Effects of thermal activation conditions on the microstructure regulation of corncob-derived activated carbon for hydrogen storage

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Abstract

Activated carbons derived from corncob (CACs) were prepared by pyrolysis carbonization and KOH activation. Through modifying activation conditions, samples with large pore volume and ultrahigh BET specific surface area could be obtained. The sample achieved the highest hydrogen uptake capacity of 5.80 wt% at 40 bar and $-196\,^{\circ}\mathrm{C}$. The as-obtained samples were characterized by N_2-sorption, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Besides, thermogravimetric analysis was also employed to investigate the activation behavior of CACs. Detailed investigation on the activation parameters reveals that moderate activation temperature and heating rate are favorable for preparing CACs with high surface area, large pore volume and optimal pore size distribution. Meanwhile, the micropore volume between 0.65 nm and 0.85 nm along with BET surface area and total pore volume has great effects on hydrogen uptake capacities. The present results indicate that CACs are the most promising materials for hydrogen storage application.

Key words

corncob-derived activated carbon; KOH activation; activation conditions; hydrogen storage

1. Introduction

The continued deterioration of environment and limited fossil energy make hydrogen (H_2) the most promising candidate to supersede traditional fuels due to its high mass energy density and pollution-free nature. It is thus widely accepted that hydrogen will play a critical role in the field of energy especially in transportation sector. The development of hydrogen fueled vehicles can bring economic and environmental benefits through a decrease in fossil fuel use, and consequently, a decrease in air pollution and other greenhouse gases [1].

However, hydrogen normally exists as gas and has a very low density, which is widely known to be a roadblock for achieving a hydrogen-based economy. Conventional hydrogen storage methods such as compressed gas storage and cryogenic storage have significant safety hazards for on-board applications due to its high pressure and low temperature operations [2]. Many efforts are made to develop new hydrogen storage materials including metal, chemical or complex hydrides and nanoporous materials to meet the target storage specifications for on-board applications. Compared with other novel porous adsorption materials like metal organic frameworks (MOF), covalent organic frameworks (COF) and porous aromatic frameworks (PAF), carbon based materials such as activated carbons (AC), carbon nanofibers (CNF) and carbon nanotubes (CNT) have been subjected to intensive research [3−6]. Among them, activated carbon derived from biomass carbonaceous source highlights the reutilization of bio-waste from agriculture (e.g. corncob, coconut shell, sawdust, etc) due to its low cost, ready availability and good chemical stability.

In previous literatures, activated carbons are mainly designed for general use as adsorbents in wastewater treatment to remove organic pollutants [7,8]. The activated carbon for water purification application possesses surface area less than $2000\,\mathrm{m^2/g}$ and large amounts of macropores which are drawbacks on hydrogen storage use. Thus, to develop activated carbons with ultrahigh surface area and optimal pore structure is of great interest to carry out the desired hydrogen storage target for on-board application. To our knowledge, the

published papers concerning the corncob-derived activated carbons rarely attained the BET specific surface area more than 3000 m^2/g [9−12]. Because hydrogen storage capacity is closely correlated with specific surface area, the as-obtained corncob-derived activated carbons are of great interest to the hydrogen storage application.

The objective of this study is to further explore the effects of activation conditions on the microsturcture of corncob-derived activated carbon. In addition, correlations between pore size distributions of corncob-derived activated carbon and their enhanced hydrogen storage capacity were also elaborated in this paper.

2. Experimental

2.1. Syntheses of corncob-derived activated carbons

The synthesis process comprises two steps: (i) pyrolysis carbonization of corncobs and (ii) chemical activation with KOH as activating agent. Detailed processes were given in our previous work [13], the as-obtained samples were hereafter designated as CACT-R (corncob activated carbon), where T is the activation temperature and R is the heating rate (Table 1).

Table 1. Different prepared conditions for different corncob activated carbon samples

Samples	Heating rate (°C/min)	Activation temperature (°C)	Activation time (h)	Ball milling time (min)	KOH/carbon ratio	Yield (%)
CAC800-3	3	800	3	30	4	40.2
CAC800-5	5	800	3	30	4	38.6
CAC800-10	10	800	3	30	4	23.5
CAC850-3	3	850	3	30	4	34.5
CAC850-5	5	850	3	30	4	32.6
CAC850-10	10	850	3	30	4	14.4
AC7	commercial activated carbon					

2.2. Characterization

The scanning electron microscopy (SEM, FEI SIRION 200/INCA, OXFORD) and transmission electron microscopy (TEM, JEM-2100F, JEOL) were adopted to determine the morphologies and texture of the samples. A high accuracy balance (METTLER TOLEDO with ±0.00001 g accuracy) was used to diminish the experimental error.

NETZSCH STA 449C apparatus was used to investigate the behavior of the activation process under nitrogen atmosphere. Sample in an alumina open cell was heated up from room temperature to 1000 °C at a heating rate of 3, 5, 10 °C/min, respectively. The flow of nitrogen was 15 mL/min.

Nitrogen-sorption isotherms and textural properties of all the samples were determined at −196 °C using nitrogen in a conventional volumetric technique by a Micromeritics ASAP 2020 sorptometer over a wide relative pressure range from 10^{-6} to 0.995. The surface area was calculated using BET method based on the adsorption data in partial pressure (p/p_0) ranging from 0.02 to 0.25 and the total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of 0.98. The micropore surface area was calculated by Dubinine Astakhov (DA) equation. The micropore volume was calculated by Dubinine Radushkevich (DR) equation. Pore size distributions (PSDs) were calculated by Density Functional Theory (DFT) Plus Software (provided by Micromeritics Instrument Corporation), which is based on the calculated adsorption isotherms for pores of different sizes. In DFT calculations, the equilibrium model of carbon slit-shaped pores was applied. All of the samples were degassed at 300 °C for 600 min prior to the measurement.

Hydrogen adsorption measurements were carried out at 25 °C over the pressure range of 0−170 bar and at −196 °C over the pressure range of 0−100 bar, respectively. Hydro-

gen adsorption measurements at high pressure were carried out with a standard pressure-composition-temperature (PCT) volumetric apparatus. The bulk gas amounts were calculated by the state equation of Modified Benedict-Webb-Rubin [14]. The hydrogen uptake under atmospheric pressure was evaluated over the pressure range of 0−1.0 bar at −196 °C by ASAP 2020 apparatus. Previous to the measurement, the samples were degassed at 300 °C for 600 min under vacuum. High-purity hydrogen (⩾99.9999%) was used for the uptake measurement.

3. Results and discussion

Through the methodology described in the experimental section, the activated carbons with ultrahigh surface area and controlled morphologies and texture can be prepared from corncob by KOH activation. The morphologies and texture of the activated carbons are obviously affected by the preparation parameters.

Figure 1 shows the SEM images of the three as-prepared typical activated carbon samples. Different from honeycomb structure reported by previous works [9,10], all the prepared samples were mainly composed of vast irregular granules. It can be concluded that original honeycomb morphologies of corncob are damaged to abundant irregular granules during the intense ball milling process before activation. In particular, sample CAC850-10 showed large amount of surface opening pores, which can be ascribed to the over-etching caused by rapid heating rate. With the increase of activation temperature and heating rate, the intensive reaction between KOH and carbide leads to the enlargement of nanopores, resulting in the decrease of micropore volume which could also be verified by the data in Table 2. Figure 2 shows the HRTEM images of two typical activated carbon samples, CAC800-5 and CAC850-5,