Large surface area sucrose-based carbons via template-assisted routes: Preparation, microstructure, and hydrogen adsorption properties

Jinjun Cai [a,b], Menglong Yang [a], Yanlong Xing [a], Xuebo Zhao [a,*]

[a] Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, PR China
[b] University of Chinese Academy of Sciences, Beijing 100049, PR China

HIGHLIGHTS

- Sucrose was selected as precursor to prepare carbons in the existence of USY zeolite.
- We studied the influence of USY zeolite on the pore structure of carbons.
- The specific surface area and pore width of these carbons can be easily adjusted.
- Hydrogen storage properties on these carbons were correlated with their pore structure.

GRAPHICAL ABSTRACT

Sucrose-based porous carbons were prepared via template-assisted method. The presence of zeolite in carbonization will inhibit graphitic degrees to some extent and enlarge surface area and pore volume of carbons, and then improve hydrogen storage capacities.
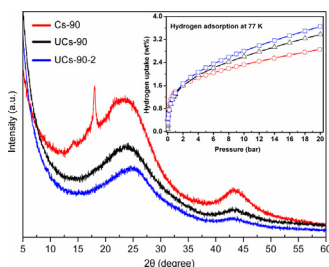
ARTICLE INFO

ABSTRACT

We report the preparation of sucrose-based nanoporous carbons via template-assisted routes using zeolite USY as the hard-template. Sulfuric acid-pretreated sucrose solution is polymerized and carbonized via adjusting the mass ratios of zeolite over sucrose and temperatures. Large surface area carbons with wide micropore size, developed mesoporosity and moderate storage capacity were obtained. We find that preparation parameters have great effects on the pore structure of carbons. Total pore volume of carbons develops with an increase of carbonization temperature and the presence of zeolite in carbonization processes can effectively enlarge the surface area and pore volume. However, the morphology of carbons is not transferred from zeolites, and micropore in the carbons is almost wholly from the sucrose precursor itself. The hydrogen adsorption properties of carbons at 77 K and 20 bar are further investigated in this work. Carbon with a surface area of 1200 m²/g exhibits a hydrogen storage capacity of up to 3.65 wt% at 77 K and 20 bar, and the hydrogen capacities at higher pressures are found to be much more correlated with surface area and micropore volume of carbons.

1. Introduction

Nowadays, the scarcity of energy resource and the environmental pollution in the evolution of human fuels have definitely aroused great attention towards searching for an alternative fuel [1]. Hydrogen is actually considered to be one of the most attractive energy carriers and fuels in the near future because its combustion creates neither air pollution nor green-house gas emission, and also with a heating value three times larger than petroleum [1–3]. For the most actual applications, however, the storage of hydrogen is the largest barrier to overcome. There is a growing interest in the development of new techniques for hydrogen storage, and the

* Corresponding author. Tel.: +86 532 80662728; fax: +86 532 80662728.
E-mail address: zhaoxb@qibebt.ac.cn (X. Zhao).

physisorption in carbon-based materials is one of the most promising methods available because of their fast kinetics, reversibility, and relatively low costs [4,5]. The surface areas and micropore volumes are found to be the most key parameters in dictating the hydrogen uptake in such materials. There are many studies to date have been conducted for hydrogen storage on various solid-state porous materials such as the activated carbons, zeolites, and metal-organic frameworks (MOF) [6–8], however, there are seldom materials can achieve the claims of DOE (Department of Energy, USA) criterion for the storage uptake on practical applications. The storage capacities of hydrogen on carbons are highly dependent on surface areas and porosities especially for microporosities, and the uptakes decrease rapidly at high temperature for the weak interaction between adsorbates and adsorbents. Therefore, the weak interaction of molecules physisorbed within pores is especially needed to be understood in order to optimize materials for hydrogen adsorption.

Porous carbons with well-developed pores have been used extensively in the area of catalysis, adsorption, separation, and electrode materials for their superior properties such as the high surface area, large pore volume, and extreme stability [9,10]. The past decade in particular has witnessed a rapidly growth in diverse applications, especially in the hydrogen storage [11–17]. In order to meet the requirements of hydrogen storage, a more refined control on the microporosities, surface chemistry and morphology of carbons is very desired [18]. Moreover, the preparation routes and precursor usually determine the ranges of physical properties for final carbons [19–21]. Therefore, there is no doubt that a sensible choice of precursors is one of the most critical issues for preparing carbons with high performance on hydrogen storage. Of late, many efforts have been conducted for preparing carbons with improved properties and lots of scientists have demonstrated that the existence of zeolites in carbonization has significant effects on the morphology, pore structure, and adsorptive behavior of carbons [22]. All previous reported data have definitely indicated a promising potential of the template-assisted method in hydrogen storage [23–25]. In general, templated-carbons were prepared via pyrolysis of precursor formed in highly ordered micro-channels or meso-channels of inorganic materials and followed the destruction of templates. In this way, pore structure of carbons can be largely manipulated via the selection of a proper inorganic template, precursor as well as pyrolytic conditions.

Sucrose is a kind of small organic molecules and has been widely used as precursor to prepare ordered mesoporous carbons using ordered silicas as hard-template [26–35]. In this paper, we report the preparation of porous carbons with sucrose as a precursor in the presence of USY zeolites via controlling the carbonization temperature and the mass ratio of zeolite to sucrose. Moreover, the adsorptive properties of hydrogen at 77 K on the carbons to 20 bar were also investigated. The purpose of this paper reported here is two-fold as follows: first to investigate the effects of preparation parameters on pores of carbons with an aim to better understanding the formation mechanism of pore structures; second to correlate the results of hydrogen storage at cryogenic temperature to the pore architecture of carbons.

2. Experimental

2.1. Materials and preparation of carbons

USY zeolite (H-form, $SiO_2/Al_2O_3 = 10$–13, Xinhong Chemical Co., Ltd, China) was chose as the template after pre-calcination at 550 °C for 6 h in air and used throughout in our experiment. Based on the information provided by manufacturer, the zeolite is an ultra-stable one which can preserve its crystal structure even up to 990 °C. Sucrose and sulfuric acid (AR, both purchased from Sinopharm Chemical Reagent Co., Ltd) were used as received. Nitrogen and hydrogen with purities above 99.999% for the gas adsorption measurements were provided by Qingdao Heli Gas Co., Ltd, China.

Sucrose-based carbons were prepared via a modified impregnation method [29,31]. Firstly, powdery zeolites dried under vacuum at 150 °C for 6 h and then 1.0 g of zeolites were impregnated with an aqueous solution consisting of 1.0 g sucrose, 0.12 g H_2SO_4, and 4.0 g H_2O under reduced pressure at 25 °C and later pressure was restored to atmospheric pressure via introducing air. Secondly, the mixture of zeolite-sucrose solution were stirred for 10 h and then heated at 100 and 160 °C for 6 h, respectively. Composites of zeolite containing partially decomposed sucrose were immersed again with an aqueous solution consisting of 0.5 g sucrose, 0.06 g H_2SO_4 and 4.0 g H_2O for stirring 10 h. After heated again at 100 °C for 6 h and followed at 160 °C for 6 h, the final brown-color composite were carbonized in a vertical quartz tube (i.d. = 16 mm) under N_2 flow at a rate of 5 °C/min to the fixed temperature (600–1000 °C) for 4 h. In contrast, two samples were also carbonized at 900 °C for 4 h via the same infiltration procedures with pure sucrose solution or doubled mass of zeolite to the first immersed sucrose. Finally, all black samples were treated with an excess amount of 40% HF for 6 h and then refluxed in a concentrated HCl at 60 °C for 3 h. The obtained carbons were washed with copious quantities of distilled water and air-dried at 120 °C overnight.

Carbons derived from the impregnation procedure that mass ratio of zeolite over the first impregnated sucrose is 1.0 were denoted as UCs-60, UCs-70, UCs-80, UCs-90, and UCs-100, corresponding to carbonization temperature of 600, 700, 800, 900 and 1000 °C, respectively. The sample carbonized at 900 °C for 4 h via the same impregnation procedure with a doubled mass of zeolite to the first impregnated sucrose was denoted as UCs-90-2. Sample derived from a pure sucrose solution was denoted as Cs-90, referring to the carbonization temperature of 900 °C for 4 h.

2.2. Characterization of porous carbons

The structural feature of carbons was studied by the X-ray diffractometer (XRD, Bruker D8) and Raman spectrometer (Renishaw-inVia Raman microscope, UK). The morphologies were performed with observations on a scanning electron microscopy (SEM, Hitachi S-4800). N_2 sorption data were collected at 77 K on a static volumetric sorption analyzer (ASAP2020, Micrometrics, USA). The surface area was calculated using Brunauer-Emmett-Teller (BET) method based on the adsorption data of N_2 in the relative pressure (p/p_0) range of 0.02–0.25. The partial pressure range (0.02–0.25) for the calculation of surface area was selected taking into accounts previous reports that lower partial pressure range (0.01–0.05) will overestimate surface area whereas partial pressure range (0.1–0.3) underestimate surface area [36,37]. Before N_2 adsorption measurements, samples were degassed for 10 h at 300 °C.

2.3. Hydrogen uptake measurements

Hydrogen adsorption measurements were performed on an Intelligent Gravimetric Analyzer (IGA-001, Hiden), which is an ultrahigh vacuum system, and incorporates a microbalance capable of measuring weight with a resolution of ±0.1 μg. The hydrogen uptakes were determined at 77 K over a pressure range to 20 bar and adsorption results were corrected for the buoyancy effect. Before adsorption measurements, samples were degassed (10^{-7} bar) at 200 °C for 5 h.