

Effects of boron source composition ratio on the microstructure and adsorption performance of hexagonal boron nitride prepared by template method

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The paper was prepared spherical hexagonal boron nitride with different microstructures under flowing ammonia atmosphere. The effect of boron source component ratios (molar ratio of borax and boric acid) on the phase composition of the sample were studied: the work also explored the effect of boron source component ratio on the microstructure and adsorption performance of h-BN. Spherical hexagonal boron nitride had corresponding to shell structure, mesoporous structure, and solid structure when the ratio of boron source components respectively was 1 : 0.5, 1 : 1, and 1 : 2. Between 1 : 1 and 1:0.5, the former had an lower adsorptions at low relative pressures. On the contrary, the adsorption of former would increased at higher relative pressures and reached up $276.02 \text{ cm}^3 \text{ g}^{-1}$, and the maximum adsorption of the latter reached only $228.20 \text{ cm}^3 \text{ g}^{-1}$. Under any relative pressure, the adsorption capacity was the lowest when the boron source composition ratio was 1 : 2.

Key words: Boron source component ratio, Hexagonal boron nitride, Microstructure, Adsorption performance.

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. In addition, h-BN is also used to make refractory crucibles [12], electrical insulator and heat-resistant material [13]. The experimental results showed that spherical h-BN powder had better filling capability, formability, and thermodynamic stability than flaked h-BN. The h-BN ceramics with good filling ability, high stability, and high adsorption have a potential application as high temperature catalyst carriers, especially as a gas

adsorbent in hydrogen storage, automobile exhausts, and meteorological haze governance. However, the crystal structure of h-BN is similar to graphite, and the micro-morphology usually appears in lamellar form [14, 15], so spherical h-BN cannot form spontaneously in nature. At present, the micro-morphology of h-BN powders that is sold on domestic and foreign markets is all lamellar and even randomly layered: it therefore cannot meet the requirements of more advanced, demanding applications. To date, research has been limited to the experimental stage and has been unable to be applied to large-scale industrial production with high synthesis temperatures, environmental pollution restrictions, and high risk and low yield factors^[16]. Although spherical h-BN, with its high filling ability, high adsorption, and high stability, has great application prospects as an adsorbent in the field of environmental protection and new energy, so far, h-BN materials have not been widely used in these areas. The main reason is that research into the preparation, its microstructure, and adsorption performance of spherical 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 h-BN powder represents an advance in this respect.

Currently, the most effective method for preparing high adsorption spherical hexagonal boron nitride uses a template [17]: the surfactant aggregates, when ordered, spontaneously become micelles when the concentration of the surfactant reaches a critical micelle concentration (CMC), and the template is formed. When the concentration

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of surfactant was in the range of CMC or 10 times that, the micelle was generally spherical [18]. In the present study, because borax and boric acid ions were negatively charged, the experiments were conducted with selected cationic surfactants (dodecyl trimethyl ammonium chloride, as DTAC) as the soft template. On the basis of a preliminary study, when the DTAC quality percentage was 10% [18], the surfactant would form spherical micelles, and globular h-BN powder could be obtained. Experimentally, the author had found that the boron source distribution ratio affected the h-BN ball rate, microstructure, and adsorption properties under certain template conditions. The main purpose of this work was to study the effect of boron source component ratios on micro-morphology and adsorption properties of h-BN to lay a theoretical foundation for later application in the field of catalyst carriers, gas adsorbents, hydrogen storage materials, etc. Research into the effect of boron source composition ratio on the preparation of spherical h-BN, its microstructure, and adsorption properties is sparse, so these research results would represent an advance therein.

Experimental materials and Methods

Experimental materials

The boron source composition ratio referred to the molar ratio of borax and boric acid. In these experiments, borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and boric acid (H_3BO_3) acted as the boron source, and boron source component ratios were respectively: 1:0, 1:0.5, 1:1, 1:2, and 1:3. Urea ($\text{CO}(\text{NH}_2)_2$) provided nitrogen, the B:N atomic molar ratio was 1:4. Dodecyl trimethyl ammonium chloride ($\text{C}_{12}\text{H}_{25}\text{N}$, (DTAC)) acted as the soft template at a concentration of 10 wt% [18]. Acrylamide ($\text{C}_3\text{H}_5\text{ON}$) was used as the monomer, N,N-methylene bis acrylamide ($\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$) was used as a cross-linking agent, ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) was used as an initiator, and the added network agent was composed of acrylamide: N,N-methylene-amide: ammonium persulfate in proportions 140 : 4 : 25.

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 ratio and urea quality designation were placed, with the required amount of DTAC, into deionized water, which was then stirred to form a transparent solution. In addition, the experiment added acrylamide and N,N-methylene-bis-acrylamide into the solution, again, blending and stirring to form a transparent solution. Secondly these solutions were added to water at a constant temperature between 60 and 70 °C, to which $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was added under continuous stirring until the entire mixture was converted into a colloid. Finally, the precursor was

dried thoroughly in box-type furnace (200 °C, 2 h) and ground. Thereafter h-BN precursors with different boron source composition ratios could be prepared.

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⁻¹ for 1 h. Then the h-BN precursor was sequentially heated to different nitriding temperatures at a rate of 10 °C min⁻¹ for 2 h and cooled. After cooling to room temperature, the products were cleaned by pickling, washing, and alcohol washing, and oven-dried at 60 °C for 24 h. Then the dried product was placed in a rapid-heating furnace to remove residual carbon at 600 °C for 3 h: high purity spherical h-BN was thus obtained at different nitriding temperatures.

Adsorption performance characterization

The method used to characterize the adsorption performance of the h-BN powder was a liquid nitrogen adsorption test. Under a liquid nitrogen temperature of 77.4 K, this study used nitrogen as a gas adsorbent and a Gemini 2380 automatic porosity analyzer to measure the adsorption-desorption isotherm for each h-BN powder. Firstly, the samples were heated to 300 °C for 1 h and weighed after vacuuming, degassing, and the removal of surface adsorbed gaseous impurities. The test sample was 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 sample was derived by testing the amount of nitrogen adsorbed by each sample.

Microstructure and phase composition characterization

The micro-morphology and microstructure of h-BN powder were observed by using an S-4800 type emission scanning electron microscopy (Hitachi Ltd, Japan) and a Tecna G²20 type transmission electron microscope (FEI Co., USA). The material phase composition was analysed by PW3040/60 type X-ray diffraction, and the tests used a copper target with a scanning speed of 15 °/min and an angle scanning range of 10 ° ≤ 2θ ≤ 90 °. By comparing the results of those diffraction peaks revealed by XRD diffraction with the card database, the phase composition of the samples could then be determined.

Experimental results and discussion

Effect of boron source composition ratio on phase composition

The effect of the ratio of boron source components on the phase composition in the same synthesis process (675 °C, 2 h) was studied. Fig. 1 shows the XRD diffraction pattern of the samples prepared with

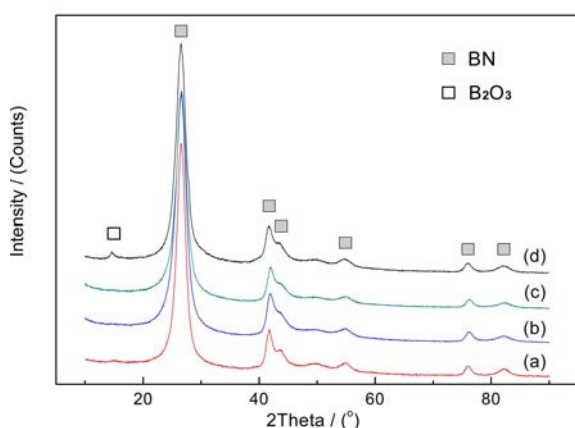


Fig. 1. The XRD diffraction spectrum of the powder (a) 1 : 0; (b) 1 : 1; (c) 1 : 2; (d) 1 : 3.

different boron source compositions: there was only the diffraction peak of h-BN present in the XRD diffraction pattern when the molar ratio of borax and boric acid was 1 : 0, 1 : 1, and 1 : 2 respectively (Fig. 1(a) to (c)). In the XRD diffraction patterns, in addition to the existing BN diffraction peak, there was a small amount of B_2O_3 indicated when the molar ratio of borax to boric acid was 1 : 3, *i.e.* when the boric acid proportion was increased, as shown in Fig. 1(d) which showed that the ratio of boron source components had no effect on the phase composition when it was varied from 1 : 0 to 1 : 2. However, when the boron source composition ratio increased to 1 : 3 (*i.e.* when the relative boric acid content increased), the synthetic reaction of BN was incomplete and it remained a part of the B_2O_3 ; because the melting point of B_2O_3 was low (460 °C) [19], the excess of molten B_2O_3 formed a dense cover-layer on the surface of the template, thus hindering ammonia diffusion so that the boron source and nitrogen source could not come into contact which, in turn, ensured that some B_2O_3 remained. Other data show that boric acid was used in the synthesis of boron nitride fibers when boric acid was the only source of boron in most cases, and the synthesis temperature was high (usually over 1000 °C) [20]. The synthesis temperature used here was 675 °C and thus excessive amounts of boric acid were obtained which was not conducive to the production of high purity h-BN although it allowed the production of high purity hexagonal boron nitride when the boron source composition ratio was changed from 1 : 0 to 1 : 2.

Effect of boron source composition ratio on microstructure

The ratio of boron source components was studied with a view to examining its effect(s) on the micro-morphology in the same synthesis process (675 °C, 2 h). Fig. 2 shows SEM micrographs of the micro-morphology of h-BN at boron source component ratios of: 1 : 0, 1 : 0.5, 1 : 1, and 1 : 2.

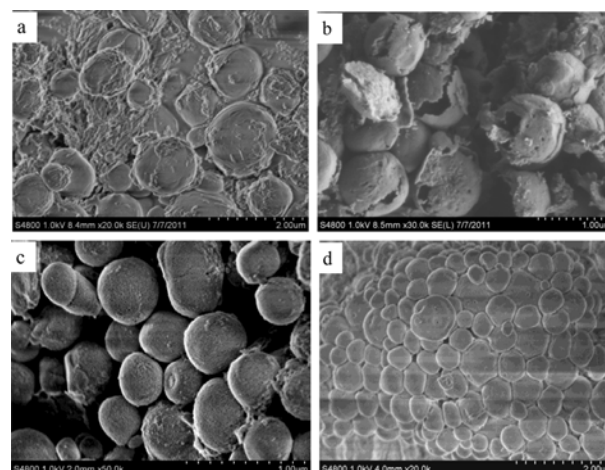


Fig. 2. The microstructure of h-BN powder under different ratio of boron source component 1:0; (b) 1:0.5; (c) 1:1; (d) 1:2.

Fig. 2 shows that when the boron source component ratio was 1 : 0, namely at a boric acid content of zero, spherical BN was formed in part of the region and laminar BN was formed elsewhere: some sheets were connected in bundles, and the rate of ball-formation was low, as shown in Fig. 2(a). The amount of spherical h-BN powder increased when the ratio of boron source components was 1 : 0.5, namely when little boric acid was added, the surface of the h-BN powder micro-morphology manifested small holes and most of the hollow balls were damaged. The ball diameter was between 700 and 1000 nm, as shown in Fig. 2(b). This was attributed to that fact that the hollow balls were damaged because the hollow balls had thinner walls, therefore reducing the stiffness of the resultant h-BN and rendering the spherical shells more susceptible to damage after the support from the template was removed by calcination. The microscopic structure of the BN powder was spherical, and the formation of globular components increased, meanwhile the ball surface had different size holes therein when the boron source component ratio was 1 : 1, (*i.e.* when the boric acid content was increased) as shown in Fig. 2(c). When the ratio of boron source components was 1 : 2, (*i.e.* when the boric acid content was further increased) h-BN powder had different sizes, irregular shapes, but was practically spherical, with a more compact surface as shown in Fig. 2(d).

In conclusion, boric acid was beneficial to the formation of spherical h-BN. The h-BN powder's micro-morphology would change along with changes in the boron source component ratio. With an increased boron source component ratio, the boric acid ratio and the quality ratio of the molten boron oxide were increased: this was advantageous to the motion of the solid borax or boron atoms, so the ball rate also increased. Under these experimental conditions, and with the composition ratio of the boron source ranging

from 1 : 0.5 to 1 : 2, high purity spherical hexagonal boron nitride could be obtained.

Effect of boron source composition ratio on hexagonal boron nitride microstructure

High purity spherical h-BN samples were analyzed after further amplification by TEM (Fig. 3). The structure of boron nitride was similar to the hollow spherical shell found when the boron source composition ratio was 1 : 0.5, as shown in Fig. 3(a). The boron nitride structure was akin to porous spheres with an aperture size of less than 50 nm when the boron source composition ratio was increased to 1 : 1. This showed that these spheres were mesoporous, and with the majority of their interiors unconnected to the outside world, (*i.e.* a closed porosity form, as shown in Fig. 3(b)). When the boron source composition ratio was increased to 1 : 2, the microcosmic structure of boron nitride was similar to a pyknotic solid sphere and there were no small pores, as shown in Fig. 3(c) and (d). Above all, with the increase of proportion of boric acid, the microcosmic structure of the boron nitride was respectively similar to a spherical shell, porous hollow spheres, and a pyknotic solid sphere. Because the quality of the boron oxide increased gradually when the amount of boric acid addition was increased, so excess molten boron oxide in the template surface would gradually penetrate to the interior of the template. The greater the amount of molten boron oxide, the greater the amount that penetrated to the interior of the template, to be converted into h-BN in the liquid ammonia atmosphere. Therefore, the amount of boron oxide in the template was insufficient when the boron source composition ratio was smaller (*i.e.* when the proportion of boric acid was reduced), and h-BN would then form a hollow spherical shell structure. With the increase of proportion of boric acid, mesoporous microspheres and dense solid spheres were

obtained in that order.

Effect of boron source composition ratio on adsorption performance

Fig. 4 showed adsorption-desorption isotherms under different boron source composition proportions. As seen in Fig. 4, when the relative pressure was lower ($P_0/P < 0.85$), the adsorption was higher when the boron source composition ratio was 1 : 0.5 than when that at a boron source composition ratio of 1 : 1. When the relative pressure was higher ($P_0/P < 0.85$), the previous result was reversed: the adsorption at a boron source composition ratio of 1 : 0.5 was lower than that at a boron source composition ratio of 1 : 1, as shown in Fig. 4(a) and (b). The highest adsorption capacity was 228.20 cm^3/g when the boron source composition ratio was 1 : 0.5, the highest adsorption capacity was 276.02 cm^3/g when the boron source composition ratio was 1 : 1. In the sample where the boron source composition ratio was 1 : 1, because mesoporous spheres, with some closed pores appeared in the interior thereof and were not connected to the outside world, these closed pores could not be opened when the relative pressure was lower, and therefore the adsorption was lower, as shown in Fig. 4(b). The sample had a hollow spherical shell structure when the ratio of boron source components was 1 : 0.5, and the stoma which connected a pore to the outside world occurred in relatively larger amounts, thus the adsorption was increased, as shown in Fig. 4(a). Some closed pores in the mesoporous spheres began to open and connect with the outside world when the relative pressure was higher, thus the adsorption capacity increased significantly. As seen in Fig. 4(c) and (d), when the boron source composition ratio was 2 : 1, since pyknotic solid spheres were formed and there were no small pores, the adsorption significantly decreased regardless of the relative pressure, as shown in Fig. 4(c).

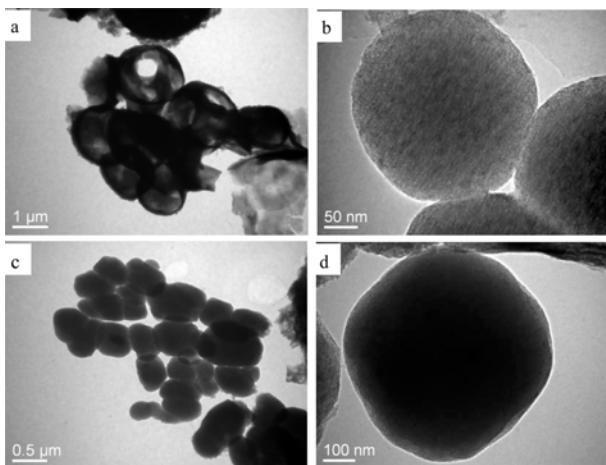


Fig. 3. The high purity spherical h-BN microstructure under different ratio of boron source component 1 : 0.5 (b) 1 : 1 (c) 1 : 2; (d) 1 : 2.

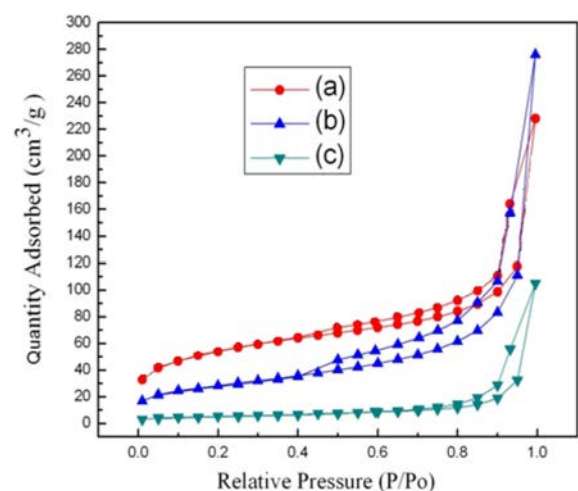


Fig. 4. The isothermal adsorption-stripping of h-BN powder under different ratio of boron source component The molar ratio of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and H_3BO_3 : (a) 1 : 0.5; (b) 1 : 1; (c) 1 : 2.

Conclusions

(1) The experiments could yield high purity hexagonal boron nitride when the boron source component proportions were respectively 1:0, 1:1, and 1:2. Phases were composed of h-BN and a small amount of B₂O₃ impurities when the boron source component proportion was 1:3.

(2) Boric acid was helpful when producing spherical h-BN, the h-BN micro-morphology was spherical when the boron source component ratio was between 1:0.5 and 1:2. The h-BN produced was similar to a hollow sphere structure when the boron source component proportions were 1:0.5. The h-BN produced was similar to a porous sphere structure when the boron source component proportions were 1:1. The h-BN had a solid sphere structure when the boron source component proportions were 1:2.

(3) Comparing boron source composition ratios 1:0.5 and 1:1, the former had a higher adsorption than the latter when the relative pressure P_0/P was less than 0.85. The latter had a higher adsorption than the former when P_0/P was greater than 0.9: the maximum adsorption capacity of the former could reach 276.02 cm³ g⁻¹, while the highest adsorption of the latter was 228.20 cm³ g⁻¹. When the boron source composition ratio was 1:2, the adsorption capacity was the lowest regardless of the relative pressure.

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