Separation and Purification Technology 66 (2009) 565–569

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Investigation of H_2 storage in a templated carbon derived from zeolite Y and PFA

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ARTICLE INFO

Article history:
Received 30 October 2008
Received in revised form 16 January 2009
Accepted 26 January 2009

Keywords:
Template carbon
Adsorption
Hydrogen storage
Activated carbon
Characterization

ABSTRACT

An activated carbon sample was synthesized using poly furfuryl alcohol (PFA) as the carbon precursor and ammonium-form zeolite Y as the template. The sample presents a specific surface area of 2545 m^2/g and a hydrogen sorption capacity of 2.4% at 10 bar and 77 K. The structure of the sample was characterized with the sorption isotherms of N_2, Ar, and CO_2, respectively. It was found that the small micropores and the specific surface area were better characterized by CO_2 sorption and Ar sorption, respectively. The existence of the small micropores was confirmed by hydrogen isosteric heat of adsorption.

1. Introduction

Template synthesis is a promising technology for preparing activated carbon (AC) samples with large surface area and relatively uniform porous structure [1–6]. This kind of carbons (referred to as templated carbon or TC) has caught some recent research attention in the energy gas (H_2) storage application, where the surface area, pore size and the microporosity dictate the uptake capacity [7,8]. A few recent studies have demonstrated the potential of TCs for H_2 storage. For example, Chen et al. [9] prepared a TC using zeolite Y as templates and propylene/butylene as carbon sources. The H_2 capacity was 2 wt% at 77 K and 1 bar. Armandi et al. [10] applied the post-treatments (activations) for TCs prepared using SBA-15 silica as template and reached a capacity of 2.0 wt% at 77 K and 1 bar. Yang et al. synthesized a TC via CVD process with zeolite β and acetonitrile. The H_2 capacity of 6.9 wt% was observed at 77 K and 20 bar [11]. A composite of TC-platinum nanoparticles reported a H_2 uptake of 1.35 wt% at 298 K and 100 bar [12]. Table 1 generalizes the synthetic methods and the related H_2 storage performance for a few TC samples.

H_2 sorption in ACs is physical sorption in nature and the small micropores (in the size range of 0.6–0.9 nm) play the dominant role for the sorption capacity [7,17]. A number of studies demonstrated the importance of small micropores. Mandoki et al. [18] reported that H_2 uptake in ACs is directly proportional to the volumes of small micropores characterized by CO_2 sorption at 273 K. Yushin et al. [19] studied H_2 storage on ACs derived from high-temperature chlorination of carbides (referred to as CDC) and found that H_2 sorption capacity at 77 K followed the linear relation with volume of small micropores (<1 nm). The CDC with a H_2 capacity of 2.8 wt% (at 1 bar and 77 K) has the maximum volume of small micropores (0.52 cm^3/g). Guan et al. [20] recently reported the advantages of CO_2 sorption in characterizing such small micropores in TCs.

This article will investigate H_2 sorption in a TC. The porous structure of the TC is characterized using the sorption isotherms of different gas adsorbates and examined by the isosteric heat of adsorption of H_2.

2. Experiments

The TC was prepared with the following procedures: (1) impregnating poly furfuryl alcohol (PFA) in ammonium-form zeolite Y (NH_4Y form, SiO_2/Al_2O_3 = 5.1, by Zeolyst international®), (2) pyrolysis at 1323 K in N_2 flow stream, and (3) acid wash to remove the template zeolite. The detailed preparation procedures can be found in the literature [5].

The morphology the TC was studied by XRD, SEM, and TEM. The bulk density was determined by the ASTM method [21]. The sorption isotherms of N_2 and Ar at 77 K and CO_2 at 273 K were measured on a pore and surface analyzer (Quantachrome, Autosorb-1). Prior to isotherm measurements, the samples were degassed overnight at 523 K and under high vacuum. The specific surface area (S_{BET}) of the TC was derived using BET method in the pressure range (P/P_0 = 0.05–0.3). The pore size distribution was derived from the isotherms via the non-local density functional theory (NLDFT) with the assumption that the pores are slit-shaped and the adsorbate–pore interaction is dispersive (for N_2 and A_r).

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doi:10.1016/j.seppur.2009.01.015

Table 1
The synthetic conditions and H_2 sorption properties of templated carbons.

Template	Carbon source	Pyrolysis temperature (K)	Hydrogen sorption			Ref.
			wt%	T (K)	P (bar)	
SBA-15 silica	Sucrose	1073	2.0	77	0.9	[10]
Zeolite NaY	Proplylene, butylenes	993–1033	2.0	77	1	[9]
Zeolite β	Acetonitrile	1123	2.6	77	1	[11]
Zeolite β	Acetonitrile	1123	6.9	77	20	[11]
SBA-15 silica	Acetonitrile	1173	3.4	77	20	[13]
Zeolite Y	Acetonitrile	1073	4.5	77	20	[14]
Silica aerosol	Sucrose	1173	2.0	77	1.1	[15]
MCM-48	Sucrose	1173	2.2	77	1	[16]

H_2 sorption was measured at three temperatures, 77 K (liquid N_2 temperature), 195 K (dry ice temperature), and 303 K (room temperature), respectively, at the pressure up to 50 bar. H_2 isotherm at 77 K was measured with the pore and surface analyzer up to 1 bar and with a high pressure volumetric rig up to 50 bar. About 0.7 g of TC sample was loaded in the sample cell of the high pressure rig. H_2 gas (purity >99.9%) was supplied by SOXIAL Singapore. During the sorption 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. The sample does not exhibit the diffraction peak at 6° (2θ) corresponding to the {1 1 1} plane of zeolite Y. The diffraction peak at 26° (2θ), which corresponds to the {0 0 2} diffraction of graphitic carbon, is very weak as well. These observations suggest that the TC is essentially amorphous in structure. Fig. 1b presents the FESEM image of the TC, which verifies that the graphite crystals are basically amorphous with large interparticle voids (confirmed by the measured ASTM density of 0.28 g/cc). The TEM image (Fig. 1c) further reveals that the graphite crystals have the heterogeneous surface with significant defects.

Fig. 2a shows N_2 isotherm measured at 77 K. The hysteresis in the desorption isotherm suggests the existence of mesopores. The PSD derived via NLDFT was embedded in Fig. 2a. A major micropore peak was seen at ~1.3 nm and two mesopore peaks were found at 2.6 and 3.8 nm, respectively. The micropore peak at 1.3 nm is corresponding to the periodicity of the microchannels of the zeolite template [4,5], while the micropores with the smaller sizes were likely developed by the pyrolysis process. The mesopores were formed probably due to (1) the incomplete infiltration of the carbon precursor into the microchannels [3,5] and (2) the carbonization process. Fig. 2b presents Ar isotherm measured at 77 K and the derived PSD. It is interesting to see that Ar isotherm predicts a higher distribution density of micropores (at ~1.3 nm) as well as a peak of small micropores at ~0.6–0.7 nm, which was undetected by N_2 sorption. Compared with N_2 molecule, Ar is an inert monoatomic gas with smaller molecular dimension and higher critical temperature (150.9 K). These properties enable Ar molecules to penetrate the small micropores with faster kinetics and less diffusion barriers so that the small micropores (as well as the ink-bottled pores) were better probed. Therefore, the BET surface area derived from Ar isotherm (2545 m^2/g) is the more realistic surface property of the TC for this application. Next, CO_2 isotherm measured at 273 K was studied. CO_2 molecules are assumed to be a 3-centered fluid with both dispersive and electrostatic interaction between the fluid molecules [22]. Fig. 2c shows CO_2 isotherm with the embedded PSD. We see that CO_2 sorption reports three micropore peaks, located at the pore size of 0.5, 0.6, and 0.85 nm, respectively. The micropore peaks at 0.6–0.85 nm were partly agreed by the PSD derived from Ar sorption (Fig. 2b). It should be noted that, in the measurements of three isotherms, the lowest sorption pressure was set at ~0.005 Torr. It might be possible for Ar or even N_2 molecule to detect the small micropores, but considerably lower sorption pres-

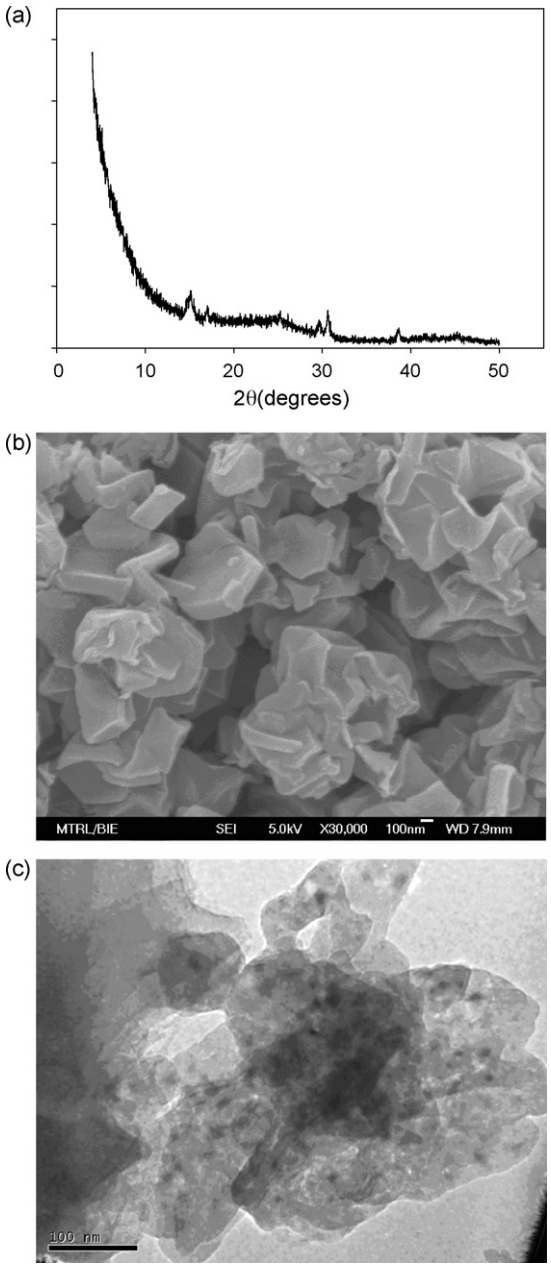

Fig. 1. The structure of the TC: (a) XRD, (b) FESEM and (c) TEM.

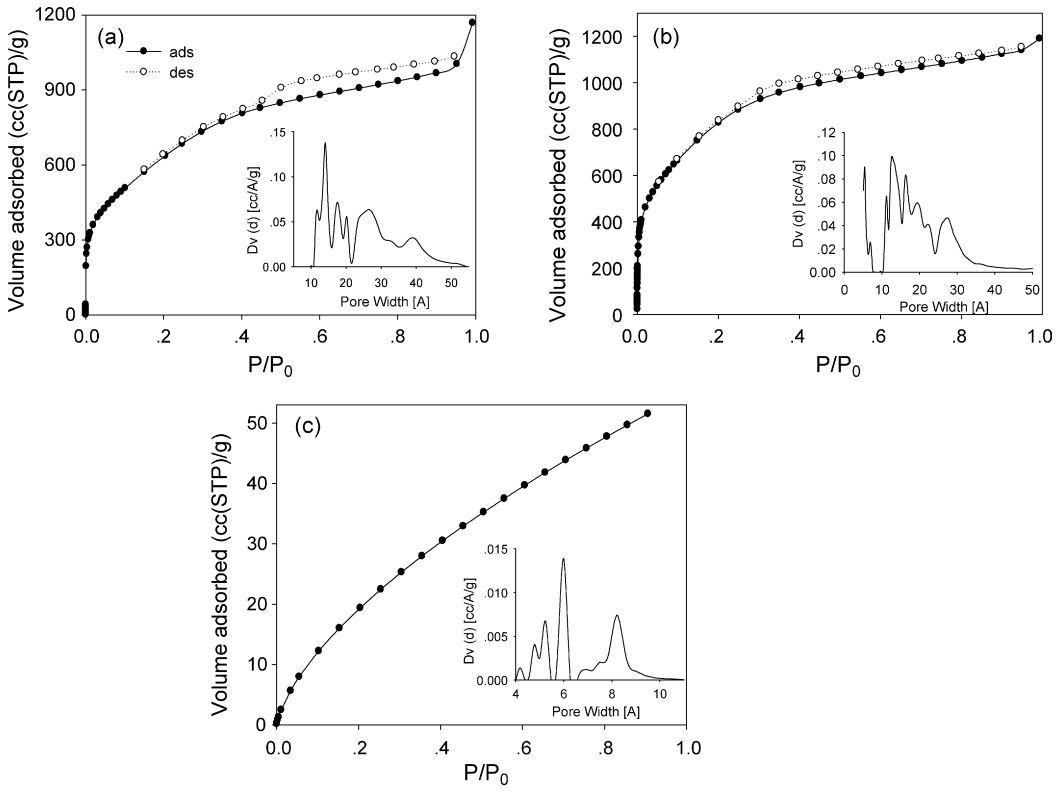

Fig. 2. Sorption isotherm and PSD on the TC: (a) N_2 isotherm at 77 K and the derived PSD; (b) Ar isotherm at 77 K and the derived PSD and (c) CO_2 isotherm at 273 K and the derived PSD.

sure will be required (e.g. $<10^{-5}$ Torr). The measurement under such conditions will take extremely long time and the results can also be unstable at such a low pressure. Therefore, this exercise confirms our previous findings with another TC that CO_2 sorption is a more reliable method for the characterization of small micropores [20]. This is expected as CO_2 molecule is more strongly adsorbed and smaller in dimension (at the favorable orientation) than N_2 and Ar molecules. This result is also in agreement with the study by Sweatman and Quirke [23] that N_2 sorption at 77 K is diffusion limited or even frozen in such small micropores.

The surface properties of the TC were derived from the three sorption isotherms and listed in Table 2. We see that Ar sorption predicts a slightly higher surface area and a larger micropore volume than N_2. This is due to the better accessibility of Ar molecules in the porous network of the TC. The difference in the BET areas detected by molecules with different dimensions was also observed in our previous experiments and attributed to the effect of size exclusion [24]. CO_2 sorption reports a very small BET surface area ($125\ m^2/g$) and a small micropore volume (0.03 cc/g by DR plot) because the sorption pressure is low ($\leq$1 bar). Considerably high sorption pressure is needed for CO_2 molecule to detect the large pores of the TC [22], which is well beyond the working range of the commercial pore and surface analyzer. The high surface area and good micropore volume suggests that the TC is a good candidate for energy storage. The existence of the mesopore volume means that its storage capacity can be further improved.

Fig. 3a shows H_2 isotherm at three temperatures as symbols. Some discrepancy was seen between H_2 isotherm measured on the low pressure rig (at 77 K, <1 bar) and that measured on the high pressure volumetric rig (77 K, 0.3–50 bar), but the agreement

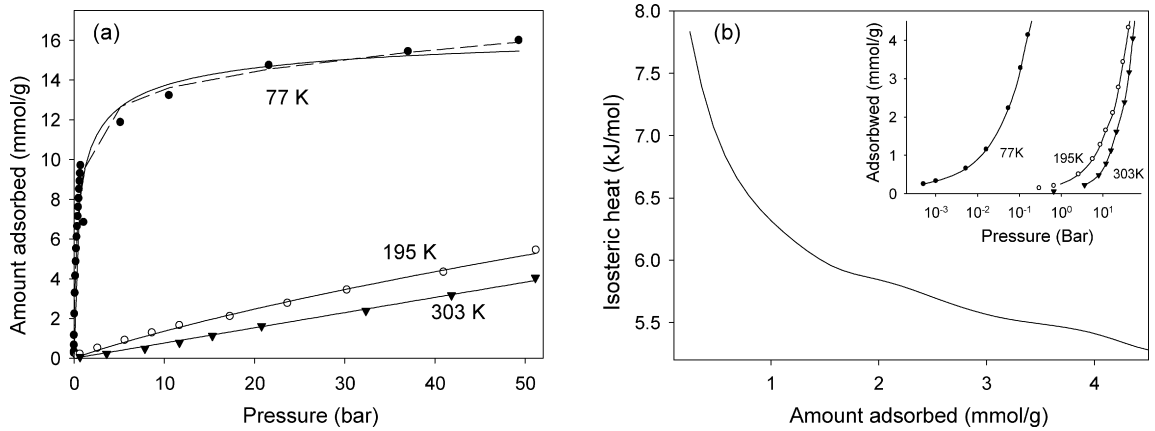

Fig. 3. H_2 sorption isotherms and isosteric heat on the TC: (a) H_2 isotherms at three temperatures. Solid line = Toth model ($C_{\mu s}$ = 17.3 mmol/g, $b = 8.66\ kPa^{-1}$, t = 0.474, at 77 K); Dashed line is Nguyen and Do's model); (b) isosteric heat of H_2 sorption on the TC. The embedded figure is the isotherm data involved in the computation.

Table 2
The surface properties of the TC from N_2, Ar and CO_2 sorption isotherms.

	S_{BET} (m^2/g)	Micropore volume (cc/g)	Total pore volume (cc/g)
N_2	2136	1.034	1.556
Ar	2545	1.129	1.402
CO_2	125.0	0.03	0.03

was reasonable. At 77 K, H_2 sorption increases quickly until 10 bar with a capacity of 12 mmol/g (~2.4 wt%). This capacity increases to ~3.1 wt% at the pressure of 50 bar. The capacity is seen to decrease significantly at the dry ice and room temperatures (~0.8 wt% at room temperature and 50 bar). Compared with other storage technologies such as metal-organic framework or metal hydrates, H_2 capacity of TC is comparable but at the lower end. For example, the above-mentioned two technologies reported storage capacities of 6.9 wt% on MOF-5 (77 K and 100 bar) [25] and 5.6 wt% on MgH_2/2LiNiH_2 [26], respectively. However, physical adsorption in carbonaceous adsorbent presents such advantages of low cost, good reversibility, and safety.

The H_2 isotherms were then fitted, respectively, to the Toth equation, $C_\mu = C_{\mu s} bP/\left[1+(bP)^t\right]^{1/t}$. The fittings were shown in Fig. 3a as solid lines while the optimal parameters (for the data at 77 K only) were listed in the figure caption. The isotherm parameter ($t = 0.474$) indicates that the TC is heterogeneous towards H_2 molecules at 77 K.

The H_2 isosteric heat of adsorption, Q_{iso}, was calculated using the Clausius–Clapeyron equation $[Q_{iso}/RT^2 = -(\partial \ln P/\partial T)_q]$ and plotted in Fig. 3b versus the surface loading. The experimental data involved in the computation was plotted in the embedded figure. It is seen that the heat of adsorption drops quickly from ~7.8 to 5 kJ/mol as the surface loading increase to 4 mmol/g. The high value of Q_{iso} is an indication of H_2 sorption in small micropores (0.6–0.9 nm) which is mainly responsible for H_2 sorption capacity [8,10,11,24] at ambient temperature. According to Table 2, only about 3% of the total micropore volume of the TC belongs to small micropores. Future efforts should be devoted to increase this volume fraction, rather than to further increase the specific surface area.

Finally, the TC was characterized by H_2 sorption isotherm at 77 K with the model proposed by Nguyen and Do [27]. The model employs isotherm data at supercritical temperature and over a wide pressure range and has been used for the structural characterization of activated carbons, carbon molecular sieves, and carbon membranes [28]. The model fitting to the isotherm data was listed in Fig. 3a as the dashed lines while the distribution of sorption capacities in pores of various dimensions were presented schematically in Fig. 4. We see that the model correctly predicts the small

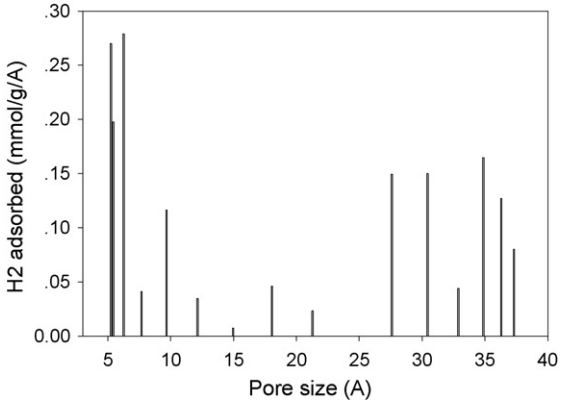

Fig. 4. The distribution of the H_2 sorption capacity of the TC derived by Cuong and Do's model.

micropore peaks at 0.5–1 nm (detected by CO_2 sorption) and the mesopore peaks at 3–4 nm (detected by N_2 sorption), although the contribution of the mesopores seems a bit high.

4. Conclusions

The templated carbon synthesized using zeolite Y as template and PFA as carbon source presents a H_2 sorption capacity of 2.4 wt% at 77 K and 10 bar. The carbon contains a small fraction of small micropores which result in an isosteric heat of adsorption of 7.8 kJ/mol. The structure of the carbon was characterized with the sorption isotherm of different adsorbates (Ar, N_2 and CO_2). CO_2 isotherm at 273 K and Ar isotherm at 77 K were found to be more reliable methods in characterizing the small micropores and the specific surface area, respectively.

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