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

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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.

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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.

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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

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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, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10\text{--}13$, 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 $\pm 0.1 \mu\text{g}$. 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.

Fig. 1. Powder XRD patterns for the USY zeolite template and sucrose-based carbons.

3. Results and discussions

The XRD patterns for sucrose-based carbons obtained from different conditions are shown in Fig. 1. For comparison, XRD pattern of original USY zeolite is also included. It is clearly observed that all carbons exhibit two broad weak diffraction peaks at around 24° and 44° regardless of the preparation processes, attributing to the (002) and (101) diffractions from the turbostratic carbons, respectively [4,30]. The absence of sharp peaks indicates that sucrose-based carbons possess low crystallinity and most of them contain large proportion of amorphous structure. However, the graphitic degree of carbons is found to be largely dependent on carbonization temperature and mass ratio of zeolites to sucrose. For example, other weak peaks apart from the 24° and 44° happen to appear in UCs-100 (Fig. 1d) while the Cs-90 has already showed some apparent peaks (Fig. 1c). A sharp peak at around 6° assigning to the (111) plane of USY zeolites is not observed in our present work, indicating that the transferability of structural orderings from zeolite for sucrose-based carbons is relatively low [30].

The porosities of USY zeolites and carbons are probed via N_2 adsorption technique and corresponding N_2 sorption isotherms are shown in Fig. 2. Detailed pore structure parameters of sucrose-based carbons are listed in Table 1. The characteristic Type I isotherm of zeolites demonstrates its relatively large surface area and developed microporosities. However, a tiny hysteresis loop appeared at the higher pressure (e.g. $p/p_0 = 0.45$ –1.0) supports the existence of narrow mesopores in the structure of zeolites which is maybe due to the formation of interparticle voids [14]. We can find that the N_2 sorption profiles for carbons except for the Cs-90 are quite similar to each other (Fig. 2). They are all the combination of Type I and II isotherms with an apparent hysteresis loop over a wide pressure range [39], and exhibit a more rounded “knee” at the low relative pressure than USY zeolites and Cs-90, indicating that the carbons contain not only large amounts of micropores but also a portion of meso- or macro-pores with slit-like pores, which are probably due to an incomplete infiltration of precursor into

Fig. 2. The N_2 adsorption (Filled symbols) and desorption (Open symbols) isotherms for USY zeolite template and sucrose-based carbons. For clarity, isotherms of UCs-70, UCs-80, and UCs-100 carbons are offset (y-axis) by 80, 200, and 320, respectively.

micro-channels of zeolites [14,17,30]. All of these observations are also supported from the pore volume analyses in Table 1. We find that the quantities of mesopores and total pore volume are almost proportional to the carbonization temperature, though mesopores in carbons only have little contributions to the surface area (Table 1). It should be noted that hysteresis seems to become narrower at an elevated temperature under the same synthesis process, that is, the hysteresis loop in UCs-80, UCs-90, and UCs-100 is obviously thinner than the one in UCs-60 and UCs-70. The narrow hysteresis loop indicates that the disordered mesopores are not isolated or entrapped within micropore structures but exposed to the external surface of the carbon particles [40]. For the Cs-90 sample in Fig. 2 derived from the pure sucrose solution, the sorption isotherm is a typical Type I isotherm, indicating mainly a microporous material.

The pore size distributions (PSDs) of carbons determined via the non-local density functional theory (NLDFT) model using the adsorption data of N_2 are shown in Fig. 3, which are in good consistent with the results of adsorption isotherms presented in Fig. 2. It is very clearly that pore width in sucrose-based carbons

Fig. 3. Pore size distribution (PSD) curves obtained via applying NLDFT method to the N_2 adsorption data of these sucrose-based carbons.

Table 1The N₂ adsorption data at 77 K for pore structure parameters and hydrogen uptake of USY zeolite and sucrose-based carbons obtained under different preparation conditions.

Sample	S_{BET} (m ² /g) ^a	V_{Total} (cm ³ g ⁻¹) ^b	V_{Micro} (cm ³ g ⁻¹) ^c	V_{Meso} (cm ³ g ⁻¹) ^d	R_{Micro} (%) ^e	Hydrogen uptake (wt%) ^f
USY zeolite	701.5	0.405	0.304	0.101	0.75	–
UCs-60	1071.9	0.731	0.488	0.243	0.67	3.32 (1.29)
UCs-70	1127.2	0.817	0.498	0.319	0.61	3.52 (1.43)
UCs-80	1088.9	0.853	0.475	0.378	0.55	3.37 (1.28)
UCs-90	1038.4	0.888	0.433	0.455	0.49	3.37 (1.30)
UCs-100	1042.1	0.996	0.414	0.582	0.41	3.23 (1.15)
UCs-90-2	1218.6	1.068	0.458	0.610	0.43	3.65 (1.34)
Cs-90	723.2	0.417	0.324	0.093	0.77	2.85 (1.39)

^a Surface area is calculated via Brunauer-Emmet-Teller (BET) method at $p/p_0 = 0.02$ – 0.25 .^b Total pore volume is estimated from the adsorption data of N₂ at $p/p_0 = 0.996$.^c Micropore volume is calculated via the Dubinin-Radushkevich (DR) equation.^d Mesopore volume is derived by subtracting micropore volume from total pore volume.^e Ratio of micropore volume.^f Hydrogen uptake is measured at 77 K and 20 bar via the gravimetric adsorption method, and the value in the parentheses is the hydrogen uptake at 77 K and 1 bar.

can be divided into four parts, that is, <1 nm, 1–2 nm, 2–10 nm, and >10 nm. Moreover, the relative amounts between different pore sizes change with the preparation conditions. In the range of pores having pore size less than 1.0 nm, the PSD curves for all carbons are quite similar to each other regardless of the presence of USY zeolites in the preparation process or not, indicating that this proportion of micropores of carbons inherited wholly from sucrose precursor itself during its carbonization processes. This is due to the fact that the carbonization of oxygen-rich organic molecules such as sucrose will generate large amounts of gaseous species (e.g., CO₂ and H₂O), resulting in the creation of considerable voids space (i.e., micropores) inside the carbon frameworks [40]. The PSD curves in the range of 1–2 nm with a maxima at around 1.4 nm for the carbons prepared in the presence of zeolites are very reasonable, and most probably transferred from the wall frameworks of zeolites via a comparison to Cs-90 [41]. In addition, the ranges of 2–10 nm and >10 nm in pore size are apparently related to the carbonization temperature and the mass ratio of zeolites to sucrose. For example, the two samples, UCs-100 and UCs-90-2, have a maximum ratio of meso- and macro-pores in the ranges compared with other samples. From the data listed in Table 1, we can also conclude that carbonization with a higher temperature and more amounts of zeolite additives to sucrose appear to favor the larger pores and total pore volumes. We believe that the

larger pores are created from the pore collapse during the etching processes in view that the sucrose binders between carbon particles may not be stable enough to maintain the carbon frameworks after the template is removed [30]. The Brunauer-Emmet-Teller (BET) specific surface areas and total pore volumes of the carbons derived in the presence of USY zeolites are of respectively up to 1038 m²/g and 0.88 cm³ g⁻¹, which are much higher than the one in the absence of zeolite (700 m²/g and 0.417 cm³ g⁻¹). Moreover, the surface area of sucrose-based carbons obtained in this work is also much larger than the previous reported data from the pure sucrose solution (603 m²/g) [26], indicating that the use of zeolite additives in carbonization process is very helpful for enlarging the surface area of carbons. Indeed, the BET surface area of Cs-90, UCs-90, and UCs-90-2 increase gradually in turn. Therefore, it can be inferred that the presence of zeolite in carbonization process plays an important role in the development of carbon's pore structure, especially for the meso- and macro-pores.

Fig. 4 shows SEM images of the original USY zeolites and carbons with the aim to further investigate the effects of carbonization temperature and zeolite additives on the microstructure of carbons. As shown in Fig. 4, the USY zeolite exhibits well-resolved hexagonal crystal morphologies while carbons display a disordered morphology without any macroscopic structure replicated from the template, which was previously observed the replication in

Fig. 4. Representative SEM pictures for USY zeolite template and sucrose-based carbons.

Fig. 5. Representative Raman spectra for the prepared sucrose-based carbons.

carbons derived from zeolite with other kinds of precursors [4,38,42]. Comparatively, Cs-90 and UCs-90-2 show well sheet-graphite-like structures with large interparticle voids on micrometer scale. The overall results of SEM images are in good accordance with the XRD results in Fig. 1 that carbons are largely amorphous.

The Raman spectroscopy is used to further illustrate the levels of graphitization of carbons and the corresponding results are shown in Fig. 5. Raman spectra measurements are performed on a Renishaw-inVia Raman microscope excited with a 532 nm laser. It is very clearly that two prominent peaks located at around 1350 cm^{-1} (D-band) and 1590 cm^{-1} (G-band) can be found for all the sucrose-based carbons, ascribing to an imperfect structure of amorphous carbons and C–C stretching vibration mode of graphene with sp^2 electronic configuration, respectively [26]. The relative intensity ratio between D-band and G-band (I_D/I_G) is usually partly utilized to evaluate the graphitic degrees of carbon-based materials. As can be seen from the Fig. 5, the variations of I_D/I_G are found and a universal observation is that the approximate value of I_D/I_G increases with an increase of carbonization temperature. The phenomenon agrees well with that reported previously by other groups [26,42] and the graphitic degree of sucrose-based carbon in our present work is very poor even at an elevated carbonization temperature, indicating that the formation of some sp^3 electronic configurations for the carbon element in amorphous carbons [43]. Furthermore, an additional broad 2D-band around 2700 cm^{-1} and a sharp peak around 2300 cm^{-1} appear in all carbons, which are maybe attribute to the overtones and combinations of vibration modes for the graphitic layer [44,45]. Their appearance indicates the existence of some graphitic-graphene structures, and Raman data are in good agreement with the XRD and SEM observations.

The hydrogen adsorption isotherms of carbons (77 K over pressure range 0–20 bar), measured from the gravimetric analysis, are shown in Fig. 6. Detailed hydrogen storage capacities at pressure of 1 and 20 bar are listed in Table 1. All the hydrogen adsorption isotherms are Type I in the IUPAC classification [39] and desorption isotherm (Inset Fig. 6) with virtually no hysteresis at 77 K confirmed from other hand that the hydrogen uptake on these carbons is totally reversible and impurities have not been adsorbed [5]. Especially, the adsorption uptakes of hydrogen at 1 bar vary between 1.1 and $1.4 I_D/I_G$ wt%, which are very comparable to the previous observations on other sucrose-based carbons obtained from different preparation routes [11,30]. We believe that the trend in hydrogen uptakes is closely related to the textural properties of carbons and maybe also relate to the levels of graphitic degree. UCs-90-2 has both the highest surface area and total pore volume,

Fig. 6. H_2 adsorption isotherms of carbons at 77 K and 20 bar. The inset is adsorption (Filled symbols) and desorption (Open symbols) isotherms for H_2 at 20 bar on the UCs-90-2.

exhibiting the highest hydrogen storage uptake at 20 bar. It is clearly observed that the saturation is not achieved at 20 bar and the trajectory of isotherms suggests that a higher uptake is possibly obtained at the higher pressures. In contrast, UCs-70 has the highest micropore volume, displaying the highest uptake at 1 bar. This observation is in excellent consistent with previous studies which have already indicated that hydrogen uptakes in carbons have close relevancy with microporities [5,11,26,30]. However, it also should be noted that increased studies have already confirmed that it is not simply the overall surface areas and microporities that determine hydrogen uptake in carbons but the surface areas associated with the ‘optimal pores’ of $6\text{--}9\text{ Å}$ [5,14,46], which has been perfectly confirmed in this work. For example, the samples Cs-90, UCs-90, and UCs-90-2 exhibit a hydrogen uptake of 1.39, 1.30, and 1.34 wt% at 1 bar, respectively, though the total surface areas and micropore volumes for Cs-90 are much smaller than other two samples. Particularly, UCs-100 with a higher micropore volume and surface area than Cs-90 also shows an uptake of 1.15 wt% at 1 bar. However, UCs-90-2 shows a larger hydrogen uptake than UCs-90 and Cs-90 at 20 bar. Therefore, we can infer that the presence of zeolites in the carbonization process can greatly enlarge the surface area and mesopore volume, and have a positive role in hydrogen storage at a higher pressure (e.g. 20 bar) but less effects at a lower pressure (e.g. 1 bar). It is reasonable from Fig. 3 that both the UCs-100 and UCs-90-2 have great quantities of large mesopores but Cs-90 has almost wholly micropores less than 1 nm only with little small mesopores, resulting in the much larger interaction energy of hydrogen molecules in these narrow micropores [11,44–46]. Moreover, it can be seen from Fig. 6 and Table 1 that the actual order of hydrogen uptake is roughly similar to that of the micropore volume, especially for pores less than 1 nm. It is expected that carbons with a higher micropore volume have more accessible adsorption sites, resulting in the larger hydrogen storage capacities. However, it is interesting to note a fact that UCs-90-2 has the highest hydrogen uptakes at 20 bar and 77 K, although its micropore volume was slightly lower than the UCs-70. As shown in Fig. 3, the PSD curve of UCs-90-2 also exhibits some macropores other than micro- and mesopores which will be work in the hydrogen storage at higher pressures, and thus the hydrogen uptake of UCs-90-2 is slightly higher than UCs-70 at 20 bar while slightly lower at 1 bar. In addition, the presence of zeolites in the carbonization process will inhibit the degree of graphitization to some extent, resulting in the increase of hydrogen storage uptakes. Therefore,

synergistic effects between the graphitization of carbons and microporosities maybe play important roles in hydrogen storage.

4. Conclusions

In summary, we prepared sucrose-based carbons via template-assisted carbonization and investigated their H₂ adsorption properties. The total pore volume and mesopore volume of carbons are almost proportional to the temperature. Furthermore, carbons obtained in the presence of zeolites exhibit much larger surface area and total pore volume than the ones obtained from the pure sucrose solution. Zeolite additives used in the carbonization process play an important role in developing mesoporosities, and carbons did not have the structural periodicity transferred from the zeolite template. The H₂ storage capacity on UCs-90-2 is up to 3.6 wt% at 77 K and 20 bar, which is proportional to the surface areas and microporosities. Overall, our findings add and enrich some useful insights to some extent in designing suitable carbon-based materials for H₂ storage. Moreover, the sucrose-based carbons with multi-pores have potential in the application of catalysis and electrode materials, though the surface modification is essential for further enlarging the levels of H₂ storage.

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