ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 177 (2004) 609–615

JOURNAL OF SOLID STATE CHEMISTRY

http://elsevier.com/locate/jssc

Micrometric BN powders used as catalyst support: influence of the precursor on the properties of the BN ceramic

José Antonio Perdigon-Melon,[a] Aline Auroux,[a] Claude Guimon,[b] and Bernard Bonnetot[c,*]

[a] *Institut de Recherches sur la Catalyse, UPR CNRS 5401, 2, Av A Einstein, 69626 Villeurbanne cedex, France*
[b] *LPCM,UMR CNRS 5624, 2 av. du Président Angot, F-64053 Pau cedex 9, France*
[c] *Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, bat Berthollet UCB Lyon I, 69622 Villeurbanne Cedex, France*

Received 2 October 2002; accepted 26 May 2003

Abstract

Thin powders and foams of boron nitride have been prepared from molecular precursors for use as noble metal supports in the catalytic conversion of methane. Different precursors originating from borazines have been tested. The best results were obtained using a precursor derived from trichloroborazine (TCB) which, after reacting with ammonia at room temperature and then thermolyzing up to 1800°C, led to BN powders with a specific area of more than $300\,m^2\,g^{-1}$ and a micrometric spherical texture. Comparable results were obtained using polyborazylene under similar conditions. Aminoborazine-derived precursors did not yield such high specific area ceramics but the BN microstructure resembled a foam with a crystallized skin and amorphous internal part. These differences were related to the chemical mechanism of the conversion of the precursor into BN. Polyhaloborazines and polyborazines yielded BN through gas–solid reactions whereas aminoborazine polymers could be kept waxy up to high temperatures, which favored the glassy foam. Catalysts composed of BN support and platinum have been prepared using two routes: from a mixture of precursor or by impregnation of a BN powder leading to very different catalysts.

Keywords: Boron nitride; Molecular precursors; Powder; Alkane oxidation; Platinum

1. Introduction

The reduction of the volatile organic compound (VOC) emissions using catalytic combustion, actually a major problem, is usually solved through an oxidation using supported noble metals like palladium or platinum. This reaction is highly energetic and the catalyst support, generally alumina or zirconia, has to bear major thermal constraints [1]. Recently, taking into account the poor properties of the oxide supports [2], research has focused on new catalysts bearing active noble metals, but with adapted supports such as activated carbon [3], carbides [4] or nitrides [5]. Boron nitride could be a good candidate because its specific properties could have potential applications in many industrial fields [6,7]. BN, under its hexagonal structure, resembles graphite and its thermal properties and chemical inertia are very promising for applications involving its use under hard conditions. Bulk BN is prepared by high-temperature reactions of inexpensive materials [8] but the powders obtained using these syntheses are not suitable for high surface area support. Unlike the carbon whose charcoal powder is stable to moisture, turbostratic BN is very easily hydrolyzed. High surface area BN substrates have been prepared from aerogels following a method described in the literature [9,10]. Recently, finely ground BN powder has been used as support for noble metal catalysts and has given better results than traditional metal oxide supports [11].

In the present work, porous boron nitride samples have been prepared from different molecular precursors. The nature and treatment of precursors have been investigated in order to determine accurately the optimal conditions leading to high surface porous boron nitride materials suitable for use as catalyst supports. The best results led to BN powders presenting surface areas of more than $300\,m^2\,g^{-1}$. To obtain catalysts two preparations have been tested: a one-step synthesis from a precursor containing BN and platinum precursors and a

---

[*] Corresponding author. Fax: 33-4-72-44-06-18.
E-mail address: bernard.bonnetot@univ-lyon1.fr (B. Bonnetot).

0022-4596/$ - see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2003.05.007

sol–gel impregnation of a BN powder prepared previously. The two syntheses led to very different physical properties of the samples.

2. Experimental

2.1. General procedure and products

2.1.1. Starting materials

All experiments were performed under an atmosphere of pure argon using a standard vacuum-line, Schlenk techniques and an efficient dry box with solvents purified using standard methods [12]. The starting materials for the synthesis of polyborazylene, $(NH_4)_2CO_3$ and $NaBH_4$ (Aldrich powder grade 99%) were used as received. The trichloroborazine (TCB) was prepared from BCl_3 (stainless steel bottle Alphagaz, 99.9%) and NH_4Cl (Aldrich, ACS reagent 99.5%). Ammonium chloride was dried under vacuum at 100°C for 12 h before the synthesis. Methylamine (Fluka, 97%), required for the synthesis of trimethylaminoborazine, was used as supplied without further purification. For platinum impregnation, Pt(II) acetylacetonate (Strem, 98%) was used with no further treatment. Ammonium hydroxide used for the sol–gel method was a 28–30% NH_3 solution in water (Aldrich, ACS reagent).

2.1.2. Characterization

^{11}B, ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 300, respectively, at 96.26 MHz (external reference Et_2OBF_3 nondecoupled, with positive values downfield), 300 MHz (reference TMS) and 75 MHz (reference TMS, total decoupling). The chemical shifts were expressed in ppm. The IR spectra were recorded on an FTIR Nicolet Magna 550 spectrophotometer in KBr pellets. The ceramic yields were determined using a TGA B70 apparatus. DSC analyses were run on a TA 8000 Mettler-Toledo under argon atmosphere. SEM images were obtained from a Jeol 55 CF (CMEABG Lyon) and TEM pictures were recorded using a Jeol 2010 (IRC Lyon). X-ray powder diffraction (XRD) patterns were obtained with Cu$K\alpha$ radiation using a Philips PW 3710/3020 diffractometer equipped with a monochromator. The BET surface areas were measured using nitrogen at 77 K. All the samples were outgassed at 673 K for 4 h prior to the absorption measurements. The XPS analysis were performed with an SSI (Surface Science Instruments) 301 spectrophotometer using a monochromatic Al $K\alpha$ Al radiation.

2.2. Synthesis and characterization of precursors

Boron nitride preparations start usually from borazinic $(BN)_3$ precursors [6,7]. Among these compounds, three types of precursors have been studied according to the starting borazine.

2.2.1. Precursor I

P I was prepared from trichloroborazine (TCB) and contained 15–20% weight TCB linear polymers. TCB and its polymers were known to yield BN through high-temperature reactions [14]. TCB was prepared using the standard method [13] and was recovered with an 80% yield. The elemental analysis clearly showed the presence of polymers by lowering of the chlorine percentage: theoretical for $Cl_3B_3N_3H_3$ (M_W 183.83): B, 17.63; H, 1.63; N, 22.83; Cl, 57.91; experimental: B, 19.6; H, 1.6; N, 27.4; Cl, 51.2.

2.2.2. Precursor II

P II was a polyborazylenic polymer obtained from thermolysis of ammonia-borane NH_3BH_3. It is a mixture of stacked borazine cycles bounded by linear –BH_2–NH_2– chains and its conversion into BN has been widely studied. P II was prepared using the classical method of pyrolysis from NH_3BH_3 in glyme [15]. The borazine was not distilled but rather polymerized in situ, directly yielding a polymer [15,16]. The presence of organic moieties in the polymer was confirmed by the elemental analysis (in wt%): B = 23.0; N = 45.8; H = 7.1; C = 18.0; the oxygen content could not be measured in the presence of boron and was calculated to be about 6 wt%.

2.2.3. Precursor III

P III was obtained from trialkylaminoborazine $(RNH[BNH])_3$. Several alkyl groups and crosslinking advancements have been tested in a previous work [17] and more convenient results were obtained from a low crosslinked polymer where the alkyl was methyl groups. Trimethylaminoborazine (MAB) was prepared by reaction between trichloroborazine and methylamine [18]. To obtain P III, MAB underwent a thermal crosslinking under an argon stream. The polymerization of MAB evolved methylamine; each methylamine molecule evolved corresponded to an intercycle bonding. The polymerization was carried out following the standard process described [19]. For P III, the ratio of the quantity of amine evolved versus the amount of monomer was 0.5, which led to a polymer with glass transition $T_g = 85.5$°C and a ceramic yield of 55% at 1000°C. The elemental analysis was (in wt%): B = 23.5; N = 47.8; H = 7.2; C = 18.8; oxygen could not be measured in the presence of boron but amounted to less than 3%. P III was a glassy compound and could be melted, so it has been used to obtain thin and long BN ceramic fibers [20]. The starting molecules used for the synthesis of the precursors are given in Fig. 1.

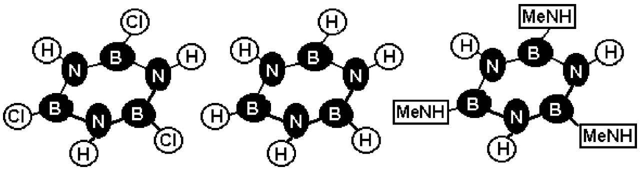

Fig. 1. Starting molecules for the synthesis of the precursors. P I: trichloroborazine, P II: borazine and P III: trimethylaminoborazine.

2.2.4. *Preparation of platinum catalysts supported by high specific surface BN*

From mix precursors containing BN and noble metal precursors: One of the aims of this work was to prepare directly noble metals supported on BN powder in a one-step synthesis. P I seemed to be the most promising, as reported in the Results section. Consequently, a synthesis has been performed by reaction between P I and an organic platinum precursor. The required quantity of platinum acetylacetonate was dissolved in ethylacetate and the corresponding quantity of P I was added. The solution was refluxed for 12 h and the solvent removed. Acetylacetone was displaced by the precursor, and a solid precursor containing platinum was recovered. This mixture was treated following the ceramization conditions of P I.

Using sol–gel impregnation: To an isopropanol suspension of high surface BN prepared from P I (150 mL of isopropanol per gram of BN powder), the necessary quantity of acetylacetonate of platinum was added. The ligand was displaced using a concentrated ammonium hydroxide (5 mL per gram of BN powder). The solvent was removed after 12 h of reaction under reflux. After drying under low pressure, the catalyst was activated at 400°C for 2 h under a hydrogen flow.

2.3. *Conversion of the precursors into boron nitride*

The conversion of the molecular precursors into boron nitride required ceramization under an ammonia flow. Ammonia was used as a reductive atmosphere, and its ability to replace halo or amino groups on the borazine framework was well known [20,21]. Ammonia was also a curing reagent in the borazine polymerization [16]. So, for the preparation of BN from molecular precursors, it was usual to perform a low temperature ceramization, up to 600°C at least, under an ammonia flow. The conversion of each precursor into BN has been studied using TGA up to 1000°C in order to optimize the ceramization conditions and the properties of the obtained ceramic. The measurements were realized in a pure ammonia flow up to 650°C and then under nitrogen. The three tested compounds exhibited original behaviors related to their formulation and their reactivity towards ammonia. Taking into account the TGA analysis, a standard procedure was established to treat the precursors.

High surface BN powders are known to be very reactive, like thin films [22], so a high-temperature stabilization of the powders was carried out up to 1800°C (heating rate 600°C h^{-1} under nitrogen atmosphere). This treatment decreases the porosity [10], but the utilization of BN under the experimental conditions for catalytic applications requires a very stable support.

3. Results and discussion

3.1. *Conversion of precursor into BN*

3.1.1. *Ceramization of the precursor P I*

The conversion of TCB into BN was well known [14], but the reaction leading to high area BN through a reaction direct with ammonia had to be investigated. When TCB was heated under an ammonia flow, the melting of this compound at 88°C lowered the reaction of the gas phase. The conversion of solid P I into boron nitride under an ammonia flow is given in Fig. 2. To avoid the melting of TCB, the reaction with ammonia was performed at room temperature on a finely ground precursor. The first step of the reaction was the addition of ammonia to the precursor. This reaction was rapid at the beginning, but like all gas/solid reactions it was slowed down by kinetic considerations. The reaction was run for more than 15 h in order to reach the limit of the addition, which occurred when 6 molecules of ammonia were added to one of TCB. This corresponds to 2 NH_3 for each BCl group of the precursor. When the addition was completed, the temperature was raised. Very little of the fixed ammonia was lost when heating up to 350°C. The reaction of ammonia with TCB led to a very stable complex. At 400°C, a white compound, which was characterized as NH_4Cl, was deposited on the silica tube of the TGA apparatus. Then, the weight loss slowed down to a value very close to the theoretical ceramic yield of TCB of 40%. This reaction of the ceramization is given in

$$\begin{aligned}&Cl_3B_3N_3H_{3\text{solid}} + 6NH_{3\text{gas}} \rightarrow [(NH_3)_2ClBNH]_{3\text{solid}}\\&\rightarrow 3NH_4Cl_{\text{gas}} + 3NH_3 + 3BN_{\text{solid}}.\end{aligned} \tag{1}$$

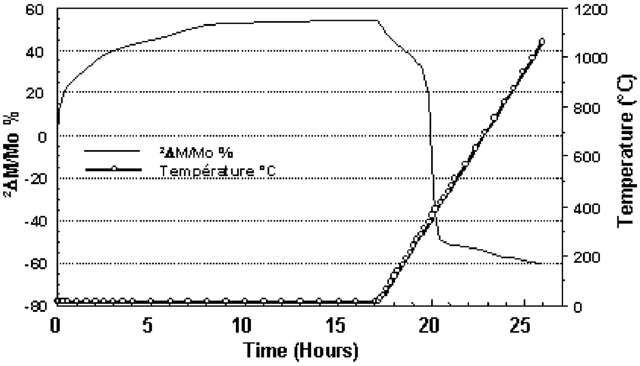

Fig. 2. TGA evolution during the reaction of P I with ammonia.

The fixation of ammonia on TCB was accompanied by a severe dilatation of the solid. This reaction involved only solids or gas and led to a white pre-ceramic BN. The i.r. spectrum of this powder showed beside the BN bands 1385 and 795 cm^{-1} a broad band at 3400 cm^{-1} characteristic of the remaining NH groups. This pre-ceramic was very air sensitive and was required to be kept under an inert atmosphere.

3.1.2. Ceramization of precursors P II and P III

The behavior of precursors P II and P III was tested under ammonia under the same experimental conditions as those used for precursor P I. No significant reaction took place at room temperature, and Fig. 3 shows the results of a ceramization. For both precursors, the reaction was very slow up to 100°C. For precursor P II, the reaction with ammonia became very significant in the range of temperature from 200 to 300°C. The total weight loss for precursor P II was more important than expected (the boron content of the polymer was consistent with a ceramic yield of 52%, while the weight loss reached 55%). This could be explained by a stripping off of volatile borazine from the precursor [23]. P III ceramization is consistent with the published results [20,21]. The role of ammonia in the stripping of the amino moieties is essential and up to 1000°C, NH_2 groups remained bonded to the cycles of the turbostratic BN which was also very air sensitive. The following equation summarizes the different reactions of the ceramization of P III:

$$
\begin{aligned}
&((NMe)_3[BNH]_3)_{n\text{solid}} + 3nNH_{3\text{gas}} \\
&\quad \rightarrow (NH_2)_3[BNH]_3)_{n\text{solid}} + 3nMeNH_{2\text{gas}} \\
&\quad \rightarrow 3nNH_{3\text{gas}} + 3nBN_{\text{solid}} \qquad (2)
\end{aligned}
$$

The chosen experimental steps for the conversion of the polymers into BN were:

Precursor P I was reacted for 48 h at room temperature with ammonia in a graphite crucible. Then the temperature was raised up to 1100°C with a heating rate of 100° C h^{-1}. The ceramization was performed up to 650°C under pure ammonia and then under nitrogen. For the precursors P II and P III, the room temperature treatment was omitted.

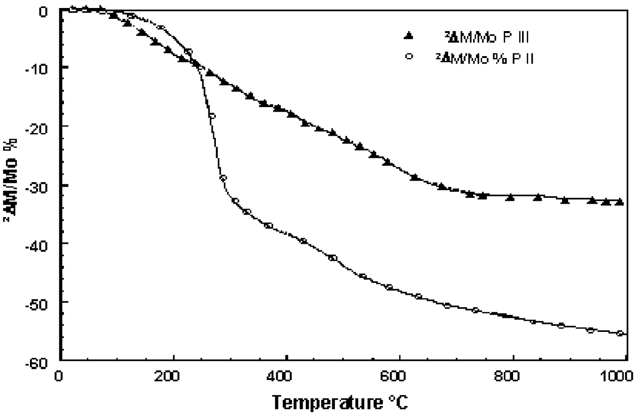

Fig. 3. Ceramization of precursors P II (curve with circles) and P III.

3.2. Characterization of the BN powders obtained

The three precursors led to the formation of porous powders or foams. The XPS measurements performed on the three samples were not significantly different. Photoelectron peaks from B_{1s}, N_{1s}, O_{1s} and C_{1s} were clearly recognized in the spectra of the three samples. Fig. 4 shows the XPS spectrum from a sample obtained from P I. The results of the deconvolution procedure showed the presence of only one possible boron chemical state centered at 190.5 eV. No B–C or B–O bonds were present. For nitrogen, the photopeak at 398.2 eV was also simple and no BN_xO_y was characterized. The presence of carbon and oxygen was related to superficial contamination. The average sample composition calculated in wt% was B: 46.3; N: 50.7; C: 1.3; O: 1.7 (Theoretical B: 43.6; N: 56.4). This composition revealed a nitrogen deficiency which was common when the composition of boron nitride was performed by XPS because the high temperatures reached during the analysis favor the evolution of gaseous nitrogen [25].

The specific areas of the samples obtained from P III were always smaller than for the samples obtained from P I or P II. The crystallization of the BN was very low although a very high temperature had been used. This was related to the important specific area which hindered the growth of the crystallites.

The crystallization of the samples was characterized by the determination of L_c, length along the c-axis, and L_a, length along the a-axis, of the graphite-like BN crystallites [24] (Table 1). Several experiments have been performed using each precursor, and the results given here are the most representative. The error on the specific area was given by the measurement apparatus. The specific areas obtained were very different depending on the precursor formulation. It turned out to be impossible to obtain specific areas of more than

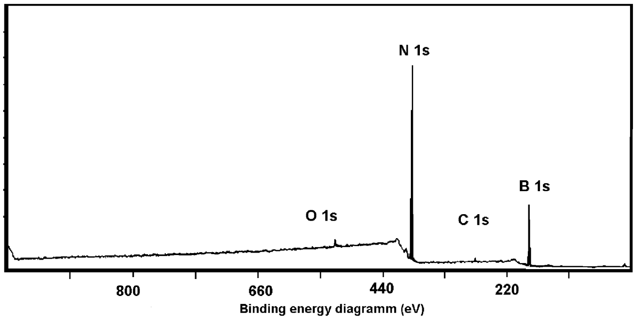

Fig. 4. XPS (0–1100 eV) spectrum of the sample obtained from P I.

Table 1
Characteristics of the obtained powders

Precursor	Crystallite size L_c (nm)	L_a (nm)	Specific area ($m^2 g^{-1}$)
P I	1.6	5.4	310.2 ± 7
P II	1.8	7.2	482.7 ± 17
P III	1.6	4.5	58.7 ± 3

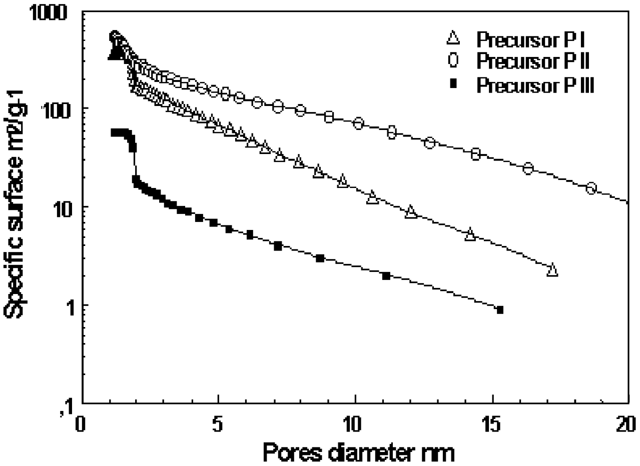

Fig. 5. Specific area of the samples as a function of pore diameter.

$100\,m^2\,g^{-1}$ using precursor P III. The specific surfaces of the samples obtained from the three different precursors as a function of the diameter of the pores are reported in Fig. 5.

Although the surfaces were very different, the pore distribution (measured using the BET technique) seemed to be comparable, no special enhancement of pore size could be characterized. Two types of pores were present: large mesopores from 2 to 20 nm and a microporosity with pores smaller than 2 nm enhancing the surface. The microporosity of the sample obtained from precursor P II was more important than for the other samples, and the pores seemed to be a little smaller, down to 1 nm, in a large number. In fact the curves obtained from these three precursors showed a homothetic repartition. The main difference pay in the global specific surface, but the pore diameter distributions were not very different.

This has been explained using SEM images, which are given in Fig. 6A and B, respectively, for powders obtained from precursors P I and P II. The samples prepared from precursor P III always showed the same microstructure: a smooth external skin covering a more porous structure (Fig. 6C). This porous structure was not open and the measured area was lowered.

The same differences have been characterized using TEM analysis and the microstructures of the ceramics obtained from the three different precursors were comparable but with changes in the crystallization and the crystal distribution in the BN powders.

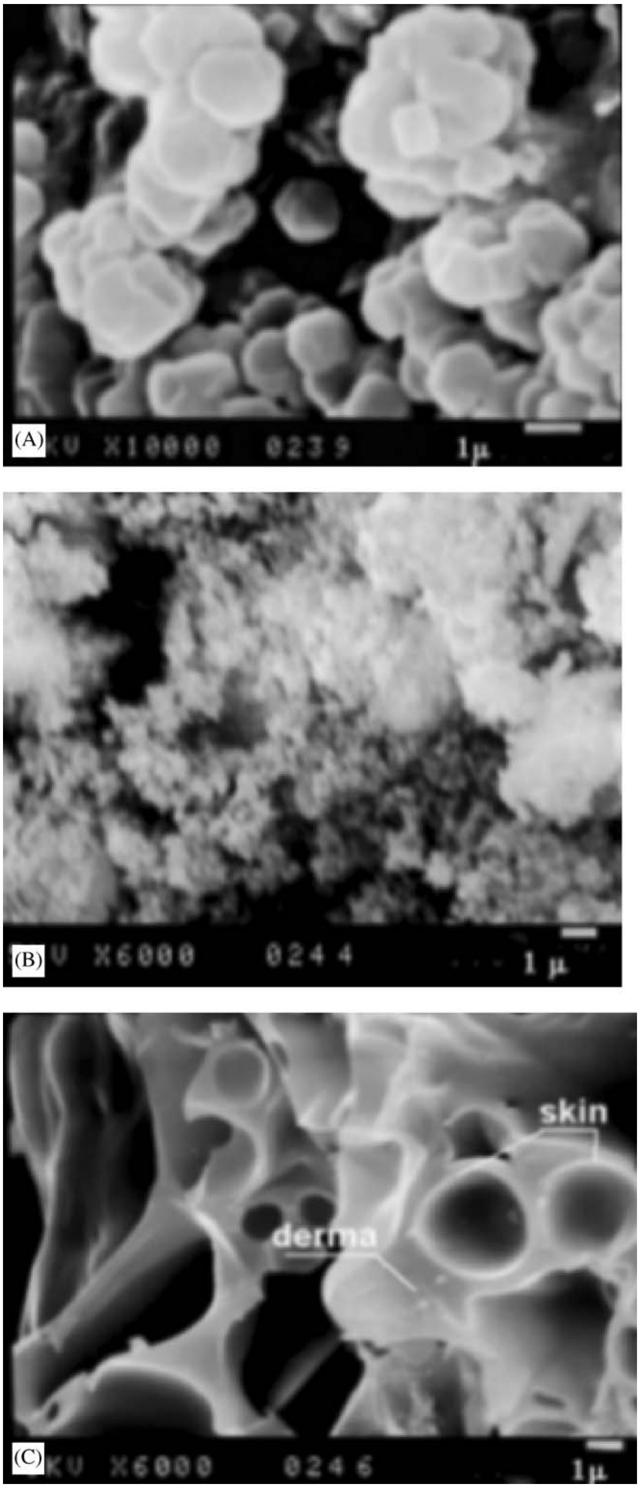

Fig. 6. SEM micrographs obtained from (A) sample from P I; (B) sample from P II; (C) Sample from P III.

The samples obtained from P I exhibit a quasifractal structure and the small spheres characterized using SEM were in fact composed of a very small and low

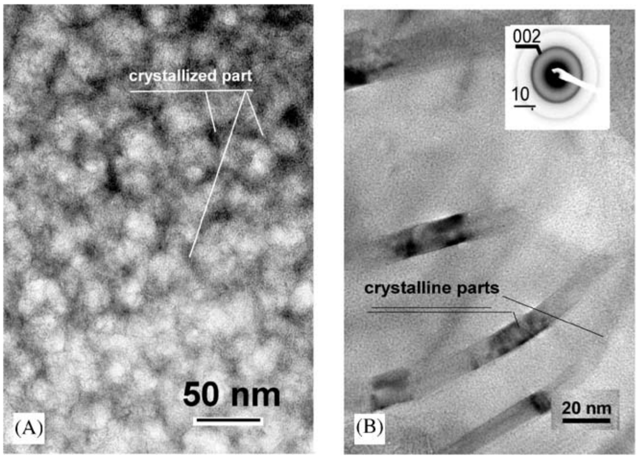

Fig. 7. TEM micrographs: (A) BN powder from P I; (B) BN powder from P II.

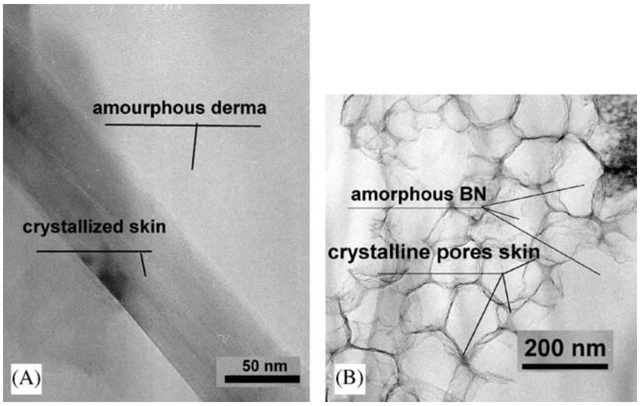

Fig. 8. TEM micrographs: (A) BN powder from P III; (B) view of the crystallized framework.

crystallized powder showing nanometric organized regions surrounding an amorphous core as shown in Fig. 7A. The nanostructure of the BN powder obtained from P II (Fig. 7B) is composed of long organized BN layers built from 5 to 10 layers of BN resembling nanotubes crossing a poor organized main part of the sample. This organization could be related to the framework of the polymer P II composed of stacked BN cycles bonded by substituted BN chains. This structure was enhanced by the ammonia treatment and yield to platelets construction close to the BN structure of powders obtained by mechanical grinding of classically prepared BN.

In the foams obtained from P III, the microstructure was more complex and had to be related to the heterogeneous structure of the powder as shown in Fig. 8A and B. Besides crystallized parts in which the BN layers were clearly present, large amorphous parts were the main parts of the sample. This amorphous "derma" bounded by a crystallized skin has been observed in BN fibers prepared from a polyaminoborazinic precursor [25]. In this case also, the crystallization of the external part of BN was related to possibilities of crystal growing of amorphous BN when oxide allowed an enhancement of the crystallization [26]. In the case of BN foams, the pre-ceramic obtained after the chemical treatment and ceramization up to 1000°C was composed of large pores which trapped water and oxygen traces as soon as the powder was in contact with air outside the furnace. These impurity traces favor the BN crystallization because the boron oxide formed was a crystallization reagent. The crystallized framework of the macroporous and mesoporous structure could be observed after annealing up to 1800°C, thermal treatment which enhances crystallization around the pores. The "net" structure of crystallized BN surrounding amorphous or turbostratic BN powder is given in Fig. 8B. An important difference from carbon had to be pointed out because, unlike the low crystallized charcoal, very porous and stable, turbostratic BN was very sensitive to oxidation and hydrolysis. A very high temperature was required to transform turbostratic BN powder into h-BN, but this transformation was not only related to the temperature and the precursor as for carbon; in this case, the presence of oxide impurity favors the crystallization.

3.3. Characterization of a PtBN-supported catalyst

As reported in the experimental part, two attempts were made using different synthesis pathways: a direct synthesis of platinum supported on BN powder starting from a precursor mixture (A) and a two-step preparation from a BN powder obtained from P I followed by an impregnation using a sol–gel method (B). The XRD pattern of the two samples are given in Fig. 9. The two syntheses led to platinum supported by BN. However, the line width of sample A clearly showed crystallized platinum mixed with the BN support. Sample B showed only a very small and broad peak corresponding to the 1 1 1 reflection. The broadness of the peak characterized disordered platinum unlike the first sample.

To know more about the platinum dispersion on the boron nitride, elemental analysis and XPS measurements have been performed on the two samples and results are given in Table 2.

The results clearly show that the sample prepared using a one-step synthesis exhibits no more platinum on the surface. Platinum is still present as shown using elemental analysis but it is scattered into the boron nitride powder. The effect of this polyprecursors technique also led to an increase in the crystallization and a lowering of specific surface of sample A. Although this method of synthesis was promising, it did not seem to be convenient for preparing catalysts. On the contrary, the second synthetic method led to very

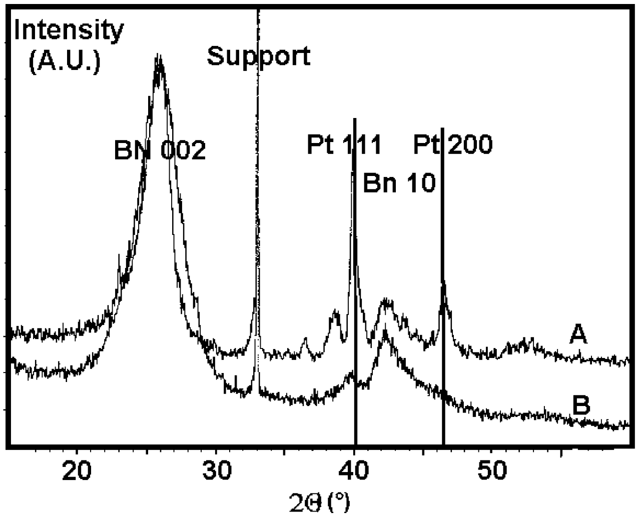

Fig. 9. XRD patterns of the BN-supported platinum samples.

Table 2
Characterization of the platinum-supported samples

Sample	Surface (m^2g^{-1})	L_c (nm)	Classical measure (wt%)	XPS measurements (wt%)		
				B	N	Pt
A	110	3.7	4.1	44.4	47.2	0
B	500	1.6	1.6	37.4	44.3	1.5

scattered platinum on the surface of the powder and this catalyst should be more preferred.

4. Conclusion

The preparation of high surface area boron nitride powders and foams from various molecular precursors has been studied. The highest specific areas were obtained using the polyborazylenic precursor. However, the difference in the measured surface area was specially related to an enhanced micro-porosity of the samples. Curiously, the foams obtained from aminoborazinic precursors always exhibited a smaller specific area. This has been related to the ability of this precursor to melt and stay in a waxy form at high temperature, which leads to a composite structure of the powder with a non-porous crystallized skin of the foam embedding an amorphous porous structure. Using haloborazinic precursors, specific areas of more than $300\,m^2\,g^{-1}$ are commonly obtained, and the preparation of samples of 10 g of BN powder is classical. A platinum catalyst supported on a BN powder has been prepared directly in a one-step synthesis but platinum was scattered inside the boron nitride powder and was inefficient for catalysis. Platinum-supported catalysts have been obtained by a more classical sol–gel deposition and highly dispersed platinum on BN high surface powders have been prepared.

References

[1] A.B. Stiles, in: Calalyst Supports and Supported Catalysts. Theoretical and Applied Concepts, Butterworths Publishers, Stoneham, MA, USA, pp. 57–85.
[2] H.C. Yao, M. Sieg, H.K. Plummer Jr, J. Catal. 59 (1979) 365.
[3] L. Pesant, G. Winé, R. Vieira, P. Leroi, C. Pham-Huu, M.J. Ledoux, in: E. Gaigneux, et al. (Eds.), Studies in Surface Science and Catalysis, Elsevier, Amsterdam, 2002, p. 193.
[4] C. Méthivier, J. Massardier, J.C. Bertholini, Appl. Catal. A Gen. 182 (1999) 337.
[5] C. Méthivier, B. Béguin, M. Brun, J. Massardier, J.C. Bertholini, J. Catal. 173 (1998) 374;
J.C. Wu, Z. Lin, F. Tsai, J.W. Pan, Catal. Today 63 (2000) 419.
[6] R.T. Paine, C.K. Narula, Chem. Rev. 90 (1990) 73.
[7] R.T. Paine, L.G. Sneddon, Chemtech 7 (1994) 29.
[8] J. Economy, R. Anderson, Inorg. Chem. 5–6 (1966) 968.
[9] C.K. Narula, R. Schaeffer, R.T. Paine, J. Am. Chem. Soc. 109 (1987) 5556.
[10] D.A. Lindquist, T.T. Borek, S.J. Kramer, C.K. Narula, G. Johnston, R. Schaeffer, D.M. Smith, R.T. Paine, J. Am. Ceram. Soc. 73 (1990) 757.
[11] J.C. Wu, Z. Lin, F.J.W. Pan, M. Rei, Appl. Catal. A Gen. 219 (2001) 117;
C.A. Lin, J.C.S. Wu, F.J.W. Pan, C.T. Yeh, J. Catal. 210 (2002) 39.
[12] D.D. Perrin, W.L. Armarengo, D.R. Perrin, in: Purification of Laboratory Chemicals, Pergamon Press, London, 1996, pp. 5–25.
[13] K. Niedenzu, J.W. Dawson, J. Am. Chem. Soc. 81 (1959) 3561.
[14] M. Houdayer, J. Spitz, D. Tran Van, French Patent No. 81 22163, 1981; US Patent No. 4 472 454, 1984.
[15] D.P. Kim, K.T. Moon, J.G. Kho, J. Economy, C. Gervais, F. Babonneau, Polym. Adv. Technol. 10 (1999) 702.
[16] P.J. Fazen, J.S. Beck, A.T. Lynch, E.E. Remsey, L.G. Sneddon, Chem. Mater. 2 (1990) 1942.
[17] J.A. Perdigon-Melon, A. Auroux, D. Cornu, P. Miele, B. Toury, B. Bonnetot, J. Organometallic Chem. 657 (2002) 98.
[18] R.H. Toeniskoetter, F.R. Hall, Inorg. Chem. 2 (1963) 29.
[19] G. Mignani, C. Richard, R. Trichon, Procédés de Préparation de Polyaminoborazines, French Patent, FR 2 695 645, 1992.
[20] S. Bernard, D. Cornu, P. Miele, H. Vincent, J. Bouix, J. Organometallic Chem. 657 (2002) 91.
[21] Y. Kimura, Y. Kubo, N. Hayashi, J. Inorg. Org. Polym. 2 (1992) 231.
[22] T. Matsuda, J. Mater. Sci. 24 (1989) 2353.
[23] E. Framery, Thesis No. 1616, University of Rennes, 1996, pp. 93–99.
[24] J. Thomas, N.E. Weston, T.E. O'Connor, J. Am. Chem. Soc. 84 (1962) 4619.
[25] F. Chassagneux, T. Epicier, P. Toutois, P. Miele, C. Vincent, H. Vincent, J. Eur. Ceram. Soc. 22 (2002) 2415.
[26] T. Hagio, K. Nonaka, T. Sato, J. Mater. Sci. Lett. 16 (1997) 795.