

Pore size effects of nanoporous carbons with ultra-high surface area on high-pressure hydrogen storage

Zhen Geng^{a,c}, Cunman Zhang^{a,b*}, Dabin Wang^{a,b}, Xiangyang Zhou^{a,b}, Mei Cai^d

a. Clean Energy Automotive Engineering Center, Tongji University, Shanghai 201804, China;

b. School of Automotive Studies, Tongji University, Shanghai 201804, China;

c. School of Materials Science and Technology, Tongji University, Shanghai 201804, China;

d. Research & Development Center, General Motors, MI 48265-3300, United States

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Abstract

In this work, the morphologies and pore structures of a series of corncob-derived activated carbons and zeolite templated carbon with ultrahigh surface area were carefully investigated by SEM, HRTEM and N₂-sorption characterization technologies. The high-pressure hydrogen uptake performance was analyzed using standard Pressure-Composition-Temperature apparatus in order to study the pore size effects on hydrogen uptake. These as-obtained porous carbons showed different characteristics of pore size distribution as well as specific surface area. The results indicate that the most effective pores for adsorbing hydrogen depended on the storage pressure. These ultramicropores (0.65–0.85 nm) could be the most effective pores on excess H₂ uptake at 1 bar, however, micropores (0.85–2 nm) would play a more important role in excess H₂ uptake at higher pressure at 77 K. At room temperature, pore size effects on H₂ uptake capacity were very weak. Both specific surface area and total pore volume play more important roles than pore size for H₂ uptake at room temperature, which was clearly different from that at 77 K. For applications in future, the corncob-derived activated carbons can be more available than zeolite templated carbons at 77 K. Element doping enhanced hydrogen uptake could be main research direction for improving H₂ uptake capacity at room temperature.

Key words

corncob; activated carbon; zeolite templated carbon; hydrogen storage; pore size effect

1. Introduction

Attentions have been intensively gained for the widespread change from fossil fuels to renewable energies. Hydrogen is being considered as an ideal alternative to fossil fuels due to its high chemical energy and pollution-free burning [1,2]. It is an excellent energy carrier especially for mobile applications. However, several scientific and technological issues need to be overcome for its economical applications and particularly its storage is one of the key hurdles.

There are four principal methods to store hydrogen, including liquefaction, compressed gas, chemical hydrogen storage with metal hydrides and hydrogen physisorption [3]. Among the approaches listed above, physisorption has gained attractions due to its rapid kinetics, reversibility and relatively high storage capacity. Several studies on hydrogen physisorption of porous solid materials, such as metal-organic frame-

works (MOFs) [4], zeolite [5] and carbon materials (e.g. carbon nanotubes, carbide-derived carbons and nanoporous activated carbons) [6–8] have been performed. Among them, nanoporous carbon materials as hydrogen storage media have attracted extensive attentions due to their low cost, light weight, high surface area and chemical stability.

It is now well demonstrated that the hydrogen physisorption capacity of porous carbons depends on the specific surface area and pore volume. A number of studies indicate that hydrogen physisorption on porous carbons occurs mainly inside the micropores especially micropores below 1 nm, and surface area associated with microporosity and fit pore size is crucial for hydrogen storage [9–12]. Recently, our research results indicate that the micropore volume between 0.65 nm and 1.5 nm is a key factor influencing the hydrogen uptakes at 77 K, which can be more important than BET surface area and total pore volume [13]. Thus, it is desirable to improve fit microporosity to enhance hydrogen storage capacity.

* Corresponding author. Tel: +86-21-69583793; Fax: +86-21-69583850; E-mail: zhangcunman@tongji.edu.cn

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Chemical activation of raw materials containing carbon offers an effective approach to obtain the activated carbons with characteristic pore structure, ultra-high surface area and pore volume, which is generally made by mixing carbonaceous materials with chemical activating agents (KOH, H_3PO_4 , $ZnCl_2$, etc.), followed by the carbonization. Among various chemical reagents, KOH is widely used since it can result in activated carbons (ACs) with defined micropore size distribution, and ultrahigh specific surface area (SSA) up to $3000\text{ m}^2/\text{g}$. Thus, KOH activation is considered as one of the effective ways to prepare microporous activated carbons with promising hydrogen storage [14].

In the previous study, correlation investigations showed the micropores between 0.65 nm and 0.85 nm could be the most effective pores for hydrogen uptakes at 77 K and 1 bar. However, the hydrogen uptake capacities at 1 bar can not reflect the full hydrogen uptake capacity of carbon materials. It is very necessary to study the hydrogen storage performance at high pressure. Are the ultramicropores between 0.65 nm and 0.85 nm still the most effective pores for excess hydrogen uptake at higher pressure?

In this work, the morphologies and pore structures of corncob-derived activated carbons (CACs) and zeolite templated carbon (ZTC) will be carefully investigated using effective characterization technologies and analysis methods. Based on the above information, the hydrogen storage performance of a series of CACs and ZTC will be investigated at a wide testing pressure. The pore size effects on hydrogen storage will be analyzed deeply.

2. Experimental

2.1. Material synthesis

Activated carbons were prepared by KOH chemical activation with biomass corncob as carbon sources. Detailed procedures were similar to previous reports [13]. Generally, dry corncob powders were carbonized at 673 K for 4 h in flowing nitrogen atmosphere. The obtained carbonized powders were then further ground into small particles with different particle size by varying ball milling time at the rate of 400 r/min. Then, carbonized powders were suspended in KOH saturated solutions with different ratios (KOH/C ratio 3–5 : 1) and magnetically stirred for 2 h at room temperature followed by drying under vacuum at 393 K for 12 h to evaporate most of the adsorbed water on the sample. Finally, the impregnated mixture was transferred to a muffle furnace and activated at different temperatures (973–1123 K), activation time (1–5 h) and heating rates (3–10 K/min) under flow nitrogen. The final products were washed with deionized water until the pH value reached about 7.0 and then dried at 393 K under vacuum. The as-prepared products were denoted as CAC_x (corncob-derived activated carbons), and x is sample's number. Among several prepared samples, some samples with typical characteristic (see Table 1) were selected to study hydrogen storage. Besides, commercial activated carbon (AC) from EnerG2 was also used to study the pore size effects on hydrogen storage as a comparison.

Table 1. Prepared conditions for different corncob activated carbon samples

Samples	Particle size (μm)	Activation temperature (K)	Activation time (h)	Heating rate (K/min)	KOH/C ratio
CAC1	<25	1123	3	5	4
CAC2	>880	1123	3	5	4
CAC3	<25	1123	3	3	4
CAC4	380–830	1123	3	5	4
CAC5	<25	1123	3	10	4
CAC6	<25	1073	3	5	3
CAC7	<25	1073	3	5	5

Zeolite templated carbon (ZTC) was prepared via nanocasting using zeolite NaY as solid template and furfuryl alcohol as carbon precursor. Detailed procedures were described as follows. First, after drying zeolite NaY at 473 K under vacuum for 12 h, the furfuryl alcohol (98%, Sigma-Aldrich) was casted into zeolite by nanocasting process at room temperature. Excess furfuryl alcohol was added into dried zeolite and magnetically stirred for 24 h under N_2 atmosphere. The mixture of zeolite and furfuryl alcohol was collected by filtration and washed with excess mesitylene (99.0%, Sigma-Aldrich). Then the filtered mixture was transferred to glass flask preheated to 353 K in N_2 flow for drying, and then the temperature was elevated to 423 K for 12 h under N_2 flow for polymerization. The mixed powders were transferred to ceramic boats and heated to 973 K at 5 K/min under N_2 flow in a horizontal quartz tube furnace, then N_2 was switched to propylene/ N_2 mixture (7% propylene) gas for

2 h, and back to nitrogen gas with increasing temperature to 1173 K at 10 K/min for 3 h. Finally, the product was transferred into aqueous solution of HF (48%, EM Industries) to remove zeolite template. The final product was washed by deionized water until the pH value reached about 7.0 and then dried at 393 K under vacuum.

2.2. Material characterization and analysis methods

The morphologies of samples were characterized by scanning electron microscopy (SEM, NOVA Nano, FEI). Porous structure of the samples was characterized by transmission electron microscopy (TEM, JEM-2100F, JEOL).

The textural properties of the samples were performed by N_2 -sorption at 77 K using a Micromeritics ASAP2020 over a wide relative pressure ranging from about 10^{-6} to 1.0. Prior

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