Materials Letters 137 (2014) 233–236

Contents lists available at ScienceDirect

Materials Letters

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

Pyrolysis reaction of squaric acid: A one-step method for producing expanded foam of mesoporous carbon

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ARTICLE INFO

Article history:
Received 28 June 2014
Accepted 28 August 2014
Available online 6 September 2014

Keywords:
Squaric acid
Carbon materials
Porous materials
Mesoporous carbon
Oxocarbon pyrolysis

ABSTRACT

A template-free approach is described for the synthesis of expanded foams of mesoporous carbon exhibiting high surface areas ranging from 550 to 1100 $m^2 g^{-1}$. The procedure is based on the exceptional carbonization reaction that occurs with squaric acid ($H_2C_4O_4$), a strained four-membered carbocycle belonging to the oxocarbon acids. Indeed the pyrolysis reaction proceeds just above 300 °C through an amazing one-step and sharp exothermic phenomenon coupled with a weight loss of 90%, thereby promoting a porous structure. This massive gas release behaves also as a "fluid" template during the carbon production, which explains the formation of expanded foams. This particular thermal behaviour seems related to the phase transition that occurs in $H_2C_4O_4$ crystals at $T_c = 121$ °C. Below T_c the planar squaric acid molecules exhibit a fully ordered structure in a monoclinic system whereas for $T > T_c$ the structure undergoes a disordered tetragonal structure where all C–O bonds of squaric acid become statistically equivalent in a perfect square, making a discrete thermal decomposition reaction possible.

1. Introduction

The pyrolytic decomposition of organic precursors constitutes a common synthesis route for producing a large variety of carbonaceous materials with various structures and morphologies depending on the used experimental conditions. In particular numerous mesoporous carbon materials can be prepared in this way, which are usually characterized by high surface areas and high pore volumes [1]. Basically, the mesostructure is the result of a templating effect that often involves the use of pre-synthesized inorganic or organic templates of various degrees of complexity. With organic precursors, many other original strategies are also known [1,2] such as the elegant concept of the polymer blend carbonization method proposed by Ozaki et al. in 1997 [3]. In the latter case, two polymers of appropriate mutual affinity but with different degrees of thermal stability (one of them tends to carbonize at high temperatures while the other decomposes into gaseous products) are first intimately mixed. The as-obtained nanostructured precursor phase serves then as a template of the target mesoporous carbon material, which is obtained by pyrolysis accompanied by volatilization of the sacrificial polymer.

Herein, we report in fact a variation of this former approach. However, in the present case, both carbon source and gas precursors (sacrificial atoms) are directly included at the molecular level within a single compound. Revisiting the chemistry of cyclic oxocarbons for the past few years [4,5], we realized indeed that the simple pyrolysis reaction of squaric acid ($H_2C_4O_4$, 3,4-dihydroxycyclobut-3-ene-1,2-dione) for $T > 300$ °C induces the spontaneous production of expanded foam of mesoporous carbon [6]. The specific feature of this carbonization process as well as morphological/structural properties of the as-obtained carbonaceous materials is presented and discussed herein based on four relevant pyrolysis temperatures (400, 600, 800 and 965 °C).

2. Results and discussion

In a typical procedure, 0.5 g of squaric acid was placed into a quartz tubular furnace under Ar or N_2. The pyrolysis program

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http://dx.doi.org/10.1016/j.matlet.2014.08.148
0167-577X/

consisted in a first heating step at 5 °C min^{-1} followed by an isothermal step at the required temperature for 3 h. Further experimental details are described in Supporting information. The as-obtained carbon cakes occupied a volume several hundred times larger than the initial volume of the starting squaric acid. TEM investigations were first performed to determine the texture and the structure of the carbon foams since no Bragg peaks were observed by X-ray powder diffraction. Basically, TEM (Fig. 1a) and HRTEM (Fig. 1b) images show a hollow nano-texture and an amorphous structure, respectively. Corresponding selected area electron patterns (Fig. 1c) indicate consistent results, namely very broad and diffuse rings corresponding to (100)* and (110)* planes of an ideal hexagonal graphite structure. Upon pyrolysis reaction the material undergoes a graphitization reaction as evidenced in Fig. 1b for T=965 °C where graphene interplane distances of about 0.3–0.4 nm are measured on the HRTEM images in accordance with (002) planes [7] while (100)* and (110)* reflections are sharper on the corresponding SAED pattern.

Raman spectroscopy was also used as a useful tool for the characterization at a local scale (Fig. 1d). Spectra show three peaks centered at 1360 cm^{-1} (D band), 1526 cm^{-1}(D_3 band) and 1595 cm^{-1} (G band). G (in-plane stretching motion) and D (related to defects in graphite) bands indicate the presence of carbon atoms in sp^2 configuration while D_3 band is related to amorphous carbon phase [8]. Some variations are also observed on Raman spectra with increasing temperature. The first one is an increase of the D peak in agreement with the production of a larger amount of graphitic rings. The second effect is a decrease of the full widths at half maximum (FWHM) for both G and D peaks meaning that the graphitic structures become more ordered (i.e., homogenisation of the bond-angular and bond-length distortions). The third effect is related to the D_3 band. For C_{400} and C_{600} samples, G and D_3 bands are superimposed due to the disorder of the Csp^2 structure: combination of amorphous and crystalline phases. For the C_{800} sample, it is interesting to note that D_3 band is clearly separated from the G peak. Additionally, this G peak appears quite similar to the one related to C_{965} whereas the contribution of D_3 band is substantially reduced for the sample prepared at 965 °C. In short, Raman study suggests that a crystallisation reaction occurs within

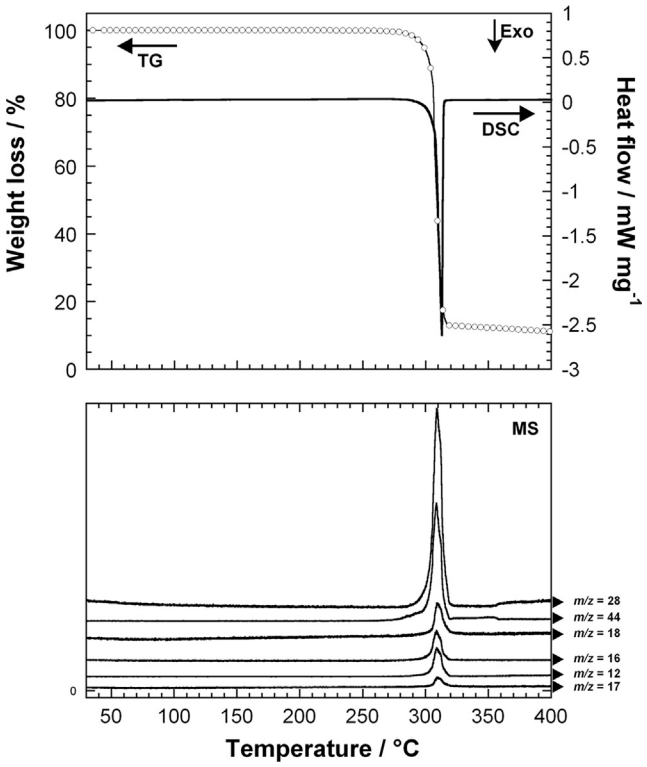

Fig. 2. Thermal analysis data of squaric acid (rate of 1 °C min^{-1} under argon).

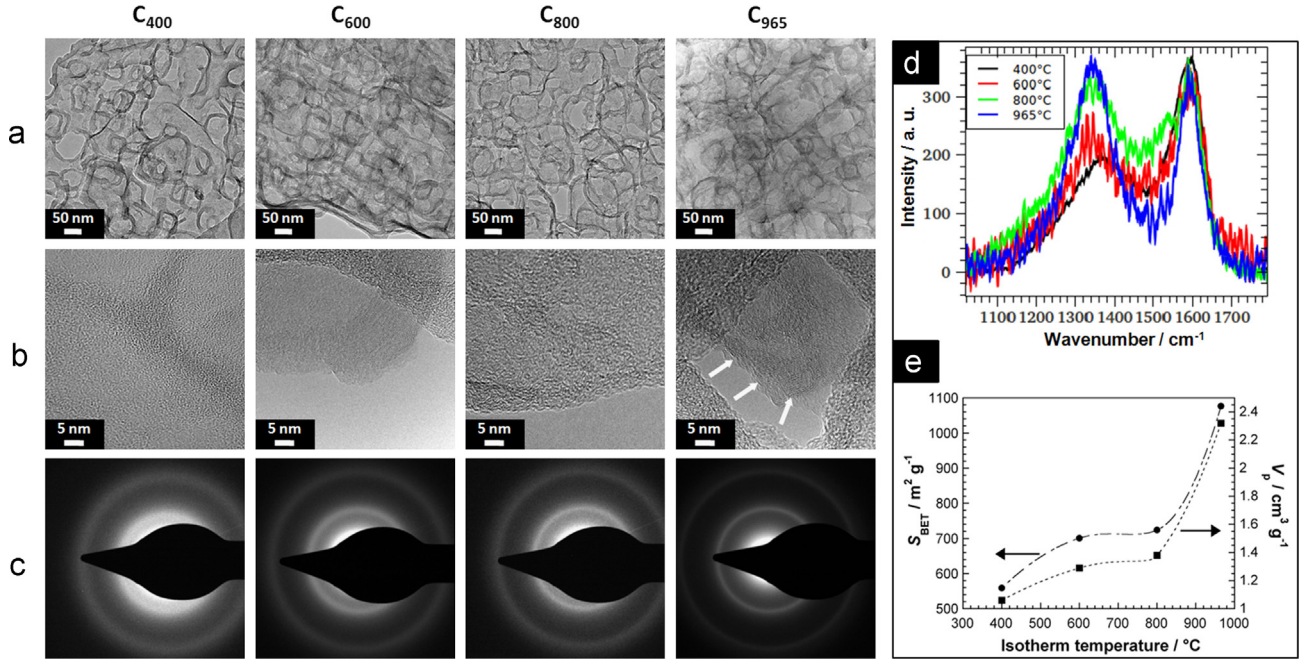

Fig. 1. Bright field (a) and HRTEM (b) images of samples prepared at 400, 600, 800 and 965 °C. Corresponding SAED patterns (c) show broad and diffuse (100)* and (110)* rings related to amorphous or poorly crystallized carbons. For the sample prepared at T=965 °C, graphitization reaction has begun as exemplified through the imaging of few graphene planes (see white arrows). (d) Superimposition of the related Raman spectra. The absence of photoluminescence on spectra indicates that carbon foams are quasi-hydrogen-free. (e) Evolution of the corresponding BET surface area (S_{BET}) and total porous volume (V_P) values.