

## Turbostratic Boron Nitride Coated on High-Surface Area Metal Oxide Templates

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Boron nitride coatings on high-surface area  $\text{MgAl}_2\text{O}_4$  and  $\text{Al}_2\text{O}_3$  have been synthesized and characterized by transmission electron microscopy and by X-ray powder diffraction. The metal oxide templates were coated with boron nitride using a simple nitridation in a flow of ammonia starting from ammonium borate adsorbed on  $\text{MgAl}_2\text{O}_4$  or  $\gamma\text{-Al}_2\text{O}_3$ .

This procedure resulted in the formation of a turbostratic boron nitride film with a thickness of a few individual BN layers.

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### Introduction

The importance of boron nitride (BN) as a ceramic material, a lubricant, and for other industrial purposes is increasing. Whereas boron nitride in many respects is similar to carbon because of the isoelectronic relation, some important differences between the properties of the two materials remain. On one hand, boron nitride, like carbon, exists in several allotropic forms, including a diamond-like cubic structure and a graphite-like hexagonal layer structure. Even boron nitride nanotubes<sup>[1]</sup> and an intriguing boron nitride nanomesh<sup>[2]</sup> were recently reported. On the other hand, white hexagonal BN (occasionally referred to as “white graphite”) is a good insulator with a bandgap around ca. 5.3 eV,<sup>[3]</sup> whereas black graphite is a semimetallic conductor. Both materials are resistant towards most reagents, but boron nitride is slightly less so due to its more polarized bonds. However, boron nitride is superior to carbon when it comes to thermal stability, in air and also in hydrogen. This has led to numerous studies on the use of boron nitride as a non-oxide ceramic material.<sup>[4–6]</sup> Due to the excellent stability of boron nitride at high temperatures and under harsh chemical conditions it has found application as a support material for heterogeneous catalysts.<sup>[7–12]</sup> The growing interest in using boron nitride as a catalyst support material, in particular for reactions where carbon is not stable, has increased the need for simple ways of synthesizing high-surface area boron nitride – an undertaking

that normally involves considerable technical difficulties.<sup>[3,13]</sup> Very recently, the use of organic-inorganic block copolymers have been used to produce BN and BCN nanostructured ceramics with very high-surface areas.<sup>[14]</sup>

### Results and Discussion

Here we present a simple, versatile procedure for the formation of high-surface area turbostratic boron nitride by high-temperature nitridation of ammonium borate adsorbed on high-surface area  $\text{MgAl}_2\text{O}_4$  or  $\gamma\text{-Al}_2\text{O}_3$  with ammonia.

Previously, reports of BN thin films on different substrates have appeared in the literature.<sup>[3,7,15,16–19]</sup> Paine et al. showed that large  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{MgO}$  single crystals could be covered by BN thin films using pyrolysis of a solid polymer formed by cross-linking chloroborazenes with hexamethyldisilazane.<sup>[4,16]</sup> Also, the preparation of BN films on metallic surfaces obtained by thermal decomposition of borazine or related compounds have been reported.<sup>[17,18]</sup>

In the present work, BN was synthesized by impregnating high-surface area  $\text{MgAl}_2\text{O}_4$  and  $\text{Al}_2\text{O}_3$  with aqueous precursor solutions of ammonium borate, using readily available boric acid as the source of boron, followed by high temperature nitridation in a flow of ammonia.<sup>[15,20]</sup> One advantage of the present procedure is its simplicity and the fact that it can be easily modified to control the extent of BN coverage on the metal oxide.  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  was chosen as the templates because they are considered completely inactive in redox processes and both known as inert support materials from the literature.<sup>[21,22]</sup> Given the stability, a removal of the metal oxides has not been attempted here even though new interesting structures could be envis-

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aged. Other templating approaches to produce high-surface area BN have been reported recently. For instance, a soft-template approach involving surfactant assembly<sup>[23]</sup> and also a hard-template method involving the use of carbon as mesopore hard-template for making boron nitride and boron carbon nitride, BCN, using  $B_2O_3$  as precursor was reported.<sup>[19]</sup> These materials were prepared by reaction with  $N_2$  which require very high reaction temperatures (1500–1750 °C) due to the thermodynamic stability of  $N_2$ . By conducting the nitridation with ammonia the reaction temperature can be lowered.

The boron content of all the samples was determined by elemental analysis using Inductively Coupled Plasma (ICP) analysis. Prior to ICP analysis, the boron nitride coated samples were pretreated with aqua regia in a microwave oven leading to decomposition of boron nitride and its dissolution as boric acid. As shown in Table 1, the measured boron contents are in good agreement with those calculated. Table 1 also lists the surface areas measured at liquid-nitrogen temperature with a Micromeritics ASAP 2020, and calculated using the BET (Brunauer–Emmett–Teller) method.<sup>[24]</sup> As seen in Table 1, the BET surface areas of all the samples are moderate to high, though not as high as the parent metal oxide templates. The surface area of the boron nitride is very much dependent on the choice of metal oxide. By choosing a high-surface area metal oxide it will give a high-surface area boron nitride. Not surprisingly, a further decrease in the surface area is observed with successive BN coatings of the  $MgAl_2O_4$  sample. This can be interpreted as encapsulation of the individual metal oxide crystals into larger agglomerates giving an overall smaller surface area.

Figure 1 shows a representative high-resolution transmission electron microscopy (TEM) image of the prepared BN-coated  $MgAl_2O_4$ , impregnated once with the precursor solution. The images were obtained by means of a JEM 2000FX microscope operated at an accelerating voltage of 300 kV. For sample preparation, ground powders were dispersed in ethanol and deposited on a 300 mesh copper grid coated with a holey carbon film. Figure 1 shows  $MgAl_2O_4$  particles coated with a thin film of BN. The BN films, which coat and apparently fully encapsulate the metal oxide particles, have thicknesses between 0.5 and 3 nm. These films consist of 2 to 6 individual BN sheets. Judged from Figure 1, the thickness of a stack of 6 sheets is estimated to be ca. 1.8 nm resulting in an interlayer distance between the sheets of ca. 0.3 nm. This distance compares well with the

0.333 nm interlayer distance of bulk hexagonal BN.<sup>[3]</sup> The composition of the BN film was qualitatively confirmed by elemental analysis using energy-dispersive X-ray (EDX) analysis. TEM analyses of the samples with higher BN content, i.e. samples impregnated two or three times with precursor solution, showed BN coating of agglomerates of metal oxide particles already coated with BN (see electronic supporting information, Figure S1).

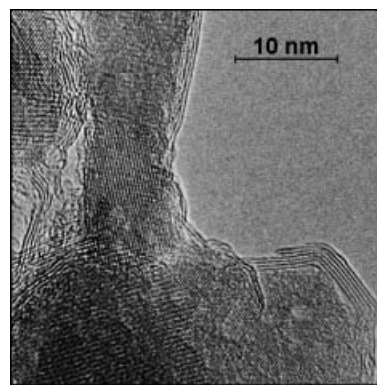


Figure 1. TEM image of BN on  $MgAl_2O_4$  impregnated once. A thin film of BN encapsulates the  $MgAl_2O_4$  particles. The film consists of 2–6 layers of BN.

Figure 2 shows a TEM image of BN-coated  $Al_2O_3$  obtained by impregnating once with the precursor solution.  $Al_2O_3$  is encapsulated by BN in a manner very similar to that of  $MgAl_2O_4$ , as 2–6 BN layers are formed. Multiple impregnations of  $Al_2O_3$  are expected to show a similar behaviour as those of  $MgAl_2O_4$ .

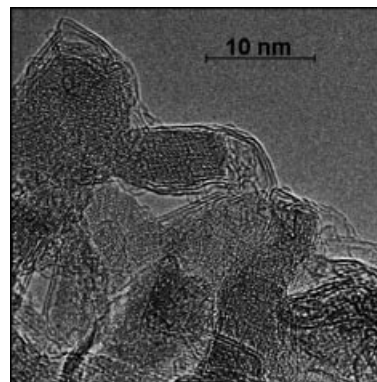


Figure 2. TEM image of BN on  $Al_2O_3$ . The  $Al_2O_3$  particles are coated with a thin BN film.

Table 1. Boron contents and BET surface areas.

| Support material | Number of impregnations | Boron content measured [wt.-%] | Boron content calculated [wt.-%] | BET Surface area [m <sup>2</sup> /g] |
|------------------|-------------------------|--------------------------------|----------------------------------|--------------------------------------|
| $MgAl_2O_4$      | 0                       | 0                              | 0                                | 72                                   |
| $MgAl_2O_4$      | 1                       | 4.67                           | 4.49                             | 39                                   |
| $MgAl_2O_4$      | 2                       | 7.77                           | 8.13                             | 27                                   |
| $MgAl_2O_4$      | 3                       | 10.70                          | 11.16                            | 14                                   |
| $Al_2O_3$        | 0                       | 0                              | 0                                | 228                                  |
| $Al_2O_3$        | 1                       | 4.30                           | 4.49                             | 175                                  |

X-ray powder diffraction (XRPD) patterns of all samples were recorded after nitridation. Figure 3 shows the XRPD patterns of the  $\text{MgAl}_2\text{O}_4$  sample coated (a) twice and (b) three times with BN; the remaining XRPD patterns are available as supplementary information (Figures S2–S3). In the XRPD patterns of BN-coated  $\text{MgAl}_2\text{O}_4$  and  $\text{Al}_2\text{O}_3$  samples that were impregnated once with precursor solution, only the parent metal oxide templates are observed, whereas the BN films are X-ray amorphous. This is because the BN film is too thin to give rise to any diffraction showing that all BN in the samples is present as film and that no bulk BN is present. However, when increasing the BN content by impregnating a second or third time, the BN phase appears as broad diffraction peaks at  $2\theta$  ca.  $26^\circ$  and  $43^\circ$  in the diffraction pattern of BN-coated  $\text{MgAl}_2\text{O}_4$ . These diffraction maxima can be assigned to a boron nitride phase which has previously been described in the literature as turbostratic BN.<sup>[25]</sup> Turbostratic materials are characterized by having a structure of roughly parallel layers, these layers, however, showing random rotation and translation about the layer normal.<sup>[26]</sup> In an X-ray diffraction pattern, turbostratic BN can be indexed on the basis of the diffraction maxima of well-defined hexagonal BN, although some reflections of hexagonal BN alter their shape and other reflections are missing. The most characteristic changes caused by the layer disorder in turbostratic relative to hexagonal BN are seen in a broadening of the (002) reflection at  $2\theta = 26.4^\circ$ , the appearance of a two-dimensional (10) reflection at  $2\theta = 42.4^\circ$  merged from the (100) and (101) reflections and the disappearance of higher indexed reflections (102), (004) and (103) above  $2\theta = 45^\circ$ .<sup>[25]</sup> These features, although partially covered by the diffraction maxima of the spinel phase, are most clearly visible in the diffraction pattern shown in Figure 3, (b).

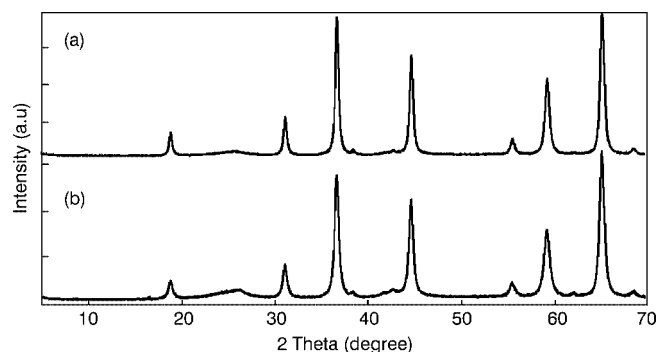


Figure 3. XRPD patterns of the BN samples coated (a) twice and (b) three times on  $\text{MgAl}_2\text{O}_4$ . The turbostratic BN phase appears at  $2\theta$  ca.  $26^\circ$  and  $43^\circ$ .

Both diffraction maxima of turbostratic boron nitride can be used for the calculation of the particle size, although different information is obtained from the three-dimensional (002) reflection and the two-dimensional (10) reflection. The (002) reflection renders information about the crystallite size along the  $c$  axis, i.e. the thickness  $L_c$  of the crystallite. From the (002) reflections in Figure 3, (a) and (b),  $L_c$  parameters of 2.5 and 2.2 nm, respectively, can be

determined. The interlayer spacings  $d_{(002)}$ , obtained from the exact position of the (002) peak maxima, are 0.344 nm in Figure 3, (a) and 0.339 nm in Figure 3, (b). This means that the BN film is, on average, 7 individual layers of BN thick confirming the impression from the TEM image shown in Figure S1. The slightly higher value for the  $d$  spacing in samples containing turbostratic BN compared to well-ordered hexagonal BN is consistent with the layer disorder in these samples, and several subpolymorphs of turbostratic BN have been discussed in the literature.<sup>[27]</sup> On the other hand, the two-dimensional (10) reflection can be used to calculate the width of the crystallite layer. However, in the diffraction patterns of the BN-coated  $\text{MgAl}_2\text{O}_4$  samples, the (10) reflection at  $2\theta$  ca.  $43^\circ$  is partially covered by the (400) reflection of spinel, preventing an unambiguous determination of the line width of the (10) reflection.

The presence of a turbostratic boron nitride phase implies the presence of boron oxynitride ( $\text{BN}_x\text{O}_y$ ) and amorphous boric oxide zones interconnecting the peripheries of the hexagonal planar boron nitride networks.<sup>[27–29]</sup> On the other hand, no indication for the presence of crystalline boric oxide with diffraction peaks at  $2\theta = 13.58^\circ$  and  $27.98^\circ$  is seen in the diffraction patterns shown in Figure 3. A removal of the oxygen impurities, coinciding with the growth and ordering of the BN layers to form crystalline BN, requires temperatures above  $1350^\circ\text{C}$ .<sup>[29,30]</sup>

The diffraction pattern of BN coated on alumina (Figure S3) shows a mixture of two alumina phases,  $\gamma$ -alumina and  $\theta$ -alumina, the latter being obtained by thermal degradation of  $\gamma$ -alumina at temperatures above  $800^\circ\text{C}$ . Remarkably, no indication was found in the diffraction pattern for the formation of the thermodynamically stable  $\alpha$ -alumina during the nitridation process, despite the thermal treatment of the coated material at  $1100^\circ\text{C}$  for 24 h.

## Conclusions

In summary, composite materials of turbostratic boron nitride coated in various concentrations on high-surface area metal oxides,  $\text{MgAl}_2\text{O}_4$  and  $\text{Al}_2\text{O}_3$ , were prepared by nitridation of ammonium borate with ammonia. This provides a simple way for the synthesis of high-surface area BN which could be an ideal support material for many heterogeneous catalytic applications.

## Experimental Section

In a typical synthesis of BN, a precursor solution was prepared by suspending  $\text{H}_3\text{BO}_3$  (5.72 g, containing 1 g of boron) in  $\text{H}_2\text{O}$  (7 mL) whilst stirring, followed by addition of aqueous  $\text{NH}_3$  (3 mL, 24 wt.-%) resulting in a clear solution. Aqueous  $\text{NH}_3$  was used to raise the solubility of  $\text{H}_3\text{BO}_3$ . The BN precursor solution (0.5 mL) was impregnated once onto high-surface area powders of  $\text{MgAl}_2\text{O}_4$  or  $\gamma\text{-Al}_2\text{O}_3$  (1 g) to incipient wetness, giving boron loads of ca. 4.5 wt.-% in each of the final samples after the formation of boron nitride. Prior to nitridation, all samples were dried for at least 30 min at  $100^\circ\text{C}$ . Nitridation was performed by passing a gentle flow of ammonia over the samples at  $1100^\circ\text{C}$  for 24 h. Attempts

to lower the reaction temperature for nitridation resulted in incomplete BN coverage of the metal oxide particles. In order to increase the amount of boron nitride, samples obtained by first impregnation were dried for 30 min at 100 °C and then impregnated a second and third time.

**Supporting Information** (see also the footnote on the first page of this article): Figure S1 shows a TEM image of BN on  $\text{MgAl}_2\text{O}_4$  impregnated three times (boron content ca. 11 wt.-%). Figure S2 and S3 show XRPD patterns of BN coated on  $\text{MgAl}_2\text{O}_4$  and  $\text{Al}_2\text{O}_3$  impregnated once.

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- [1] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, A. Zettl, *Science* **1995**, 269, 966–967.
- [2] M. Corso, W. Auwärter, M. Muntwiler, A. Tamai, T. Greber, J. Osterwalder, *Science* **2004**, 303, 217–220.
- [3] R. T. Paine, C. K. Narula, *Chem. Rev.* **1990**, 90, 73–91.
- [4] C. K. Narula, R. Schaeffer, R. T. Paine, *J. Am. Chem. Soc.* **1987**, 109, 5556–5557.
- [5] R. W. Rice, C. V. Matt, W. J. McDonough, K. McKinney, C. C. Wu, *Ceram. Eng. Sci. Proc.* **1982**, 3, 698.
- [6] S. D. Peteves, *Ceram. Int.* **1996**, 22, 527–533.
- [7] T. W. Hansen, J. B. Wagner, P. L. Hansen, S. Dahl, H. Topsøe, C. J. H. Jacobsen, *Science* **2001**, 294, 1508–1510.
- [8] J. C. S. Wu, W.-C. Chen, *Appl. Catal. A* **2005**, 289, 179–185.
- [9] G. Postole, M. Caldararu, N. I. Ionescu, B. Bonnetot, A. Auroux, C. Guimon, *Thermochim. Acta* **2005**, 434, 150–157.
- [10] C. J. H. Jacobsen, *J. Catal.* **2001**, 200, 1–3.
- [11] G. Postole, A. Gervasini, C. Guimon, A. Auroux, B. Bonnetot, *J. Phys. Chem. B* **2006**, 110, 12572–12580.
- [12] G. Postole, B. Bonnetot, A. Gervasini, C. Guimon, A. Auroux, N. I. Ionescu, M. Caldararu, *Appl. Catal.* **2007**, 316, 250–258.
- [13] J. A. Perdigon-Melon, A. Auroux, D. Cornu, P. Miele, B. Toury, B. Bonnetot, *J. Organomet. Chem.* **2002**, 657, 98–106.
- [14] P. R. L. Malenfant, J. Wan, S. T. Taylor, M. Manoharan, *Nature* **2007**, 2, 43–46.
- [15] S. E. Nielsen, C. J. H. Jacobsen, H. Udesen, T. Shim and N. K. Sørensen, *U. S. Patent*, 7 025 944.
- [16] R. T. Paine, C. K. Narula, R. Schaeffer, A. K. Datye, *Chem. Mater.* **1989**, 1, 486–489.
- [17] M. Corso, T. Greber, J. Osterwalder, *Surf. Sci.* **2005**, 577, L78–L84.
- [18] F. Müller, K. Stöwe, H. Sachdev, *Chem. Mater.* **2005**, 17, 3464–3467.
- [19] A. Vinu, M. Terrones, D. Golberg, S. Hishita, K. Ariga, T. Mori, *Chem. Mater.* **2005**, 17, 5887–5890.
- [20] A. Meller, *Gmelin Handbuch der Anorganischen Chemie, Borverbindungen*; Springer-Verlag: Berlin, **1974**, vol. 1, p. 1.
- [21] M. Trueba, S. P. Trasatti, *Eur. J. Inorg. Chem.* **2005**, 3393–3403.
- [22] C. H. Christensen, B. Jørgensen, J. Rass-Hansen, K. Egeblad, R. Madsen, S. K. Klitgaard, S. M. Hansen, M. R. Hansen, H. C. Andersen, A. Riisager, *Angew. Chem. Int. Ed.* **2006**, 45, 4648–4651.
- [23] P. Dibandjo, L. Bois, F. Chassagneux, P. Miele, *J. Eur. Ceram. Soc.* **2007**, 27, 313–317.
- [24] S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **1938**, 60, 309–319.
- [25] J. Thomas Jr, N. E. Weston, T. E. O'Connor, *J. Am. Chem. Soc.* **1963**, 84, 4619–4622.
- [26] J. Biscoe, B. E. Warren, *J. Appl. Phys.* **1942**, 13, 364–371.
- [27] M. Hubáček, T. Sato, T. Ishii, *J. Solid State Chem.* **1994**, 109, 384–390.
- [28] T. Masui, H. Hirai, R. Hamada, N. Imanaka, G. Adachi, T. Sakata, H. Mori, *J. Mater. Chem.* **2003**, 13, 622–627.
- [29] M. Hubáček, M. Ueki, T. Sato, V. Brožek, *Thermochim. Acta* **1996**, 282/283, 359–367.
- [30] Brožek, M. Hubáček, *J. Solid State Chem.* **1992**, 100, 120–129.

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