

# Synthesis and Application in the CO Oxidation Conversion Reaction of Hexagonal Boron Nitride with High Surface Area

Liangxu Lin,<sup>‡,§</sup> Zhaohui Li,<sup>¶</sup> Ying Zheng,<sup>‡,‡</sup> and Kemei Wei<sup>||</sup>

<sup>‡</sup>College of Chemistry & Materials Science, Fujian Normal University, Fuzhou 350007, China

<sup>§</sup>Zhejiang Zanyu Technology Co., Ltd, Hangzhou 310009, China

<sup>¶</sup>Research Institute of Photocatalysis, Fuzhou University, Fuzhou 350002, China

<sup>||</sup>National Engineering Research Center of Chemical Fertilizer Catalyst, Fuzhou University, Fuzhou 350002, China

Hexagonal boron nitride (h-BN) with high surface area has been synthesized via a simple method. Pt/h-BN catalyst has been prepared from the as-prepared h-BN for the CO conversion reaction. Experimental results indicate that the as-prepared h-BN particles have a surface area of 125 m<sup>2</sup>/g, a mesoporous volume of 0.29 cm<sup>3</sup>/g, and a pore diameter of 4.2 nm. The supported Pt/h-BN catalyst showed high catalytic performance on the CO conversion reaction.

## I. Introduction

RECENTLY, hexagonal boron nitride (h-BN) has received much attention due to its intriguing properties, such as high thermal conductivity, acid–base resistance, oxidation resistance, high-temperature stability, and so on.<sup>1</sup> These properties make BN a potential excellent material in advanced ceramic, catalyst and so on. In contrary to the traditional oxide supports for the catalyst, h-BN exhibits much advantage in the processes like ammonia synthesis,<sup>2</sup> combustion catalysis,<sup>3</sup> deep oxidation of volatile organic compounds (VOCs),<sup>4</sup> and propane oxidation,<sup>5</sup> etc. However, BN has less been used as supports for catalysts than traditional oxide materials, such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, etc., partly due to the difficulties in the syntheses of BN with high surface area.<sup>6</sup>

Many approaches have been developed to prepare BN with high surface area.<sup>7–11</sup> For example, ordered porous h-BN was obtained via the substitution reaction of porous template (SBA-15, CMK-3, activated carbon, etc.)<sup>7–9</sup> and h-BN with high surface area was reported to be prepared from special molecular precursors.<sup>10,11</sup> However, a complex control process is required in these reported methods. In the meantime, the impurity templates is difficult to be removed completely and effectively. The impurity, in most case, would play a negative effects on the activity of the catalyst.<sup>1</sup> In addition to these, the molecular precursors usually used are expensive and highly toxic materials. This also makes the synthetic method based on molecular precursor unattractive.<sup>7</sup>

Herein, a new method has been developed to synthesize h-BN powders with high surface area. This is a simple, efficient, and economical synthetic method. The application of the as-prepared BN in the CO conversion reaction was also studied in this communication.

## II. Experimental Procedures

4 (11 g) powder and NH<sub>4</sub>Cl solution (20 g dissolved in 150 mL of deionized water) were put in three-neck flask. Then, the flask was maintained at 120°C and regurgitate for 48 h. A white solid material was obtained after the water was distilled. This white solid material was washed with ice-cold deionized water for several times to obtain the precursor. After that, the dried precursor (1 g), NH<sub>4</sub>Cl (4 g), and KCl (4 g) were mixed and put in an Al<sub>2</sub>O<sub>3</sub> tube and react at 1000°C for 4 h under N<sub>2</sub> atmosphere. The resultant product obtained was washed with 40% aqueous HF and 10% NaOH solution to remove KCl, NH<sub>4</sub>Cl, and potential SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> to obtain the final product of h-BN.

To prepare BN based catalyst, the as-prepared BN was impregnated with a solution of H<sub>2</sub>PtCl<sub>6</sub> (Alfa Aesar, Tianjin, China) to yield a catalyst with 1 wt% metal loading. The impregnated powder was dried at 110°C overnight, then calcined at 500°C for 3 h (heating rate, 10°C/min) in a flowing synthetic air (30 mL/min). Finally, the calcined catalyst was reduced at 300°C for 1 h (heating rate, 10°C/min) in a flowing hydrogen (30 mL/min).

X-ray diffraction (XRD) pattern was carried out on a Philips X'Pert SUPER powder X-ray diffractometer (Philips Analytical Inc., Cambridge, UK) with CuK $\alpha$  radiation ( $\lambda = 1.5418$  Å). Infrared (IR) spectra was obtained using a Nicolet Model 759 (Nicolet Instrument Inc., Madison, WI) Fourier transform IR spectrometer by using pressed KBr disks. Scanning electron microscopy (SEM) was recorded on a FEI XL30 (FEI Company, Hillsboro, OR) scanning electron microscope. Transmission electron microscope (TEM) was operated on a Tecnai G2 F20 S-TWIN TEM (FEI Company) with an accelerating voltage of 200 KV. A Gatan-2000 (Gatan Inc., Pleasanton, CA) spectrometer (attached on TEM) with energy electron beam of 200 eV was used for parallel detection of electron energy-loss spectroscopy (EELS). N<sub>2</sub> adsorption isotherm of the sample was determined at –196°C using N<sub>2</sub> in a conventional volumetric technique by Quantachrome Nova 4200 (Quantachrome Instruments, Boynton Beach, FL). Preferential CO oxidation in H<sub>2</sub>-rich gas was carried out in a fixed-bed flow reaction system at atmospheric pressure using 100 mg of the catalyst (total flow rate = 900 mL · (min · g)<sup>–1</sup>. The feed stream contained 1% CO, 1% O<sub>2</sub>, and it was balanced with helium. The effluent gas was analyzed using an online gas chromatograph (GC) system equipped with a thermal conductivity detector.

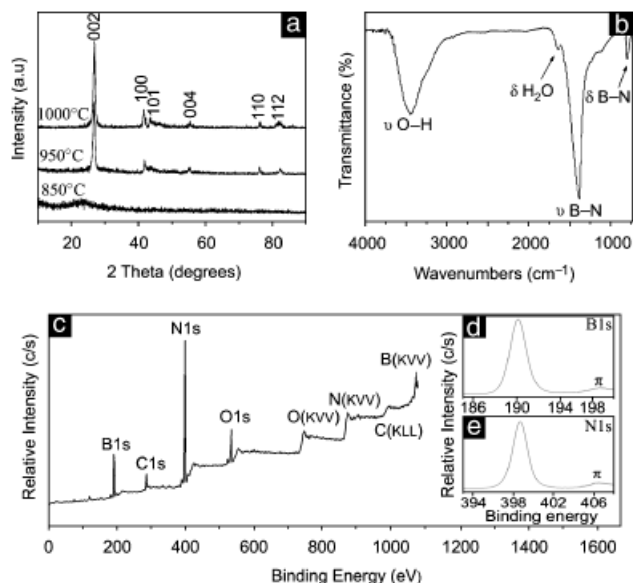
## III. Result and Discussion

The XRD pattern (Fig. 1(a)) shows peaks indexed to h-BN (JCPDS: 34-0421), and no other impure phase exists. The intense and sharp diffraction peaks indicates that the h-BN sample is well crystallized and implies that the reaction temperature (1000°C) is suitable for this reaction. The XRD of the product obtained at the synthetic temperature of 850°C shows no crys-

V. Domnich—contributing editor

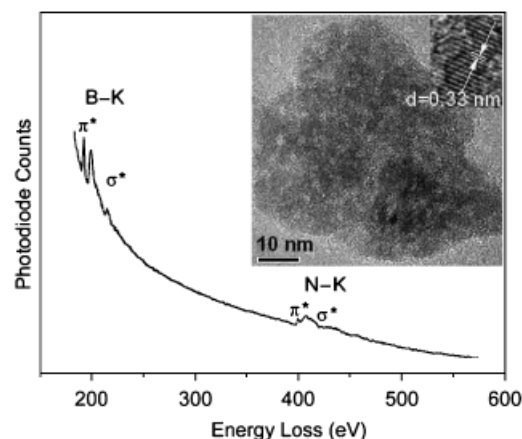
Manuscript No. 25199. Received September 16, 2008; approved December 23, 2008. This work was supported by National Natural Science Foundation of China (20576021), the Science Foundation of Fujian Province of China (E0710004).

<sup>†</sup>Author to whom correspondence should be addressed. e-mail: zhn63200@163.com



**Fig. 1.** (a) X-ray diffraction patterns of boron nitride (BN) samples; (b) infrared spectra of the as-prepared BN sample; (c)–(e) XPS spectra of the as-prepared BN sample.

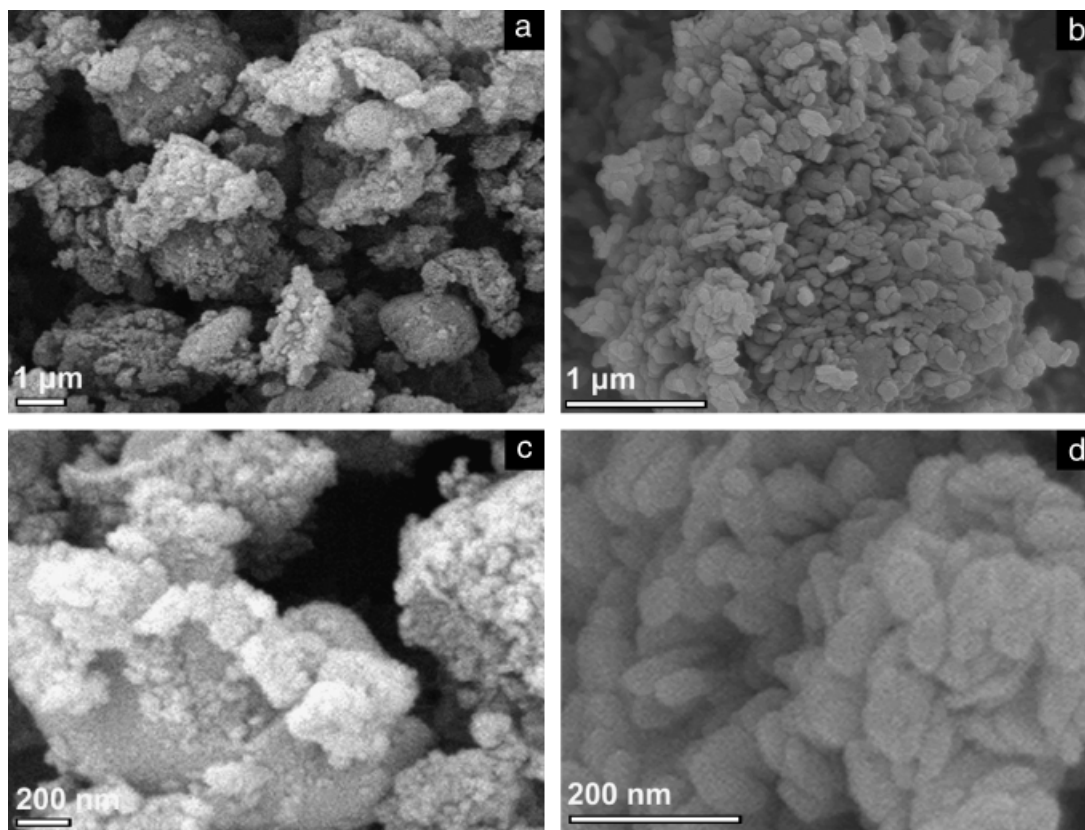
talline reflections. The (100) and (101) peaks in the XRD pattern of the product obtained at reaction temperature of 950°C is not well separated and indicates that well-crystallized h-BN could not be obtained at 950°C.<sup>12</sup> IR spectra (Fig. 1(b)) of the sample shows characteristic in-plane B–N stretching and out-of-plane B–N–B vibrations at about 1409 and 804  $\text{cm}^{-1}$ . The existence of boron, nitride in the sample is evident as shown in the full range survey XPS spectrum (Fig. 1(c)). The existence of O comes from



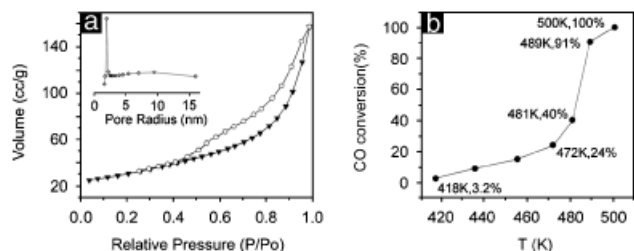
**Fig. 3.** Electron energy-loss spectroscopic spectra of as-prepared sample; (inset) corresponding transmission electron microscopic image of one boron nitride particle.

the surface oxidation. The high-resolution XPS spectra (Figs. 1(d) and (e)) show peaks at binding energy near 190.3 eV for B 1s and 398 eV for N 1s respectively.<sup>13</sup> Figures 1(d) and (e) also provided qualitative evidence for the presence of  $sp^2$  (h-BN) bonding through the identification  $\pi$  plasmon ( $\pi^*$ ) loss peaks at approximately 9 eV higher away from the B 1s and N 1s peaks.<sup>14</sup> The B/N atomic ratio calculated from XPS data is about 0.98:1, which agrees well with the stoichiometric composition of BN.

SEM images of the powder (Figs. 2(a) and (c)) indicate that the particles are loose in nature. They have coarse surface and are up to a diameter of micron scale. On the surface of these particles, some nanoparticles could be observed clearly (the TEM image of one of these nanoparticles is shown in Fig. 3). The coarse surface and the loose nature are both advantageous



**Fig. 2.** Scanning electron microscopic images of different boron nitride samples. (a, c) Synthesized with the presence of flux KCl; (b, d) synthesized without the presence of flux KCl.



**Fig. 4.** (a) Nitrogen adsorption/desorption isotherms of as-prepared boron nitride (BN) sample; (inset) pore size distributions of as-prepared BN sample; (b) reaction temperature dependence of CO conversion.

for the loading of metal particles and can improve the diffusion of the reactants and products in the catalytic reactions. It is proposed that the introduced flux KCl is responsible for the formation of the product with coarse surface and loose nature since in the absence of the flux KCl, only solid product with smooth surface can be obtained (Figs. 2(b) and (d)).

EELS spectra (Fig. 3) of one particle (Fig. 3 inset) shows two distinct absorption features at 189 and 404 eV, which correspond to the known K-edges onsets for boron and nitrogen, respectively.<sup>15</sup> The inset TEM image exhibits clear lattice fringes at 0.33 nm, in consistent with the interplanar distance of (002) crystallographic plane in h-BN.<sup>16</sup>

Nitrogen adsorption/desorption isotherm (Fig. 4(a)) of the as-prepared sample shows that the adsorption and desorption isotherms change abruptly when the relative pressure is in the range 0.42–0.91 and indicates that the BN powders have a mesoporous nature.<sup>17</sup> In addition to this, the isotherm still rises above the relative pressure of 0.9, indicating that the sample also has some macroporous structure.<sup>18</sup> The pore size of the sample calculated from desorption isotherm measurements based on the BJH (Barrett–Joyner–Halenda) method is center at 4.2 nm. The calculated BET (Brunauer–Emmett–Teller) surface area of the as-prepared sample is 125 m<sup>2</sup>/g and the mesoporous volume of 0.29 cm<sup>3</sup>/g.

Pt/h-BN catalyst was prepared and used in the CO conversion reaction. Figure 4(b) shows the dependence of CO conversion in the preferential CO oxidation in He-rich gas (1% CO+1% O<sub>2</sub>+98% He) over this Pt/h-BN catalyst. Results indicate that the oxidation quickly attained a conversion >90% at 210°C and a conversion ratio of near 100% at 227°C. This conversion temperature is much lower than the result reported on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts,<sup>19,20</sup> although we used lower Pt loadings and higher CO concentrations in our experiment.

#### IV. Conclusion

In summary, a simple, efficient and economical synthetic method was developed for synthesizing h-BN material with high surface area. Results indicate that the as-synthesized BN have a surface area of 125 m<sup>2</sup>/g, a mesoporous volume of 0.29 cm<sup>3</sup>/g, and a pore diameter of 4.2 nm. The as-prepared BN

powders are loose in nature and have coarse surface. Both features are advantageous for the loading of metal particles and can improve the diffusion of the reactants and the products during the catalytic reactions. Therefore, it is regarded as a promising catalyst support for various catalytic reactions. The Pt/h-BN catalyst based on the as-prepared BN powder shows high catalytic performance for the CO conversion reaction.

#### References

- <sup>1</sup>R. T. Paine and C. K. Narula, "Synthetic Routes to Boron Nitride," *Chem. Rev.*, **90** [1] 73–91 (1990).
- <sup>2</sup>C. J. H. Jacobsen, "Boron Nitride: A Novel Support for Ruthenium-Based Ammonia Synthesis Catalysts," *J. Catal.*, **200** [1] 1–3 (2001).
- <sup>3</sup>G. Postole, B. Bonnetot, A. Gervasini, C. Guimon, A. Auroux, N. I. Ionescu, and M. Caldararu, "Characterisation of BN-Supported Palladium Oxide Catalyst Used for Hydrocarbon Oxidation," *Appl. Catal. A—Gen.*, **316** [2] 250–8 (2007).
- <sup>4</sup>J. C. S. Wu, Z. A. Lin, J. W. Pan, and M. H. Rei, "A Novel Boron Nitride Supported Pt Catalyst for VOC Incineration," *Appl. Catal. A—Gen.*, **219** [1–2] 117–24 (2001).
- <sup>5</sup>S. H. Taylor and A. J. J. Pollard, "Silica and Boron Nitride Supported Molybdenum and Vanadium Oxide Catalysts for Propane Oxidation," *Catal. Today*, **81** [2] 179–88 (2003).
- <sup>6</sup>G. Postole, A. Gervasini, M. Caldararu, B. Bonnetot, and A. Auroux, "Is BN an Appropriate Support for Metal Oxide Catalysts?," *Appl. Catal. A—Gen.*, **325** [2] 227–36 (2007).
- <sup>7</sup>W. Q. Han, R. Brutchey, T. D. Tilley, and A. Zettl, "Activated Boron Nitride Derived from Activated Carbon," *Nanoletters*, **4** [1] 173–6 (2004).
- <sup>8</sup>A. Vinu, M. Terrones, D. Golberg, S. Hishita, K. Ariga, and T. Mori, "Synthesis of Mesoporous BN and BCN Exhibiting Large Surface Areas Via Templating Methods," *Chem. Mater.*, **17** [24] 5887–90 (2005).
- <sup>9</sup>P. Dibandjo, F. Chassagneux, L. Bois, C. Sigala, and P. Miele, "Comparison Between SBA-15 Silica and CMK-3 Carbon Nanocasting for Mesoporous Boron Nitride Synthesis," *J. Mater. Chem.*, **15** [19] 1917–23 (2005).
- <sup>10</sup>C. K. Narula, R. Schaeffer, and R. T. Paine, "Synthesis of Boron Nitride Ceramics from Poly(borazinylamine) Precursors," *J. Am. Chem. Soc.*, **109** [18] 5556–7 (1987).
- <sup>11</sup>I. P. Borovinskaya, V. A. Bunin, and A. G. Merzhanov, "Self-Propagating High-Temperature Synthesis of High-Porous Boron Nitride," *Mendelev Commun.*, **7** [2] 47–8 (1997).
- <sup>12</sup>J. Thomas Jr., N. E. Weston, and T. E. O'Connor, "Turbostratic Boron Nitride, Thermal Transformation to Ordered-Layer-Lattice Boron Nitride," *J. Am. Chem. Soc.*, **84** [24] 4619–22 (1963).
- <sup>13</sup>C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy*. Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, MN, 1979.
- <sup>14</sup>R. Trehan, Y. Lifshitz, and J. W. Rabalais, "Auger and X-Ray Electron Spectroscopy Studies of hBN, cBN, and N<sub>2</sub><sup>+</sup> Ion Irradiation of Boron and Boron Nitride," *J. Vac. Sci. Technol. A*, **8** [6] 4026–32 (1990).
- <sup>15</sup>C. Weissmantel, *Thin Films From Free Atoms and Particles*. Chapter 4, edited by K. J. Klabunde. Academic, New York, 1985.
- <sup>16</sup>R. S. Pease, "An X-Ray Study of Boron Nitride," *Acta Crystallogr.*, **5** [2] 356–61 (1952).
- <sup>17</sup>K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouqu  rol, and T. Siemieniewska, "Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity," *Pure Appl. Chem.*, **57** [4] 603–19 (1985).
- <sup>18</sup>S. J. Gregg and W. Sing, *Adsorption, Surface Area and Porosity*, p. 111. Academic, London, 1982.
- <sup>19</sup>H. L. Liu, L. Ma, S. B. Shao, Z. H. Li, A. Q. Wang, Y. Q. Huang, and T. Zhang, "Preferential CO Oxidation on Ce-Promoted Pt/ -Al<sub>2</sub>O<sub>3</sub> Catalysts under H<sub>2</sub>-Rich Atmosphere," *Chinese J. Catal.*, **28** [12] 1077–82 (2007).
- <sup>20</sup>F. C. Galisteo, R. Mariscal, M. L. Granados, M. D. Z. Poves, J. L. G. Fierro, V. Kr  ger, and R. L. Keiski, "Reactivation of Sulphated Pt/Al<sub>2</sub>O<sub>3</sub> Catalysts by Reductive Treatment in the Simultaneous Oxidation of CO and C<sub>3</sub>H<sub>6</sub>," *Appl. Catal. B—Environ.*, **72** [3–4] 272–81 (2007).