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A meso-macroporous borosilicate monolith prepared by a sol–gel method

Shao-Ting Wang, Ming-Luan Chen, Yu-Qi Feng *

Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry, Wuhan University, Wuhan 430072, PR China

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ABSTRACT

A meso-macroporous borosilicate monolith was prepared for the first time using a sol–gel method. The proposed material was subsequently characterized by FTIR-ATR and solid-state NMR experiments to investigate the chemical environment of boron in the silica framework. The results showed that boron formed Si–O–B bonds and largely existed as three-coordinated symmetrical structure as well as some tetrahedral structure in the skeleton. According to the ICP-AES experiment, the highest [B]/[Si] molar ratio was 0.15 in the final product. And a bimodal porosity was investigated by SEM, mercury porosimeter and nitrogen adsorption–desorption experiments. This new borosilicate monolithic material could have potential application in both chemical and biological sciences for separation, enrichment or catalysis.

1. Introduction

In these few decades, the preparation of bimodal porous monolithic materials has attracted much attention. This kind of materials exhibits distinct hierarchical porosity [1]. The mesopores on the skeleton give the monolith high specific surface area. And the continuous macropores in the framework provide rapid mass transportation. These advantages make monoliths very critical in both analytical chemistry (as extraction or separation media) [2,3] and catalytic chemistry (as catalytic supports or solid catalysts) [4–6].

Borosilicate materials have been comprehensively studied and widely used in microarray systems [7], catalyst supports [8] and chemosensors [9] based on their high chemical inertness and excellent thermal, mechanical stability. However, the preparation of such materials is limited by the high susceptibility of boron precursors and water hydrolysis of Si–O–B bonds before the conformation of the skeleton [10]. The precipitation of boron in the form of boric acid instead of incorporating into the network at molecular level has always been regarded as the most serious problem during the synthetic process. Lots of efforts have been devoted to deal with this problem. Irwin's group [11] prepared borosilicate glasses through a water-containing sol–gel strategy and studied the mechanism of the formation and decomposition of borosiloxane bonds in the reaction solution. They found that most of boron was leaching as boric acid in the initial gel. The incorporation could only occur after thermal treatment of the dry gel. On the other hand, Beckett's group [12,13] taking metaborate esters as the source of boron successfully synthesised glass films by a non-aqueous route. And recently, Martin's group [14] carried out an exothermic phase separation process to create borosilicate nanoparticles by mixing a binary silicon-boron oxide solution with water. However, to the best of our knowledge the borosilicate material with monolithic structure has not been achieved hitherto, which is somewhat not that conductive for the further application of such type of material. So in this work, we present the synthesis of a meso-macroporous borosilicate monolithic material for the first time by a modified sol–gel method [1,15,16], in which tetramethylorthosilicate (TMOS) and boric acid function as sources of silicon and boron, respectively.

2. Experimental

2.1. Materials and reagents

Tetramethoxysilane (98%, TMOS) was obtained from the Chemical Factory of Wuhan University (Wuhan, China). Acetic acid, poly (ethylene glycol) (PEG, *Mw* = 10,000), urea and boric acid of analytical grade were purchased from Shanghai General Chemical Reagent Factory (Shanghai, China). All the chemicals used in the experiments were analytical grade without further purification. Double-distilled water was used in all experiments.

2.2. Preparation of borosilicate monoliths

The composition of all the monoliths was shown in Table 1. Firstly, all the components were mixed in a vessel. After stirring and ultrasonic treatment (both for 10 min), the resultant transparent solution was allowed to gel and age at 40 °C for 12 h in the closed system. During this period of time, through-pores were formed in the skeleton owning to the phase separation process. Then the wet gel was transferred to a suitable autoclave to be

* Corresponding author. Tel./fax: +86 27 68755595.
E-mail address: yqfeng@whu.edu.cn (Y.-Q. Feng).

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Table 1
Starting composition of sample monoliths[a].

Sample	HOAc	PEG	Urea	TMOS	H_3BO_3
T250B0	600	30	40	250	0
T250B14	600	30	40	250	14
T250B28	600	30	40	250	28
T250B42	600	30	40	250	42
T240B28	600	30	40	240	28
T230B28	600	30	40	230	28

[a] The concentration of HOAc solution was 0.015 mol/L. And all the units mentioned above were milligram for solids and microliter for liquids.

treated at 120 °C for 3 h allowing the decomposition of urea, which could create a basic environment to promote the formation of mesopores and prevent cracking in the drying process. The monolith was then completely dried at 80 °C to promote the formation of Si–O–B bonds and then heat treated at 600 °C for 3 h to strengthen the incorporation of boron as well as remove the organic constituents. Finally the white monolith was substantially washed by water and ethanol and dried again. The shape of the obtained material was controlled by the initial vessel. A cylindrical example was shown in the photographic image in Fig. 1(d).

2.3. Characterizations

The microscopic morphology of the monolith was examined by a Quanta 200 scanning electron microscopy (SEM) (FEI, Holand). The FTIR-ATR spectra were obtained by using a Thermo Scientific Nicolet 6700 FT-IR spectrometer with a Smart Orbit accessory inserted. The solid-state NMR experiments were carried out on the

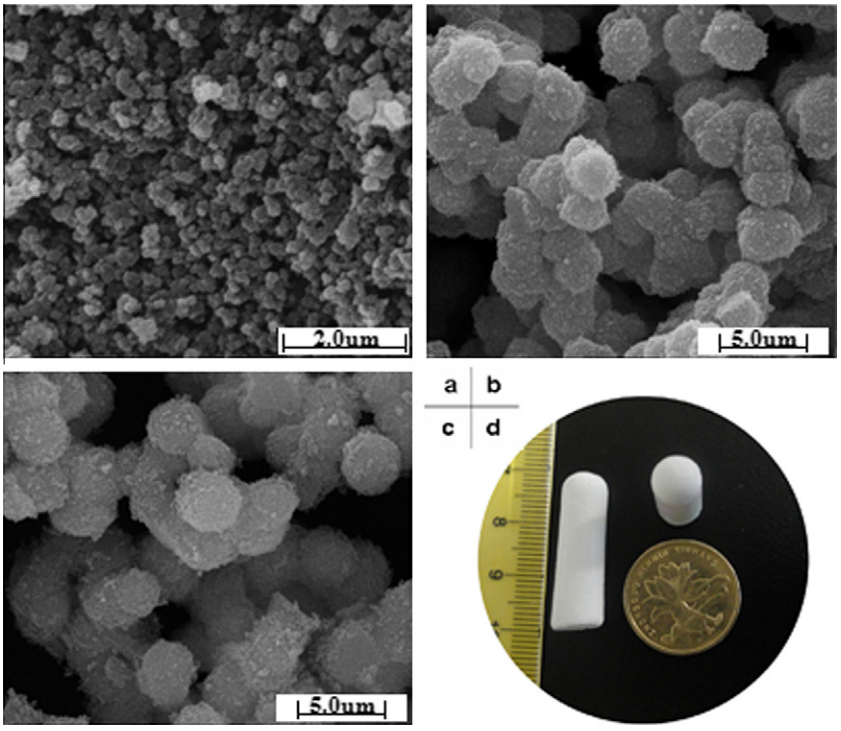

Fig. 1. SEM and photographic images of monoliths from T250B28 (a), T250B14 (b), T230B28 (c) and actual scale of T230B28 monoliths (d).

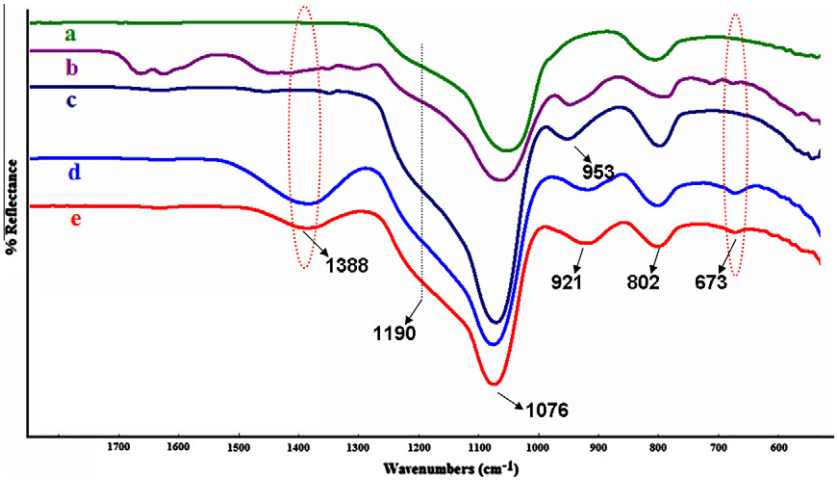

Fig. 2. FTIR spectra of T250B0 (a), T250B28 before calcination (b), (b) after washing (c), T250B28 after calcination (d), (d) after washing (e).