Journal of Analytical and Applied Pyrolysis 100 (2013) 153–157

Contents lists available at SciVerse ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

The structural development of zeolite-templated carbon under pyrolysis

X.H. Song[a], R. Xu[a], K. Wang[b,*]

[a] School of Chemical & Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore
[b] Department of Chemical Engineering, The Petroleum Institute, Abu Dhabi, United Arab Emirates

ARTICLE INFO

Article history:
Received 2 June 2012
Accepted 11 December 2012
Available online 3 January 2013

Keywords:
Activated carbon
Template synthesis
Zeolite
Pyrolysis
Adsorption
Pore size distribution

ABSTRACT

Three activated carbon samples were synthesized via the pyrolysis of furfuryl alcohol (FA) impregnated in the porous framework of zeolite Y. The pyrolysis temperature was set at 900, 1050, and 1150 °C, respectively, to investigate its role on structural development. The surface properties of the carbon samples were characterized using XRD, SEM, Raman, and gas adsorption technologies. It is found that a low pyrolysis temperature is in favor of the structural regularity and the formation of small micropores ($d < 1.0$ nm), while a high temperature is necessary for the surface area/pore enhancement. However, a too high temperature will result in the collapse of micropores and the formation of mesopores.

1. Introduction

The template carbon (TC) is synthesized via the controlled pyrolysis of a carbonaceous precursor contained in the micro-channels of a template material such as zeolite or silica [1,2]. The carbon precursor, which can be a liquid polymer or a hydrocarbon vapor, is generally infiltrated into the pores of template material by the means of impregnation or chemical vapor deposition (CVD). Compared with conventional activated carbons, TCs constitute large surface area (up to 4000 m^2/g), good porosity (up to 1.6 cm^3/g), and pores of relatively uniform sizes, which make them the ideal adsorbents for the application of energy gas storage (CH_4/H_2) [3,4]. Some high quality TCs may even contain graphite domains of highly ordered replicas (long range periodicity) which resemble the structural characteristics of the template material [1,5].

The pyrolysis process is critical for the structural development of TCs [6,7]. For example, Kyotani's group investigated the synthesis of TCs with different template materials and carbon sources and found that a low pyrolysis temperature at 700 °C and a CVD temperature of 800 °C are critical for the complete structural development [1,8]. Su et al. synthesized high quality TCs with NaY zeolite and furfuryl alcohol (FA) and a pyrolysis temperature of ~700 °C [9,10]. They employed the various forms of zeolite Y as the templates and FA/sucrose as the carbon source and found that a high pyrolysis temperature of ~1150 °C is necessary for the surface area to be fully developed. Our previous study demonstrated that the pyrolysis temperature of 1050 °C can produce a TC with good surface area for energy storage [4,11].

The pyrolysis process predominates the structural properties of TCs. In this research, TCs were synthesized using FA and zeolite Y under different pyrolysis temperatures. The structures of the TCs were fully characterized and based on which the effects of pyrolysis temperature were discussed.

2. Experimental

TC samples were prepared via the method described in our previous studies in [3,4]. In summary, about 1 gram of template zeolite Y sample (NH_4Y, $SiO_2/Al_2O_3 = 5.1$, Zeolyst international®) was firstly dried at 200 °C overnight and then impregnated with 4 ml of FA (98%, Aldrich®) in a flask for 72 h at room temperature and under stirring. The polymer–zeolite composite was filtered out and washed twice with mesitylene to remove the residual FA on the external surface of the zeolite particles. After air-drying for 6 h in a fume hood, the composite was shifted into a quartz boat (20 ml) and then loaded into the tube furnace (Carbolite HST 12/1200). The pyrolysis was under the N_2 flow rate of 100 cm^3/min and started with the ramp rate of 10 °C/min. The soak time is 3 h while the soak temperature was set 900, 1050, and 1150 °C, respectively, for each sample. After pyrolysis, acid wash (HF, ~40%) was used to dissolve the zeolite framework at the room temperature for 24 h. The resulted raw carbon was filtered out and then washed with warm deionized water (at 60 °C). The purified TC sample was filtered out again and dried in a conventional oven at 50 °C overnight. The overall yield of TC was approximately 50 mg per batch. The 3 TCs were

* Corresponding author. Tel.: +971 2607 5116; fax: +971 2607 5200.
E-mail address: kwang@pi.ac.ae (K. Wang).

0165-2370/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jaap.2012.12.011

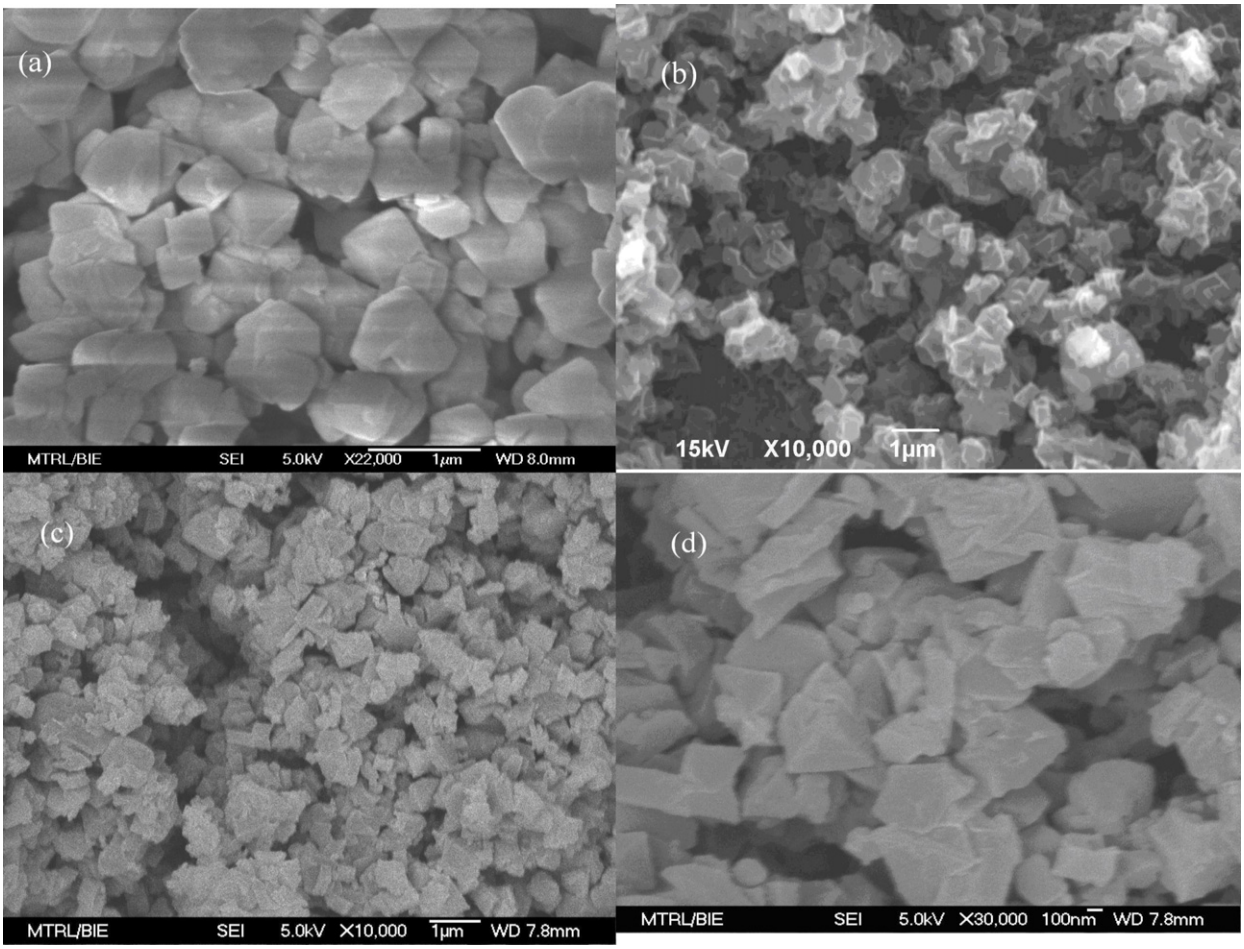

Fig. 1. SEM images of (a) NH_4Y zeolite template, (b) C1150, (c) C900, (d) C1050.

designated as C900, C1050, and C1150, respectively, with respect to its pyrolysis temperature.

N_2 adsorption at 77 K and CO_2 adsorption at 273 K were measured on the TCs using a commercial pore and surface analyzer (Quantachrome, Autosorb-1), respectively. The specific surface area (S_{BET}) was determined from N_2 isotherm in the pressure range of $P/P_0 = 0.05–0.3$. The pore size distribution (PSD) was derived from CO_2/N_2 isotherms using the non-local density functional theory (NLDFT) with the assumption of slit-shaped pore geometry [12]. The structures of the TCs were also characterized by such standard instruments as: SEM (JEOL JSM-6390LA), X-ray diffraction or XRD (Bruker D8), and Raman spectra (Renishaw inVia Reflex, HeNe Laser, 633 nm).

3. Results and discussion

Fig. 1a–d shows the SEM images of 3 TCs and the zeolite template. It is seen that while the zeolite consists of crystals with the average size of ~500 nm (Fig. 1a), the TCs are comprised of interparticle voids and largely amorphous carbon crystals with the size from ~100 nm to ~1000 nm (Fig. 3b–d). No significant difference was found between the morphologies of the 3 TCs.

Fig. 2 shows the XRD patterns of 3 TCs and the zeolite Y (the inset). The diffraction patterns of C1050 and C1150 are similar in nature, without obvious peaks at 26° (2θ) and at 43° (2θ) [which characterize the diffraction pattern of graphitic carbons]. This indicates the amorphous structure of the two TC samples. On the other hand, a small XRD peak at ~6° (2θ) can be seen on C900, which corresponds to the {1 1 1} peak of zeolite Y. This suggests that the lower temperature of 900 °C is in favor of the structural regularity (transferred from the zeolite template) of the TC while a too high temperature is detrimental to this process.

Fig. 3a–c shows the PSD of big micropores (with the diameter $d = 1–2$ nm) and mesopores ($d = 2–5$ nm) derived from the N_2 isotherm on each TC. The PSD of small micropore ($d < 1.0$ nm), which was derived from CO_2 isotherm at 273 K, is embedded in each figure as the inset. It is seen in Fig. 3d that the adsorption isotherm of C900 is largely type I while those of C1050 and C1150 are more of

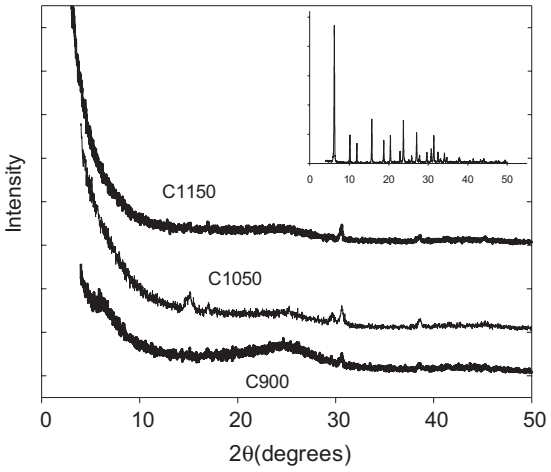

Fig. 2. XRD patterns of TC samples and zeolite Y (the inset).