Materials Chemistry and Physics 163 (2015) 331–336

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

The effect of the boron source composition ratio on the adsorption performance of hexagonal boron nitride without a template

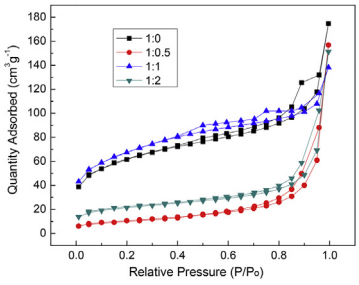
Ning Zhang*, Tong Zhang, Hongmin Kan, Xiaoyang Wang, Haibo Long, Xingyu Cui

Liaoning Key Laboratory of Advanced Materials Manufacturing Technology, Shenyang University, Shenyang, 110044 Liaoning, PR China

HIGHLIGHTS

- Spherical h-BN was synthesized by controlling the boron source composition ratio.
- Without extra spherical template, solid Na_2O was equal to a spherical template.
- At boron source composition ratio of 1:1, h-BN had best adsorption performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 January 2015
Received in revised form
27 May 2015
Accepted 17 July 2015
Available online 30 July 2015

Keywords:
Ceramics
Inorganic compounds
Nitrides
Microstructure

ABSTRACT

An inexpensive boric acid (H_3BO_3) and borax ($Na_2B_4O_7 \cdot 10H_2O$) mix was used as a source of boron with different composition ratios, and urea was used as a nitrogen source, in flowing ammonia atmosphere, for the preparation of hexagonal boron nitride (h-BN) with different micro-morphologies. Under a certain synthesis process, the effects of the molar ratio of borax and boric acid (or simply the boron source composition ratio for short) on the phase composition of the sample were studied; the work also explored the effect of boron source composition ratio on the micro-morphology, adsorption desorption isotherm and specific surface area of the h-BN powder. The main purpose of this work was to determine the optimum composition ratio of preparing spherical mesoporous h-BN and ensure that the micro-mechanism underpinning the formation of spherical mesoporous h-BN was understood. The results showed that at the optimum boron source composition ratio of 1:1, globular mesoporous spheres with a diameter of approximately 600–800 nm could be obtained with the highest pore volume and specific surface area (230.2 m^2/g).

1. Introduction

Boron nitride (BN) is a non-metal, oxide ceramic material. Its crystal structure is similar to that of carbon [1–3] and mainly contains four types of isomers which are respectively: hexagonal boron nitride (h-BN), trigonal boron nitride (r-BN), cubic boron nitride (c-BN), and wurtzite boron nitride (w-BN) [4]. The h-BN has excellent heat resistance, good corrosion resistance, a lower thermal expansion coefficient, high thermal conductivity, a low density, excellent lubricity, chemical stability, etc [5–7]. It has higher application value in the electronic information industry, new energy, and other hi-tech fields [8,9]. For instance, h-BN fiber can be used as a microwave antenna window, missile radome material, and h-BN powder can be used for the preparation of cubic boron nitride ceramic [10,11] or as a ceramic microwave tube transport energy window or clamping rod, etc [12,13]. The experimental results showed that

* Corresponding author.
E-mail address: zhangning5832@163.com (N. Zhang).

http://dx.doi.org/10.1016/j.matchemphys.2015.07.047
0254-0584/

spherical mesoporous h-BN powder had better filling capability, formability, and thermodynamic stability than flaked h-BN powder. The h-BN ceramics with good filling ability, high stability, and high adsorption have a broad application prospects as high temperature catalyst carriers, especially as a gas adsorbent in hydrogen storage, automobile exhausts, and meteorological haze governance. For example, the activated carbon has poor thermal stability. It begins to slowly oxidize and at 300 °C and quickly oxidize at about 600 °C. But h-BN begins to oxidize and at 900 °C, especially the chemical stability of h-BN makes it have good chemical inertness for most of the material. So h-BN has certain application value. However, the crystal structure of h-BN is similar to graphite, and the micro-morphology usually appears in lamellar form [14,15], so spherical mesoporous h-BN cannot form spontaneously in nature. At present, the micro-morphology of h-BN powders that are sold on domestic and foreign markets is all lamellar: it therefore cannot meet the requirements of more advanced, demanding applications. To date, research has received considerable attention and has been limited to the experimental stage and unable to be applied to large-scale industrial production with high synthesis temperatures, high cost, environmental pollution restrictions, and high risk and low yield factors [16]. Although spherical mesoporous h-BN, with its high filling ability, high adsorption, and high stability, has great application prospects as an adsorbent in the fields of environmental protection and new energy, so far, it has not been widely used in these areas. The main reason is that research into the preparation, its microstructure, and adsorption performance of spherical mesoporous h-BN material remains sparse and the relevant theoretical basis is also imperfect. Therefore, this study of the preparation, micro-morphology, and adsorption performance of spherical mesoporous h-BN powders represents an advance in this respect.

Currently, the effective method for preparing high-adsorption spherical h-BN uses a template [17]; the surfactant spontaneously becomes orderly micelles when the concentration of the surfactant reaches a critical micelle concentration (CMC), and the template is formed. According to the literature, when the concentration of the surfactant was in the range of CMC to ten times CMC, the micelle was generally spherical [18]. So spherical h-BN can be obtained on a template. For example in 2004 Wei Qianghan et al. [19] successfully synthesized h-BN with specific surface area (167.8 m^2/g) with a template. But in the post-processing of the product, this method also met with some difficulties. The template components were difficult to be effectively removed which directly affected the performance of the catalyst carrier. The specific surface area of h-BN on the market at present is 120 m^2/g and it is expensive. However, in this study without adding any surfactant and relying on an additional template, spherical mesoporous h-BN can be synthesized only by controlling the boron source composition ratio. At the optimum boron source composition ratio of 1:1, spherical mesoporous h-BN could be obtained with the highest specific surface area (230.2 m^2/g). Herein lay the novelty of this research. Now related report has not been appeared on the preparation of spherical mesoporous h-BN without any template. Therefore this research results are advanced and innovative to some extent.

2. Experimental materials and methods

2.1. Materials

In these experiments, borax and boric acid acted as the boron source, and boron source composition ratios were respectively: 1:0, 1:0.5, 1:1 and 1:2. Urea ($CO(NH_2)_2$) provided nitrogen, the B:N atomic molar ratio was 1:4. Acrylamide (C_3H_5ON) was used as the monomer, N,N-methylene bis acrylamide ($C_7H_{10}N_2O_2$) was used as a cross-linking agent, ammonium persulphate ($(NH_4)_2S_2O_8$) was used as an initiator, and the added network agent was composed of acrylamide: N,N-methylene-amide: ammonium persulphate in proportions 140:4:25.

2.2. Preparation of the h-BN precursor

The h-BN precursor was prepared with the use of a polymer network, and its materials were uniformly mixed to molecular grade.

Firstly, borax and boric acid for each different boron source composition ratios and a certain quantity of urea were placed into deionized water, under continuous stirring until a transparent solution is obtain. To the formed solution, acrylamide and N,N-methylene-bis-acrylamide were added into the solution, again, blending and stirring to form a transparent solution.

Secondly the solution was placed into water at a constant temperature between 60 and 70 °C, to which $(NH_4)_2S_2O_8$ was added under continuous stirring until the entire mixture was converted into a colloid.

Finally, the precursor was dried thoroughly in a rapid-heating furnace (200 °C) and ground. Thereafter h-BN precursors with different boron source composition ratios could be prepared.

2.3. Synthesis of spherical h-BN

On the basis of previous research work [18], the synthesis process of this study was as follows: in a flowing ammonia atmosphere, the h-BN precursor was placed into a tube furnace and heated to 300 °C at a rate of 5 °C/min for 1 h. Then the h-BN precursor was sequentially heated to a certain nitriding temperatures (675 °C) at a rate of 10 °C/min for 2 h and cooled. After cooling to room temperature, the products were cleaned by pickling, water washing, and alcohol washing, and dried at 60 °C for 24 h in the oven. Then the dried products were placed in a rapid-heating furnace to remove residual carbon at 600 °C for 3 h: high purity spherical h-BN was thus obtained.

2.4. Adsorption performance characterization

The method used to characterize the adsorption performance of the h-BN powders was a liquid nitrogen adsorption test. Under a liquid nitrogen temperature of −195.75 °C, this study used nitrogen as a gas adsorbent and a Geminiv2380 automatic analyzer of porosity produced by American Mike Instruments Company to measure the adsorption−desorption isotherm for h-BN powders. Firstly, the samples were heated to 300 °C for 1 h and weighed after vacuuming, degassing to remove the adsorbed gaseous impurities on the surface of the samples. The test samples were then placed in liquid nitrogen. At a certain liquid nitrogen temperature and under different relative pressures (P/P_0), the adsorption−desorption isotherm for each test samples was derived by testing the amount of nitrogen adsorbed by each samples.

2.5. Microstructure and phase composition characterization

The micro-morphology and microstructure of h-BN powders were observed by using an S-4800 type emission scanning electron microscopy (Hitachi Ltd, Japan) and a Tecnal $G^2$20 type transmission electron microscopy (FEI Co., USA). The phase composition was analyzed by PW3040/60 type X-ray diffractometer, and the tests used a copper target with a scanning speed of 15°/min and an angle scanning range of $10° \leq 2\theta \leq 90°$. By comparing the results of those diffraction peaks revealed by X-ray diffraction (XRD) with the card database, the phase composition of the samples could then be determined.