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Materials Research Bulletin 41 (2006) 1259–1265
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Preparation of ZnO bulk porous nanosolids of different pore diameters by a novel solvothermal hot press (STHP) method

Mei Li, Xiu-lin Liu, De-liang Cui *, Hong-yan Xu, Min-hua Jiang

State Key-Lab of Crystal Materials, Shandong University, Jinan, 250100, PR China

Received 20 June 2005; received in revised form 26 October 2005; accepted 5 January 2006
Available online 31 January 2006

Abstract

ZnO bulk porous nanosolids were prepared by a novel solvothermal hot press (STHP) method with different pore-forming agents using ZnO nanoparticles. The samples were characterized with SEM, XRD, FTIR, a mercury intrusion porosimeter and N_2 adsorption–desorption method. Experimental results showed that pore size of the nanosolids was between 20–32 and 20–100 nm when de-ionized water and CTAB solution were used as pore-forming agents, respectively. There was no obvious morphological change in the samples when all pore-forming agents were removed from the autoclave.

Keywords: A. Oxides; A. Structural materials; A. Nanostructures; C. Electron microscopy; C. X-ray diffraction

1. Introduction

Mesoporous molecular sieves have attracted much attention because of their potential use in many fields since MCM-41 was successfully synthesized [1–5]. The pore of the mesoporous material is inside the particle and it is difficult to widen pore size. Surfactants and co-polymers have been used as templates to control pore size, pore shape and morphology in the process of mesoporous materials, but it is still a challenge to expand pore size to nanometers [6–13]. In addition, almost all the mesoporous materials are powders therefore difficult to prepare as bulk materials. So we proposed a novel solvothermal hot press (STHP) method to prepare porous bulk nanosolids. Compared with mesoporous materials, porous bulk nanosolids are compacted with nanoparticles. Furthermore the pore size of porous bulk nanosolids can be easily adjusted over a broad range using different solvents. The nanoparticle channel wall is strong and flexible. The porous bulk nanosolids retain the reactive activity and catalytic ability of the nanoparticles, so they can still be used as absorbents and catalysts. This STHP method is a simple way to get macroporous material; because they are bulk nanosolids, they can be used as reactor-carriers. Technically, because of their bulk and strength, porous bulk nanosolids can be recycled thus greatly reducing the cost.

Several bulky porous nanosolids such as TiO_2 and ZrO_2 have been successfully prepared since we began using the STHP method [14–16]. In this paper, ZnO bulky porous nanosolids were synthesized using, respectively. deionized water and CTAB solution as pore-forming agents. The pore size of the latter being larger than the former, its surface area decreases and porosity increases slightly.

* Corresponding author. Tel.: +86 531 88362871; fax: +86 531 86466331.
E-mail address: plum3lm@yahoo.com.cn (D.-l. Cui).

0025-5408/$ – see front matter
doi:10.1016/j.materresbull.2006.01.005

2. Experimental

2.1. Materials

ZnO nanoparticles (with an average particle size of 50 ± 10 nm, purchased from Mingri Nanometer Materials Co. Ltd., China), cetyltrimethyl ammonium bromide (CTAB) ($C_{19}H_{42}BrN$, A.R.) and deionized water.

2.2. Sample preparation

Three grams ZnO nanoparticles were added to 8 ml deionized water and stirred for 10 min. The mixture was then transferred into an autoclave (Fig. 1) for hydrothermal treatment at 200 °C for 20 h at an average heating rate of 0.5 °C/min. At the same time, 62.5 MPa pressure was exerted on both ends of the autoclave when the temperature arrived at 200 °C. After cooling to room temperature, we got the sample named S-1.

Fourteen milligrams CTAB was dissolved into 8 ml of deionized water and stirred for 10 min. We repeated the process, as in S-1 and got sample S-2.

2.3. Characterization

XRD patterns of the samples were recorded using a D/max-γA X-ray powder diffractometer, which employed Cu Kα radiation and was operated at 5 kW with a scanning velocity of 4° min^{-1}. The SEM images of the samples were taken with an S-520 scanning electron microscope (accelerating voltage = 20 kV). The pore-size distribution was analyzed by an American Quantachrome Pore Master-60 mercury intrusion porosimeter at 20 °C. N_2 adsorption–

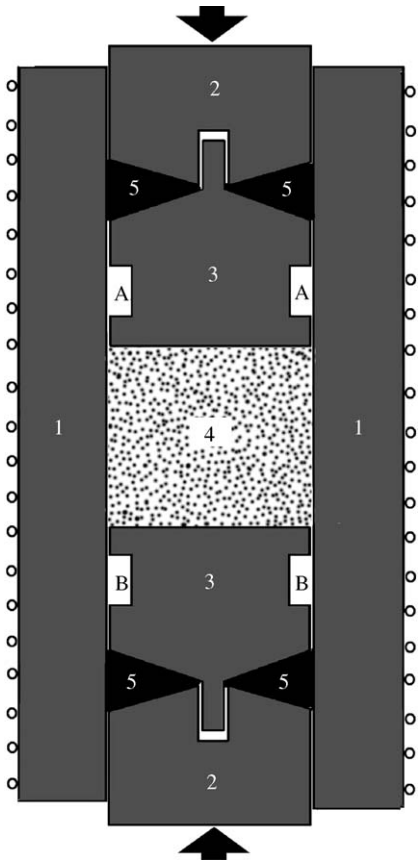

Fig. 1. Structure of solvothermal hot press autoclave: (1) cylinder; (2) piston; (3) gasket; (4) sample; (5) Teflon ring.