



High-pressure hydrogen storage and optimizing fabrication of corncob-derived activated carbon



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ABSTRACT

The corncob-derived activated carbons (CACs) with ultrahigh surface area have been prepared by KOH activation. The as-obtained samples were characterized by N₂-sorption, scanning electron microscopy (SEM), and high resolution transmission electron microscopy (HRTEM). The pore size distribution (PSD) was analyzed by using DFT method integrated slit-shaped pore model. An activated carbon sample (CAC4) shows BET surface area of 3708 m² g⁻¹ and pore volume of 2.0 cm³ g⁻¹. The size effect of carbonized particle mixed with KOH was analyzed with the change of activation temperature. The results show the high activation temperature and smaller particle size are suitable to prepare activated carbons with high surface area and large pore volume, and the low activation temperature and bigger particle size are helpful to prepare activated carbons with smaller pore size and narrow pore size distribution. The hydrogen storage results show corncob-derived activated carbons have high hydrogen uptake capacity. The excess hydrogen uptake of sample CAC4 was 3.21 wt% at 1 bar and 77 K, and 5.80 wt% at about 40 bar and 77 K (the H₂ uptake gets the highest at about 40 bar for CACs). The high-pressure hydrogen uptake at 298 K is different from the data at 77 K. The sample CAC3 shows the highest hydrogen uptake capacity of 1.05 wt% at 298 K and 164 bar, and higher than sample CAC4. This means that the changes of H₂ uptake are related to textural characters materials caused by the preparation parameters as well as storage temperature and pressure.

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1. Introduction

Hydrogen is the one of the most promising alternate fuel due to its high mass energy density and pollution-free nature; it will play a very important role in the field of future energy. The fuel cell electric vehicles (FCEVs) using hydrogen are considered as the most promising vehicles in the 21st century with numerous advantages compared with conventional cars. Firstly, FCEVs not only have higher energy conversion efficiency and environment-friendly, but also the using fuel (hydrogen) for FCEVs can be got by renewable sources, and make the cars independent from the fossil fuels [1]. While, before the FCEVs dominate the global car market, the hydrogen storage is one of main hurdles. The many storage methods (liquefaction, compression, metal hydride and physisorption) used to solve the hydrogen storage problem are being extensively studied [2–4].

Among all the approaches listed above, physisorption has gained much attention than the others due to its better kinetics performance, reversibility, and relatively high storage capacity. In general, physisorption employs high specific surface area adsorbent that can effectively adsorb hydrogen, such as activated carbon. Comparing with other novel sorption materials like metal organic frameworks, covalent organic frameworks (COF), and porous aromatic frameworks (PAF), activated carbon shows good chemical stability, ready availability, high packing density, and low cost, all of these make activated carbon become a favorable candidate material for hydrogen storage [5–7]. Varieties of activated carbons with high specific surface area have been prepared over the past decade by chemical activation. Typically, the preparations of activated carbon with high surface area from biomass wastes such as sawdust, bamboo leaves, coconut shell, corncob, hemp, etc., have attracted much attention [8,9]. Among these carbon sources, corncob is a good renewable precursor to prepare activated carbon with high surface area [10]. In our lab, a series of corncob-derived activated carbons (CAC) with ultrahigh surface area have been prepared [11]. In the previous works, some

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preparation parameters such as activation temperature, activation time, heating rate and KOH/carbon ratio were investigated in order to regulate microstructure of activated carbons. In the preparation process, the carbonized powders need be grounded by ball milling. Although fine powders are easier to make KOH and carbonized powders mix homogeneously, which could be helpful to obtain uniform activated carbons, the preparation processes are more complicated. In addition, the particle size of carbonized powder could affect the yield as well as pore size distribution (PSD) and hydrogen storage performance of activated carbon products.

In the previous researches about hydrogen storage performance of activated carbons, most reports focused on hydrogen uptake at low pressure and 77 K [12–14]. For possible application in future, the research of high-pressure hydrogen storage for porous carbons could be more useful.

In this work, the size effect of carbonized particles was investigated in the fabrication of CACs. The hydrogen storage performance of CACs at high pressure was systematically investigated at 77 K as well as ambient temperature. It was demonstrated that activated carbon with ultrahigh surface area and smaller pore size could be fabricated from larger carbonized particles. The porous structure effect of CACs on enhanced hydrogen storage capacity was also illustrated in this paper.

2. Experimental

2.1. Preparation of activated carbon

The corncobs used are No. 9 Jinkun from Chifeng city, the Mongol Autonomous Region, located in the northeast of China. The corncobs were firstly carbonized, then following by KOH activation. The detailed procedures are described as follows.

Initially, after drying for 12 h at 397 K, corncobs were grounded and sieved into powders with typical size of 380–830 μm and more than 880 μm . Secondly, the corncob powders were placed into a furnace and heated to 673 K with a heating rate of 3 K/min for 4 h in flow nitrogen. Part carbonized powders were then further ground into small particles with size of less than 25 μm by ball milling. Thirdly, the carbonized powders were soaked in KOH saturated solution and magnetically stirred for 1 h at room temperature without air, then drying in flow nitrogen at 397 K overnight to evaporate most of the adsorbed water on the sample. Finally, the impregnated mixture was transferred to box-type atmosphere furnace and activated at different temperatures under flow nitrogen with 2.5 L/min. The final products were washed with deionized water until the pH value reached about 7.0 and then dried at 110 °C under vacuum. The as-prepared products were here after designated as CAC x and x is sample's number (see Table 1).

2.2. Characterization and analysis methods

The textural properties of the samples were studied by N_2 -sorption at 77 K with automatic instrument (ASAP2020, Micromeritics)

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

Sample	Activation temperature (K)	Carbonized particle (μm)	Activation time (h)	Heating rate (K/min)	KOH/carbon ratio	Yield (%)
CAC1	1073	<25	3	5	4	32.6
CAC2	1073	380–830	3	5	4	37.9
CAC3	1073	>880	3	5	4	39.3
CAC4	1123	<25	3	5	4	28.5
CAC5	1123	380–830	3	5	4	29.4
CAC6	1123	>880	3	5	4	30.2

over a wide relative pressure range from about 10^{-6} to 0.995. Prior to the measurements, all samples were degassed at 300 °C for 600 min. The specific surface area was assessed by standard BET method (software available in the ASAP2020) using adsorption data in the relative pressure ranging from 0.02 to 0.25. The microspore surface area was calculated by the Dubinin Astakhov (DA) equation. The total pore volume was calculated by converting the amount of N_2 adsorbed at a relative pressure of 0.98 to the volume of liquid adsorbate. The micropore volume was calculated by the Dubinin Radushkevich (DR) equation. Pore size distributions (PSD) were calculated by using the Density Functional Theory (DFT) Plus Software (provided by Micromeritics Instrument Corporation), which is based on calculated adsorption isotherms for pores of different sizes. In the DFT calculations, the equilibrium model of carbon slit-shaped pores was applied.

The morphologies of the samples were characterized by scanning electron microscopy (SEM, FEI SIRION 200/INCA, OXFORD) and high resolution transmission electron microscopy (TEM, JEM-2100F, JEOL).

Hydrogen storage performance was carried out on ASAP2020 adsorption analyzer for low pressure measurement at 77 K, and typical pressure–composition–temperature (PCT) apparatus for high pressure measurement at 77 K and 293 K, respectively. All of samples were evacuated to ultrahigh vacuum at 300 °C for 600 min before the test. The high-purity hydrogen (99.999%) was used for the H_2 uptake measurements.

3. Results and discussion

Fig. 1 shows the SEM pictures of the as-prepared six activated carbon samples. The morphologies of samples CAC2, CAC3, CAC5, and CAC6 show typical honeycomb structure, whose carbonized particle size is more than 380 μm and 880 μm . However, the morphologies of samples CAC1 and CAC4 whose carbonized particle size is less than 25 μm are completely different from honeycomb structure, and were composed of amount of irregular granules. In order to get less than 25 μm carbon powders before KOH activation, a ball milling process was taken into consideration. The ball milling process damaged the origin honeycomb morphologies of carbonized particle and formed irregular granules. After KOH activation, the original morphologies of carbonized particles can be maintained basically. Fig. 2 shows HRTEM images of sample CAC1 and CAC4. The HRTEM image shows that numerous slit-shaped smaller nanopores were formed like zeolite templated carbon, and pore size distribution is very uniform through KOH activation. The pore size of sample CAC4 looks like larger than CAC1, which indicates that low activation temperature could be helpful to form smaller pores.

The N_2 -sorption isotherms and pore size distributions (PSDs) of CACs samples prepared at different preparation conditions are shown in Figs. 3 and 4. The inset figures are logarithmic scale isotherms. The results of Figs. 3(a) and 4(a) show that origin carbonized particle size can significantly influence on N_2 adsorption properties of activated carbons prepared. On the whole, the isotherms of all samples belong to type I in the IUPAC classification, a characteristic of microporous materials. The samples CAC2, CAC3, CAC5 and CAC6 were fabricated from larger carbonized particles, and samples CAC1 and CAC4 were fabricated from smaller carbonized particles. This information indicates bigger carbonized particles are helpful to prepare microporous carbons. Comparing Fig. 3(a) with Fig. 4(a), it was clearly found the difference of isotherms caused by carbonized particle size is more remarkable with the increase of activation temperature. The smaller carbonized particle and high activation temperature could be suitable to fabricate activated carbon with ultrahigh surface area.

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