperature in nitrogen atmosphere. It was heated at 120 °C for 8 h under vacuum before adsorption measurement.

The precursors were subject to three different treatments before thermal degradation:

(a) Without any treatments at all
(b) Dried at 120 °C for about 6 h
(c) Soaked in water until water content is about 10%

Porous solids are usually characterized using the adsorption isotherms of N_2 at 77 K [12] or by the adsorption isotherms of CO_2 at 273 K [13]. Nitrogen adsorption was adopted to characterize carbon samples as a routine analysis, but CO_2 adsorption was also measured for some samples. The DRK equation [12] was applied to estimate the surface area (A). Pore volume (V_p) was estimated by the amount adsorbed at $p/p_s \approx 0.95$ dividing by the density
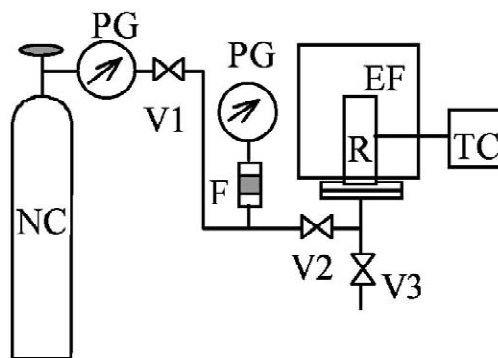

Fig. 1. The setup for thermal degradation. NC: nitrogen cylinder; PG: pressure gauge; F: filter; R: reactor; EF: electric furnace; TC: temperature controller; V1–V3: valves.

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of liquid nitrogen at 77 K (0.809 g cm^{-3}) [12]. Average pore size was determined as $4V_p/A$. A PSD oriented isotherm model [13] was used to evaluate pore size distribution.

3. Result and discussion

Typical results are presented in Table 1. Product quality is directly reflected in the adsorption isotherms of nitrogen at 77 K shown in Fig. 2. T-1 is the sample without thermal degradation, but carbonized directly at 850 °C, and was taken for a reference to evaluate samples subject to other processing. Samples starting with letter N did not receive any pre-treatment before thermal degradation, and those starting with letter D received pre-drying, and those starting with letter S received pre-soaking in water. It is shown that samples subject to thermal degradation possess higher specific surface area and pore volume than those that were directly carbonized. Sample N-8, which was obtained from sample N-1 by one more hour carbonization at 850 °C, shows the largest pore volume and surface area. It might be the result of further structural change or the consequence of oxidation due to the oxygen or water adsorbed on the sample when exposing to atmosphere considering its higher value of burn-off. Sample D-1 and S-2, respectively, represent the best result of receiving pre-treatments before thermal degradation. Comparing them with the runs without pretreatment, one can conclude that pre-drying is not necessary, and pre-soaking gives no advantage. The coconut shells began to soften at temperatures around 300 °C and volatile matter was released. As a consequence, the pressure in the airtight reactor increases faster than before, as shown in Fig. 3. The result shows that 325 °C is better than the others as the temperature of thermal degradation.

The natural cell structure of coconut shells must experience changes during thermal degradation and the following adiabatic expansion process. Such changes bene-
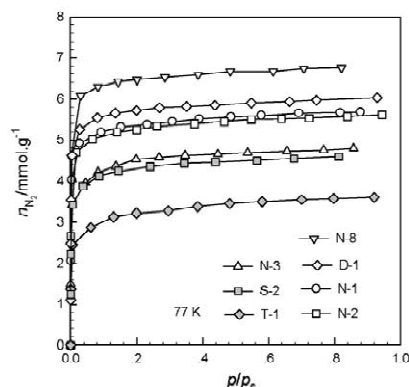

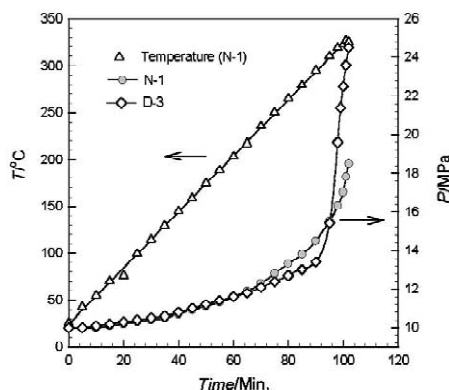Fig. 2. Adsorption isotherms of N_2 at 77 K on typical carbon samples.

Fig. 3. The temperature and pressure course during thermal degradation.

fit the creation of micropores in the carbonized samples, as shown by the experiment.

An adsorption isotherm of CO_2 at 273 K was obtained for sample N-8. The specific surface area obtained from the DRK plot of the isotherm is 609 m^2 g^{-1}, quite close to

Table 1
Representative results of activation tests

Sample	Temperature of degradation (°C)	Degradation time (min)	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Average pore size (nm)	Total burn-off (%)
T-1	–	–	354	0.12	1.36	72.5
N-1	325	102	558	0.20	1.43	73.2
N-2	325	108	548	0.19	1.39	73.6
N-3	311	95	469	0.16	1.37	73.8
N-5	275	95	554	0.19	1.37	73.9
N-6	275	105	470	0.16	1.36	74.6
N-8[a]	–	–	663	0.23	1.39	76.8
D-1	322	99	589	0.21	1.42	70.7
S-2	325	102	452	0.16	1.42	72.4

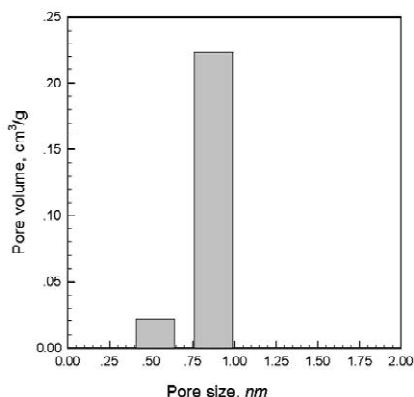[a] Obtained by one more hour of carbonization at 850 °C on sample N-1.

Fig. 4. Pore size distribution of sample N-8.

that reported by the nitrogen adsorption data. The pore size distribution of sample N-8 was also evaluated using the method proposed by Ref. [13]. The result (Fig. 4) shows most pores are narrower than 1 nm, which differs from the average pore size listed in Table 1. The value of $4V_p/A$ gives only a crude measure of pore dimension, which is affected by the reliability of V_p and A, and both of them involve large uncertainty.

In summary, adiabatic expansion at the state of thermal degradation followed by carbonization can create a microporous structure of activated carbon using coconut shells as precursor. Although the specific surface area is not high, such activated carbon has a narrow distribution of pore size in the range, possibly less than 1 nm. Therefore,

it might be a good precursor of carbon molecular sieves or superactivated carbons.

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Skeletal isomerization of 1-butene on tungsten oxide catalysts supported on activated carbons with various surface oxygen contents

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The skeletal isomerization of 1-butene is catalyzed by solids with acid surface sites of the Brönsted type [1].

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Tungsten oxide is one of the strongest acid solids among the metal oxides of the transition elements. This is due to the high oxidation state of tungsten and to the existence of double W=O bonds which allow delocalization of the ionic charge from the donation of protons, which in turn results in the stabilization of the conjugated base of the oxide [2].