

Characterization of a zeolite-templated carbon for H₂ storage application

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ABSTRACT

Hydrogen storage was investigated in an activated carbon with a specific surface area of 1500 m²/g prepared using sucrose as carbon precursor and ammonium-form zeolite Y as template. The carbon sample exhibits a hydrogen storage capacity of 2.4 wt% at 77 K and 10 bar. The isosteric heat of adsorption was found about 8 kJ/mol at a low surface loading. CO₂ adsorption isotherm at 273 K was used to characterize small micropores in the sample and was found to be more applicable than N₂ isotherm at 77 K.

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1. Introduction

Hydrogen storage via adsorption technology has been under active studies [1,2]. Compared with the chemical reactive storage technologies such as metal hydrates, the physical adsorption in nanoporous adsorbents has a number of advantages, such as fast kinetics, reversibility, and relatively low cost [3]. While some studies identified the potential of this technology to achieve the DOE (Department of Energy, USA) target of H₂ storage (6.0 wt% of hydrogen and a volumetric density of 1.5 kW h/L at ambient conditions, by 2010) [3,4], many other studies suggested that this technology could meet the DOE target only at cryogenic temperature [5,6].

A number of adsorbents have been under intensive investigations, such as activated carbons (AC) and graphite [1,3], carbon nanofibers and tubes [1,7], metal organic framework (MOF) [8]. The micropore volume and specific surface area have been found to be the two key parameters dictating the H₂ uptake in such materials [9]. For example, a sorption capacity of 7 wt% (at 77 K, 1 MPa) was reported on a carbon microbead with a BET surface area of 3180 m²/g and a pore volume of 1.9 cm³/g [10], while a capacity of 6 wt% (77 K, 4 MPa) was found on an AC with the surface area of 3808 m²/g and the pore volume of 1.52 cm³/g [11]. Pore size is another important parameter (although it is largely related to surface area), as H₂ adsorption capacity reside mainly in pores with the diameter less than four or five molecular dimensions and the

interaction between the non-polar H₂ molecules and the slit-shaped graphite pores is predominantly dispersive. Many simulations/experimental studies have indicated that the optimal pore sizes for H₂ adsorption should be around 0.65–0.9 nm in carbonaceous adsorbents [5,6,12]. Bhatia and Myers found that the optimal pore size is ~0.92 nm, by considering the weight, volumetric, as well as the deliverable H₂ storage capacities [5].

Efforts were also reported to modify the microstructure (pore size and porosity) of carbonaceous adsorbents to improve their H₂ uptakes. Such methods include chemical activation (e.g., with KOH) [11,13], physical activation (e.g., with CO₂) [14], doping with metal ions (e.g., Pt) [15], or substitution with heteroatom into nanostructures (e.g., with boron) [16], etc. In the above examples, the H₂ storage capacities were increased by a factor of 6 [13], 2 [14,15], and 3 [16], respectively.

Template synthesis is a promising technology to prepare novel porous carbon materials with large surface area and relatively uniform pores [17]. This kind of carbons (referred to as templated carbon or TC) are generally fabricated via the pyrolysis of a carbonaceous precursor in the micro-channels of a porous template, such as zeolites or silica gels [18–20]. The structure of TCs can be largely manipulated via the selection of template, carbon precursor, as well as the pyrolytic conditions [19,20]. A few recent studies have demonstrated the potential of this technology in H₂ storage. For example, Chen et al. prepared a TC using zeolite Y as templates and propylene/butylene as carbon sources [21]. The H₂ capacity was found to be 2 wt% at 77 K and 1 bar. Armandi et al. applied the post-treatments (physical and chemical activations) for TCs prepared using SBA-15 silica as template and reached a H₂ capacity

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of 2.0 wt% at 77 K and 1 bar [9]. Yang et al. synthesized a TC via CVD process with zeolite β as template and acetonitrile as carbon precursor. A H_2 capacity of 6.9 wt% was reported at 77 K and 20 bar [22].

This paper reports the hydrogen adsorption in a TC prepared using zeolite Y as template. The structure of the TC was characterized and H_2 isotherms were measured at different temperatures.

2. Experiments

The TC was prepared by soaking sucrose solution in ammonium-form zeolite Y (NH_4Y form, $SiO_2/Al_2O_3 = 5.1$), pyrolyzed at 1100 °C and followed by acid wash. The detailed preparation procedures can be found elsewhere [17].

The structure of the TC was analyzed with TEM, SEM, and XRD. Thermogravimetric analysis (TGA) was conducted with a thermogravimetric analyzer (Thermal Analysis Instruments, USA). The porous structure of the TC was characterized with N_2 isotherm measured at 77 K using a pore and surface analyzer (Quantachrome, Autosorb-1). Prior to the measurements, the TC sample was degassed overnight at 250 °C and under high vacuum. The specific surface area (S_{BET}), total pore volume (V_T) and the micropore volume (V_m) were obtained from the N_2 isotherm accordingly. The bulk density was determined using the ASTM method [23]. The helium density was measured on a pycnometer (Ultra pycnometer 1000, Quantachrome). The pore size distribution (PSD) of the TC was derived from the N_2 isotherm via the non-local density functional theory (NLDFT), with the assumption that the pores are slit-shaped and the adsorbate–pore interaction is dispersive.

A high pressure rig was fabricated to measure H_2 isotherms on the TC using the volumetric method. About 0.7 g of the TC was loaded in the sample cell with H_2 isotherms measured at 77 K (liquid nitrogen temperature), 195 K (dry ice temperature) and 303 K (room temperature), respectively. H_2 gas (purity >99.9%) was supplied by SOXIAL Singapore. During the adsorption measurement, the sample cell was submerged in a thermal bath with the controlled temperature.

3. Results and discussion

Fig. 1a shows the XRD pattern of the TC while the embedded Fig. 1b shows the XRD pattern of the zeolite NH_4Y . The two peaks at around $\sim 25^\circ$ and 43° (2θ) in Fig. 1a are assigned to the (002) and (100) diffractions of graphitic carbon [24,25], indicating a quasi-crystalline carbon structure. The shift of the peak (002) from 26.3° (2θ) to $\sim 25^\circ$ (2θ) was also observed previously [21]. The peak

at 6° (2θ), which is corresponding to the (111) planes of zeolite Y and was observed in TCs derived from zeolite Y by other studies [21,22] was not clearly seen in the present study, indicating that the structural ordering of the sample is low.

The SEM image shown in Fig. 2a reveals that the TC has the layered-graphite structure with large interparticle voids, which is in agreement with the XRD result that the TC is largely amorphous and the density measurement that its bulk density is low (0.23 g/cm^3 by the ASTM method, Table 1). The TEM image (Fig. 2b) of the carbon crystal shows a thick graphite core surrounded by thin graphite shells. Some defects can be clearly seen at the edge of the crystal as well. These observations suggest that the graphite crystal presents a high degree of structural heterogeneity and many amorphous domains.

The TGA and the derivative thermogravimetric analysis (DTGA) of the sample are presented in Fig. 3a and b, respectively. It is seen from Fig. 3a that the oxidation (combustion) of the TC was nearly complete, indicating that the acid wash treatment is effective in removing the zeolite template and the sample is a pure carbon. As the weight loss above 250 °C is related to the combustion of amorphous carbons, the broad peak at 550–630 °C (Fig. 3b) suggests that the TC sample prepared in this work is highly amorphous.

Fig. 4a shows the N_2 isotherm at 77 K. The small desorption hysteresis suggests the existence of a portion of mesopores, which is probably due to the incomplete infiltration of the carbon precursor in pore channels of the zeolite template [19]. Fig. 4b shows the PSD derived from the N_2 isotherm using the NLDFT. A major micropore peak was seen at the pore size of $\sim 0.11 \text{ nm}$. Small mesopore peaks were found at 0.26 nm and 0.38 nm, respectively. The properties of the TC are listed in Table 1.

The H_2 adsorption isotherms were measured at three temperatures (77 K, 194.5 K, and 303 K), respectively. The H_2 isotherm at 77 K was measured with the PSA rig up to 1 bar and with the high pressure rig up to 50 bar. Fig. 5 shows the isotherm data as symbols and it is noted that the two sections of the isotherm data at 77 K agree with each other reasonably well. It is also seen that, at 77 K, the H_2 sorption increases quickly until $P = 10$ bar with a capacity of $\sim 12 \text{ mmol/g}$ ($\sim 2.4 \text{ wt\%}$), then the isotherm becomes flat quickly and the capacity reaches 2.7 wt% at 50 bar. The isotherm data were fitted, respectively, to the Toth equation, $C_\mu = C_{\mu s} bP / [1 + (bP)^t]^{1/t}$. The fittings are shown in Fig. 5 as solid lines and the optimal isotherm parameters for data at 77 K are listed in the figure caption. It can be seen that the H_2 capacity decreases significantly at dry ice temperature ($\sim 0.2 \text{ wt\%}$ at 10 bar) while the isotherm is largely linear at 303 K.

The Toth isotherm parameter ($t = 0.491$ at 77 K) indicates that the TC is heterogeneous towards H_2 molecules. This is confirmed by the isosteric heat of H_2 adsorption, Q_{iso} , calculated using the Clausius–Clapeyron equation [$Q_{iso}/RT^2 = -(\partial \ln P / \partial T)_q$]. Fig. 6a plots Q_{iso} versus the adsorbed phase concentration of H_2 while the embedded Fig. 6b shows the range of the isotherm data involved in the computation (i.e., interpolation within the experimental data was employed to draw the smooth curve of Fig. 6a. Extrapolation outside the range of experimental data, however, was not used). It is seen that the heat of adsorption decreases quickly from $\sim 8 \text{ kJ/mol}$ to 5 kJ/mol as the H_2 bulk pressure increases from $\sim 10^{-3}$ bar to 0.2 bar.

The heat of adsorption is predominantly dictated by the pore size and $Q_{iso} = 8 \text{ kJ/mol}$ suggests that the TC possesses a portion of micropores in the size range of 0.65–0.7 nm [22,26]. Such a value is a bit higher than the common carbonaceous adsorbents (e.g., commercial activated carbons) in which the pore sizes disperses in a large range and the average Q_{iso} is generally around 6 kJ/mol [5]. Rao et al. [27] showed that the heat of adsorption is 4.39 kJ/mol for H_2 adsorbing onto a graphite basal plane, which suggests that the

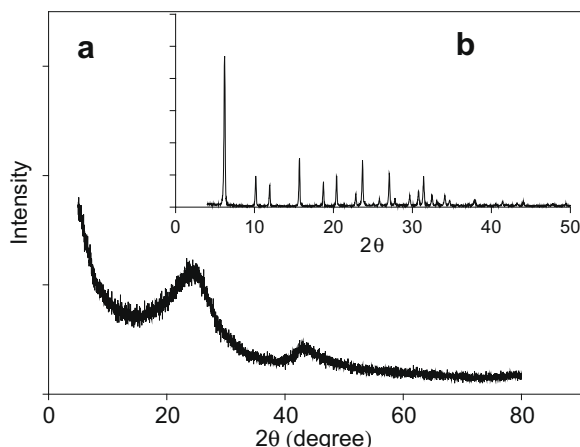


Fig. 1. The XRD pattern of (a) the TC, and (b) zeolite NH_4Y .

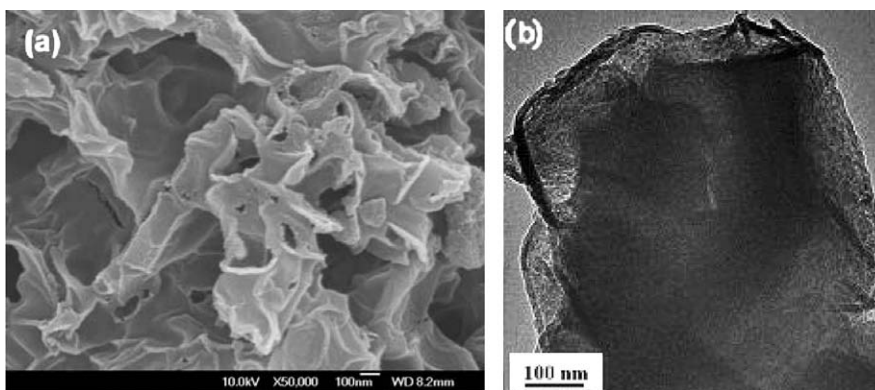


Fig. 2. (a) The SEM image of the TC. (b) The TEM image of the TC.

Table 1

Surface properties of the TC.

Surface areas (m ² /g)	Micropore volume (cm ³ /g)	Total pore volume (cm ³ /g)	Bulk density (g/cm ³)	Helium density (g/cm ³)
1500	0.78	1.30	0.23	2.15

heat of adsorption can be as high as 8.8 kJ/mol in a slit graphite pore. Yang et al. [22] also found that $Q_{iso} > 8$ kJ/mol in their TC sample at low loadings. Yushin et al. [26] even found that the heat of adsorption can reach 11 kJ/mol in their carbide-derived carbon (CDC). It is noted that the pores in the CDC may not be slit-shaped.

The high value of the heat of adsorption of H₂, however, was not supported by the PSD of the TC derived from the N₂ isotherm using NLDFT (Fig. 4b), which indicates no major contribution of pores with the size below 1 nm. To confirm the PSD in Fig. 4b, CO₂ adsorption was measured on the sample at 273 K and analyzed with the NLDFT (in which CO₂ molecules are treated as the 3-centered fluid with 12–6 as well as electrostatic interaction potentials) [28] and the HK method [29], respectively. The CO₂ isotherm is presented in Fig. 7 as symbols while the derived PSDs are shown in the embedded figure as the solid line (NLDFT) and dashed line (HK), respectively. We see that both methods confirm the existence of small micropores in the size range of 0.6–0.9 nm.

The findings suggest that CO₂ sorption is a more reliable method for the structural characterization of adsorbents with small micropores, such as zeolite-templated carbons. This is in line with our expectations, because (1) CO₂ molecule is more strongly ad-

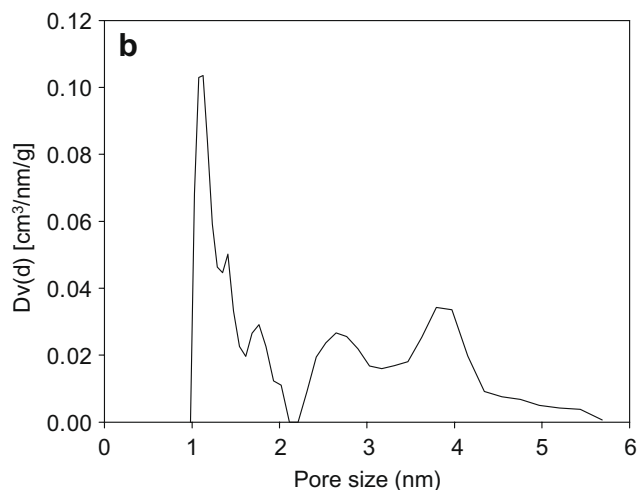
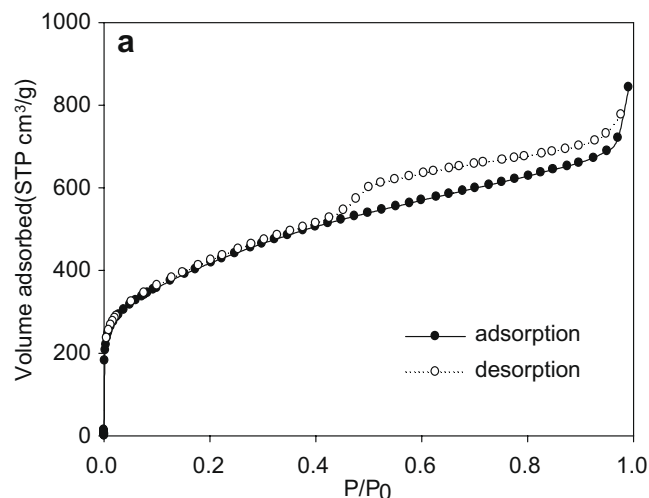


Fig. 4. The N₂ isotherm on the TC at 77 K (a) and PSD of the TC derived using NLDFT (b).

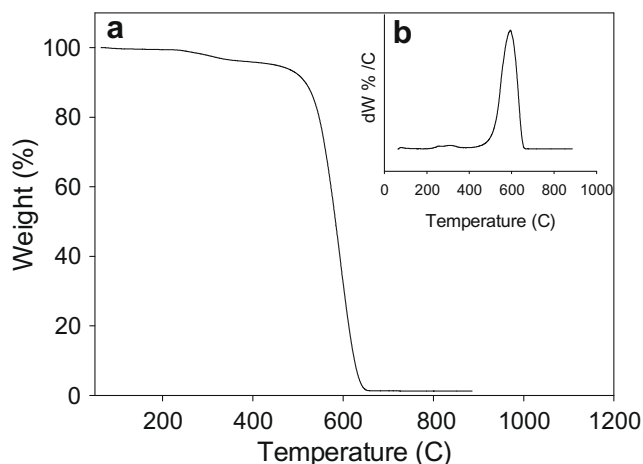


Fig. 3. The thermogravimetric analysis of the TC, (a) TGA, and (b) DTGA.

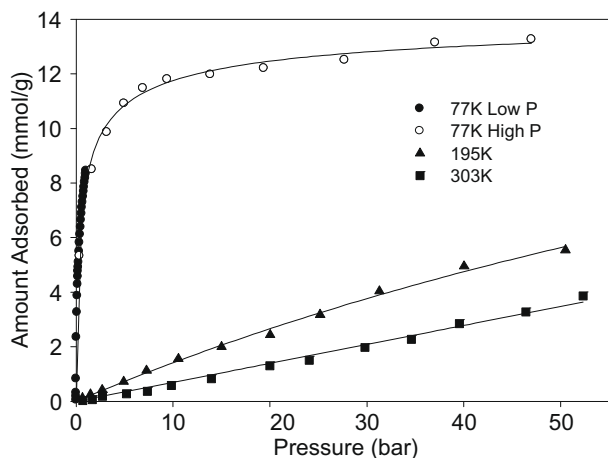


Fig. 5. Hydrogen isotherm data (symbols) and the model fittings with the Toth equation (lines). The isotherm parameters for 77 K data are: $C_{\text{H}_2} = 15.5$ (mmol/g), $b = 9.03$ (bar $^{-1}$), and $t = 0.491$.

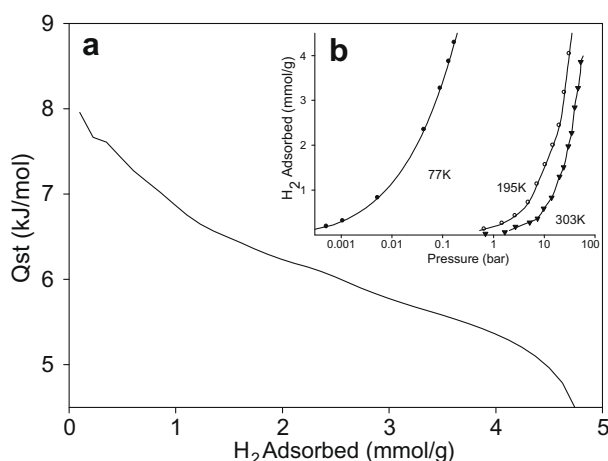


Fig. 6. (a) The isosteric heat of adsorption of H_2 on the TC (a), and the isotherm data involved in computation (b).

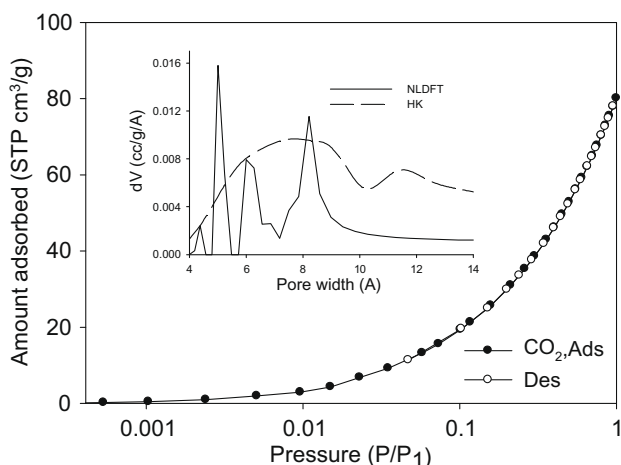


Fig. 7. The CO_2 isotherm at 273 K ($P_1 = 1.05$ bar) and the derived PSDs with NLDFT (—) and HK (---).

tates CO_2 molecule to penetrate into small micropores with much faster kinetic rates than N_2 molecules at 77 K. Another possible reason (although speculative at this point) is that the TC sample may have some ink-bottle-like micropores. Such a structural feature is common for carbon molecular sieves (CMS), of which the ultramicroporosity and the strong pore mouth barrier limit the use of N_2 adsorption at 77 K [30]. Therefore, CO_2 adsorption at ambient temperature should be preferred for characterizing the small micropores (0.6–0.9 nm) in carbonaceous materials for H_2 storage.

The advantage of CO_2 adsorption at ambient temperature for structural characterization was also reported in other studies. For example, Mandoki, et al. [31] reported that the H_2 uptakes are directly proportional to the micropore volumes of the carbon samples derived from CO_2 isotherm at 273 K (however, this is not applicable to N_2 isotherm at 77 K). Jagiello and Thommes [32] found that CO_2 sorption is more applicable in characterizing small micropores of carbonaceous adsorbents. As small micropores provides the main H_2 sorption capacity [5,6,12,22], CO_2 adsorption at 273 K should be preferably used to characterize the structure of the adsorbent for the application, or at least used to double check the structural information derived from N_2 isotherm at 77 K. The N_2 adsorption at 77 K, on the other hand, is more convenient and reliable for characterizing large micropores (1–2 nm) and mesopores. Such large pores may also be characterized by CO_2 adsorption at 273 K but requires a bulk phase pressure considerably higher than the upper limit of the bulk phase pressure (~ 1 bar) in the current commercial PSA rigs.

4. Conclusions

A templated carbon was synthesized, characterized, and investigated for hydrogen storage. The hydrogen adsorption capacity was recorded as 2.4 wt% at 77 K and 10 bar. The high value of the calculated isosteric heat of adsorption reveals the existence of small micropores in the sample. CO_2 adsorption at 273 K was found superior to the popularly used N_2 isotherm at 77 K in characterizing such small micropores.

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sorbed and smaller in dimension (favorable orientation) than N_2 molecule, and (2) the high adsorption temperature (273 K) facili-

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