Microporous and Mesoporous Materials 234 (2016) 162–165

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Synthesis of mesoporous carbons with narrow pore size distribution from metal-organic framework MIL-100(Fe)

Xinlong Yan [a, *], Yingli Yang [a], Xiaoyan Hu [a], Min Zhou [a], Sridhar Komarneni [b]

[a] School of Chemical Engineering & Technology, China University of Mining and Technology, Xuzhou 221116, PR China
[b] Department of Ecosystem Science and Management, Materials Research Institute, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA

ARTICLE INFO

Article history:
Received 15 May 2016
Received in revised form
3 July 2016
Accepted 9 July 2016
Available online 14 July 2016

Keywords:
Mesoporous carbon
Metal-organic frameworks
Carbonization
Narrow pore size distribution

ABSTRACT

Mesoporous carbon materials are of great interest in the field of environmental applications, gas separation and storage, electrode materials for fuel cells, batteries, and etc. Here, we report the synthesis of mesoporous carbons with Fe or Fe_3C embedded via carbonization of furfuryl alcohol impregnated metal-organic framework, MIL-100(Fe). The produced carbon materials are featured by nano sheet-like structure, reasonably high specific area (376 m^2/g) and narrow mesopore size distribution (centered at around 4.0 nm).

1. Introduction

Porous materials such as zeolites, carbons, metal oxides and metal-organic frameworks are of significant importance due to their promising applications in many areas, e.g. adsorption, separation, catalysis, energy storage and biomedical applications [1–5]. Among them, nanoporous carbon materials featured by high surface area, large pore volume and narrow pore size distribution have attracted extensive attention, due to their superior thermal and chemical stability [6–8]. However, most of the carbons such as activated carbon and carbon nanotubes belong to the category of microporous materials, whose application is not desirable for fuel cells, lithium-sulfur battery and water treatment et al. [9–11]. Thus, great efforts have been devoted towards preparing mesoporous carbon materials with varied pore structure.

The templating approach have been proposed as a feasible method for the synthesis of mesoporous carbon, according to the results reported by Ryoo et al. [12] and Hyeon et al. [13]. Various porous templates such as zeolites, silica, and alumina etc. were utilized [14–16]. However, this method is time consuming, costly and of small synthesis capacity.

In recent years, porous coordination polymers (PCPs) or metal-organic frameworks (MOFs), as typical inorganic-organic hybrid materials with highly crystalline structures, were employed as precursors for the formation of highly porous carbons [17–21]. However, most of the carbons prepared above were of highly microporous nature [22–24]. The preparation of mesoporous carbon with narrow pore size distribution is still a challenge. Recently, Cheetham et al. [25] reported that the carbonization of metal-organic framework-5 (MOF-5) would produce carbons with micropore/mesopore hierarchical structure. Xu et al. [26] prepared MOF-derived carbons with a structure of mesopore-connected micropores and/or macropores by pyrolysis of Cu loaded Al-MIL-101-NH_2 MOFs. Through calcination of the 5-aminotetrazole impregnated MIL-100, micro/mesoporous carbons were synthesized by Feng et al. [27]. However, the mesopore size distributions of the above carbons are rather broad or disordered.

In this study, we have successfully synthesized mesoporous carbons by thermal decomposition of furfuryl alcohol impreganted MOF-100(Fe). The produced carbon materials have high BET surface areas and narrow pore size distribution, and exhibit nano-sheet structure with Fe or Fe_3C nanoparticles embedded.

* Corresponding author.
E-mail address: yanxl@cumt.edu.cn (X. Yan).

http://dx.doi.org/10.1016/j.micromeso.2016.07.012
1387-1811/

2. Experimental

2.1. Materials

Iron powder, hydrofluoric acid, 1, 3, 5-Benzenetricarboxylic acid (H3BTC), furfuryl alcohol (FA), nitric acid, hydrochloric acid, hexane and ethanol were supplied by Sinoreagent Company (China). All solvents and chemicals are of analytical reagent grade and used without further purification.

2.2. Synthesis of porous carbons

MIL-100(Fe) was synthesized according to Yoon et al. [28]. Briefly, iron powder (555 mg), H_3BTC (1375 mg), hydrofluoric acid (35%, 400 μL), and nitric acid (65%, 380 μL) were well mixed with pure water (40 mL) in a Teflon lined steel autoclave. The autoclave was then placed in an oven at 150 °C for 12 h. After cooling, the solid product was collected by centrifugation, thoroughly washed with ethanol and water. The as-synthesized MIL-100(Fe) was further purified with hot water at 80 °C for 5 h to remove residual unreacted ions. The resulting material was characterized by XRD and N_2 adsorption-desorption experiments, and the results is included in the supporting information.

The as-prepared MIL-100(Fe) was degassed at 150 °C for 3 h to remove the solvent molecules accommodated in the pores. 200 mg of the degassed sample was soaked in the 20 mL of FA ethanol solution (Containing 100 mg FA) and the mixture was stirred until the solution became dry. Subsequently, the FA/MIL-100(Fe) composite was transferred into an alumina boat. Pyrolysis of the composite was performed in the tube furnace at temperature ranging from 700 to 900 °C under N_2 flow for 1 h. The as-obtained solid was immersed in 5 M HCl aqueous solution and kept under stirring for 24 h, followed by filtration and washing with H_2O and ethanol. The final products were named as MC-700, 800 and 900 for samples calcined at 700, 800, 900 °C, respectively. Fig. 1 shows the entire synthetic route for the carbons.

2.3. Characterization

X-ray diffraction (XRD) patterns for the samples were recorded on a Bruker D8 ADVANCE diffractometer with Cu Kα radiation at 40 KV and 30 mA. The Raman spectra of samples were acquired on a SENTERRA spectrometer (Bruker) with an excitation laser beam wavelength of 523 nm. The N_2 adsorption-desorption isotherms were collected at 77 K using IQ2 Quantachrome porosimeter. Prior to the measurement, the samples were degassed at 300 °C overnight. The total pore volume (Vt) was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.99. The pore size distributions were determined by using non-local density functional theory (NLDFT) methods for carbon with slit-like pores as a pore model. The micropore volume (V_{micro}) was estimated using t-plot method and mesopore volumes were obtained by subtracting V_{micro} from the total pore volume. Transmission Electron Microscope (TEM) and selected area electron diffraction (SAED) characterizations were carried out using a FEI Tecnai G2 F20 device operated at 200 KV. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific Escalab 250Xi instrument equipped with Al Kα radiation ($h\nu$ = 1486.6 eV).

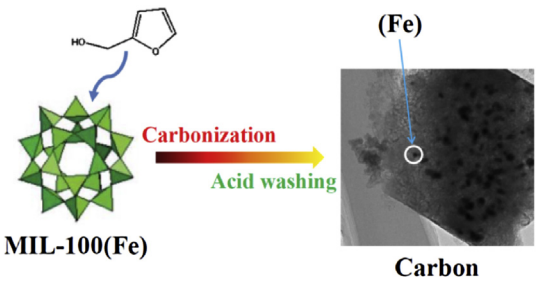

Fig. 1. Schematic illustration of the synthesis procedure of MIL-100(Fe) derived carbons.

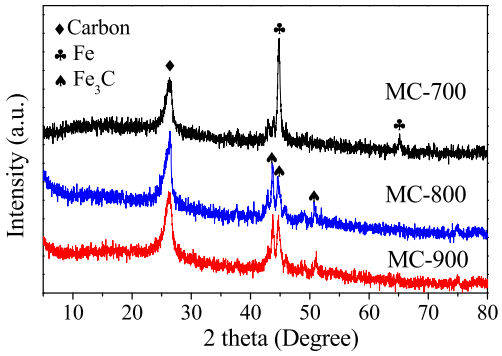

Fig. 2. XRD patterns of carbons obtained at different calcination temperatures.

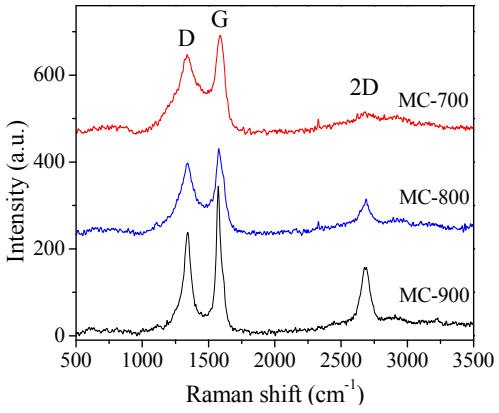

Fig. 3. Raman Spectra of as-prepared MC Carbons.

3. Results and discussion

Fig. 2 displays XRD patterns of the carbon materials obtained at different pyrolysis temperatures. The diffraction peak at around

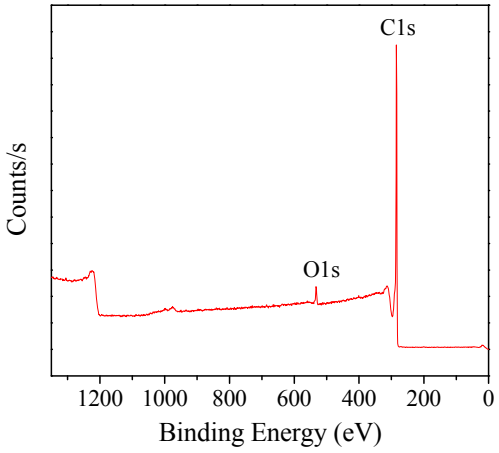

Fig. 4. XPS survey scan of sample MC-800.