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Porous boron nitride supports obtained from molecular precursors. Influence of the precursor formulation and of the thermal treatment on the properties of the BN ceramic

José Antiono Perdigon-Melon [b], Aline Auroux [b], David Cornu [a], Philippe Miele [a], Bérangère Toury [a], Bernard Bonnetot [a,*]

[a] *Laboratoire des Multimatériaux et Interfaces, Université C. Bernard Lyon I, UMR-CNRS 5615, Bat Berthollet, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France*

[b] *Institut de Recherches sur la Catalyse, CNRS, 2, Av. A. Einstein, 69626 Villeurbanne Cedex, France*

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Abstract

Boron nitride (BN) porous samples have been prepared in order to be used as noble metal catalyst support from various molecular precursors, using classical thermal methods to expand and preceramise the precursors. Three types of precursors have been tested: ammonia borane, polyborazylene and several aminoborazines and derived polymers. Using trimethylamino borazine (MAB) and MAB polymers, the surface of the foams was shown to be decreasing when the polymerisation advancement of the precursor increased meanwhile the crystallisation of the samples decreased. All the samples issued from MAB presented the same SEM morphology: large pores with a glassy skin surface covering a disorganised inner part, hidden under the thin homogeneous BN skin, which appeared through the sample breaks. This was related to the melting property of MAB polymers which imbedded the internal part of the sample and avoided its expansion. Attempts were made, using the bulkier amino group as anilino- and benzylaminoborazine to enhance the porosity of the samples using a precursor with a lower ceramic yield. The change in the specific area was not important. However, a surface of 30 $m^2 g^{-1}$ was currently obtained. The ability of the precursor to lead to high specific area seemed to be correlated to the expansion possibilities of the precursor in the solid state prior to fusion. Foams exhibiting a surface of more than 50 $m^2 g^{-1}$ have been obtained when polyborazylene based precursor was pyrolysed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Boron; Nitride; Catalysis; Support; Powders

1. Introduction

Catalytic oxidation of gasoline volatile was actually an important subject with respect to environment concern. The catalyst supports were usually made from highly divided oxides providing a large specific area on which an active noble metal was deposed. In fact, traditional metal oxides, such as Al_2O_3, SiO_2 and zeolithe possessed rather low thermal conductivity, thus metal sintering on hot spots might be severe [2,3]. The high oxidation energy of hydrocarbon species led to a high temperature localised on the metal active catalyst. The oxide supports were mainly isolators so the high oxidation energy could not be spread over the support. Moreover, a certain degree of metal-support interaction existed in most oxide-supported metal catalysts that brought a negative influence on the catalytic activity [4] thus non-oxide supports have been considered [5]. Boron nitride (BN) was one of the more interesting non oxide ceramic material because of its low density, excellent resistance to chemical attack, high melting point, good thermal conductivity and its higher stability towards oxidation than carbon [1]. The combination of these specific properties focused the attention on the possibility to prepare high surface area/high porosity BN specially useful in the fields of high temperature composites and ceramic support for catalysis. The high

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* Corresponding author. Tel.: +33-4-72-431234; fax: +33-4-72-440618

E-mail address: bernard.bonnetot@univ-lyon1.fr (B. Bonnetot).

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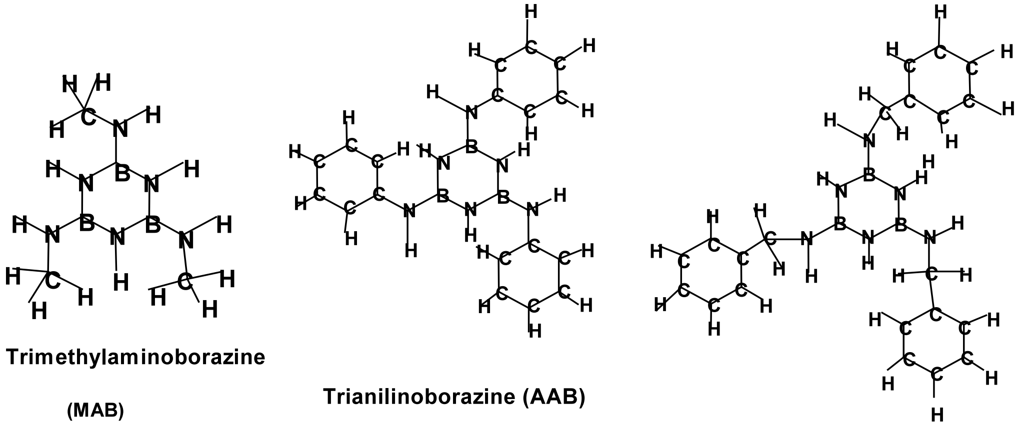
thermal conductivity of BN [6] could be a solution to disperse the important oxidation energy cleared on the metal active site and to preserve the catalyst efficiency for a longer time. Another point that had brought our interest to BN was its higher stability towards oxidation than carbon. When a catalyst was used in the destruction of gasoline volatile, small amounts of carbon were usually deposed during the oxidation and the efficiency of the catalyst was lowered. A reactivation of a BN supported catalyst could be realised by burning the residual carbon without effect on the catalyst. However, the classical ways used to get BN led to powders which were hardly converted into high specific surface supports [7,8]. The preparation of high surface samples of boron nitride had to be performed from very different molecular precursors. Starting from boron oxide, melamine diborate [9] could be converted into BN. Very thin BN powder had been obtained trough a high temperature nitruration of boron coming from diborane pyrolysis [10]. However, the main part of the molecular precursors used to obtain BN was derived from a borazine framework [7,8]. High surface BN substrates had been prepared from aerogels obtained in a THF solution using a low temperature reaction between TCB and hexamethyldisilazane following a described method [11]. The gel suspension had been treated by ammonia before it was dried using a critical point drier with CO_2 as a solvent. The surface area was shown to be very dependant on the ceramisation temperature of the sample and a surface of more than 800 m^2 g^{-1} at 1200 °C was described as dropping to 400 m^2 g when BN was stabilised at 1600 °C, the smaller pore of about 0.1 nm being closed by annealing of the aerogel [12,13]. Recently, a first boron nitride supported catalyst had been prepared from BN powder with a great specific area but not indication was given on the support preparation [14]. In the present work, several molecular BN precursors have been used under different expanding conditions to obtain polymeric foams which have been ceramised to lead to BN stabilised foams. This stabilisation had been performed up to 1800 °C in order to get very stable supports although this high temperature of treatment was known to lower the surface of the foams [13]. Very different results have been obtained which could be related to the precursor but also to the chemical and thermal treatment used to expand the precursors before and during the preceramisation. The main part of the precursors was issued from aminoborazines bearing different amino moieties. Trimethylaminoborazine, MAB, used as BN fibre precursor [15] is well known, but attempts have been made using trianilino, tribenzyl aminoborazine, polyborazylene and ammonia borane. SEM observation of the main part of the samples had shown large pores leading to a 30 m^2 g^{-1} specific area with a smooth glassy surface, always obtained using MAB or MAB issued polymers. Benzylaminoborazine led to a black carbon containing ceramic due to bad stripping of the amino group of amino borazine during ceramisation. Using non fusible precursors such as ammonia borane, polyborazylene derivative or heavy aminoborazine, thin powders were obtained exhibiting various specific areas in the range of 20–35 m^2 g^{-1} depending of the precursor and the thermal ceramisation profile, but also of the temperature of ceramisation and of impurities as described for such compounds [10,13,16].

2. Results and discussion

2.1. Molecular precursors used

Samples of porous boron nitride have been obtained using different precursors and various thermal and physical treatments. All the precursors were only constituted from boron, nitrogen and hydrogen. The simplest compound used (P I) was ammonia borane NH_3BH_3. Its pyrolysis had been studied in order to get borazine $(HBNH)_3$ at moderate temperature [17] and to get BN coatings [18]. The thermolysis of ammonia–borane under ammonia led to thin white BN powder. The other precursors were build from a borazinic framework $(BN)_3$ as the major part of the compounds used in BN preparation from molecular precursors. Two different kind of precursors have been studied one starting from borazine $(HBNH)_3$ and its polyborazylene issued polymers and the other from aminoborazines $(RNHBNH)_3$ and their derived polymers. The polymerisation of borazine [19–21] had been widely studied to get spinnable polymers. The main interest of polyborazylene was its very high ceramic yield but the chemistry of this compound was difficult [19]. However, a polyborazylene derivative sample had been prepared (P II) using the polymerisation protocol used for BN matrix preparation [22,33]. Another kind of precursors was obtained from amino-borazines. The monomers were prepared using a reaction between trichloroborazine and primary amines. Three different amines have been used, methylamine, aniline and benzylamine to prepare the corresponding aminoborazines, respectively the trimethylamino-borazine or MAB, $(CH_3NHBNH)_3$ leading to the precursor (P III), the trianilinoamino-borazine, AAB, $(C_6H_5NHBNH)_3$ leading to (P IV) and the tribenzylaminoborazine, BAB, $(C_6H_5CH_2\text{-}NHBNH)_3$ used as precursor (P V). The molecular structure of these aminoborazines were shown on Fig. 1.

The changes in the amino group corresponded to two criteria: the bulkiness of the group would change the ability of the aminoborazine to polymerise [23] and their reactivity toward ammonia used in the preceramisation. Some amino group, effectively considered as ‘good leaving’ group in the precursor which means amino


Trimethylaminoborazine (MAB)

Trianilinoborazine (AAB)

Tribenzyaminoborazine (BAB)

Fig. 1. Aminoborazines used.

groups easily replaced by ammonia, could lead to an important change in the behaviour of the preceramic during the chemical and thermal treatment and induced differences in the ceramic obtained [24]. Taking into account the bulkiness of the amino group, the aminoborazines underwent polymerisation leading to polymers of various structure depending on the condensation reaction. The classic thermal treatment yielded the reaction between two amino groups from two monomer molecules with the evolution of a molecule of amine and a new bonding between the two molecules through a bridge. The ability of aminoborazine to led to polymer was shown to depend upon the amino group, its bulkiness and its reactivity [25]. Among the aminoborazine prepared, the more reactive monomer was MAB and the less reactive one was BAB. MAB had been transformed into a polymer following a polycondensation reaction described elsewhere [25]. The physico-chemical properties of the polymer obtained were described in the experimental part, this polymer was very similar to the polymer used for polymer fibre spinning [27]. The other aminoborazines AAB and BAB had been thermolysed without polymerisation. Their reactivity had been shown as very different related to the amino group associated.

2.2. *Results and discussion*

2.2.1. *Specific treatments*

Several types of thermal treatments had been performed on the different samples in order to get foams from the fusible precursors. On some samples, a first prethermolysis with the goal to prepare a more reactive and more expanded preceramic had been made using various conditions. Then the pretreated or untreated samples were preceramised following two protocols as described in the experimental part. To stabilise and to crystallise the samples in order to avoid any changes in their properties, the samples were annealed after the preceramisation up to 1800 °C in a nitrogen flow. All the experiments were presented in Table 1 with the experimental conditions and the main characteristics of the obtained samples. Out of the specific area, the crystallinity of porous BN had been measured but only along the *c* axis of h BN [28].

The two attempts were performed using the precursor P I and similar condition without any expansion pretreatment. After annealing at 1800 °C, the samples JA 13 and 18 looked like a ‘flour’ powder of BN and have shown very similar properties. The specific area was more than 30 m^2 g^{-1} and the samples exhibited a very high crystallisation characterised by a crystallite length along the *c* axis $Lc = 150$ Å which correspond to 45 BN layers.

Using the polyborazylene derived precursor P II, two experiments JA 12 and 15 were made without any expansion treatment because this polymer decomposed rapidly when heated [22]. The heating rate and the ammonia flow were the two modified parameters (preceramisation protocols A and B, respectively) and the results were different specially for the crystallisation of the sample with Lc value dropping from 125 to 20 Å while the surface increased from 20 to 53 m^2 g^{-1}.

The main part had been run on P III because, as it could be molten, a larger number of thermal treatments could be done. The expansion of the P III had been done under low pressure with a very rapid heating and a 1 h hold at various temperatures for samples JA 01, 02 and 03; a heating in a closed autoclave followed by a rapid gas release for samples JA 04, 05 and 06, a high mechanic pressure application while heating followed by a quick pressure release was applied for samples JA 07, 08, 16 and 17. A flash thermolyse (100 °C min^{-1}) under vacuum had been realised on sample JA 11. The preceramisation of all this samples had been done using the protocol A. The precursors P IV and P V have only

Table 1
Series of samples prepared from molecular precursors

Sample	Precursor	Conditions expansion	Temperature treatment (°C)	Time (h)	Surface ($m^2\ g^{-1}$)	Crystallisation (Lc Å)
JA 0	P III				25	150
JA 1	P III	Vacuum	250	1	20	123
JA 2	P III	Vacuum	360	1	4	28
JA 3	P III	Vacuum	470	1	3.6	22
JA 4	P III	Gas pressure 1b	225	4	18	140
JA 5	P III	Gas pressure 2b	225	4	20	150
JA 6	P III	Gas pressure 5b	360	4	28	112
JA 7	P III	Press 42 daN	250	1	1.5	30
JA 8	P III	Press 42 daN	250	2	23	100
JA 11	P III	Vacuum	550	0.2	7	86
JA 12	P II	No exp/preceram A	–	–	20	125
JA 13	P I	No exp/preceram A	–	–	34	163
JA 14	P III	No exp/preceram B	–	–	12	101
JA 15	P II	No exp/preceram B	–	–	53	20
JA 16	P III	Press 40 daN	200	1	28	90
JA 17	P III	Press 40 daN	250	1	12	75
JA 18	P I	No exp/preceram A	/	/	30	140
JA 19	P IV	No exp/preceram A	/	/	21	26
JA 20	P V	No exp/preceram A	/	/	25	16

been treated following the preceramisation procedure A without pretreatment because they carried bulky amino groups which render the polymerisation very difficult. From precursor P III, the thermal treatment under vacuum on sample JA 01, 02 and 03 lowered drastically the specific area and the crystallinity of the samples. However, after pretreatment, a very light foam of preceramic was recovered and the decomposition and the polymerisation of the sample JA 03 correspond to about 50% of weight loss when a ceramic yield was achieved on the sample. It seemed that the expanded polymer could not react easily when preceramised and that the inside part of the polymeric foam was kept into a solid skin of BN. This morphology will be more efficiently shown using SEM. An example of the difference of crystallinity observed on the samples related to the precursor was given on Fig. 2.

These three samples JA 17, 19 and 20 have been ceramised in the same run under exactly the same conditions but staring from three precursors, P III, IV and V. If the surface value of the three samples were comparable, about 20 $m^2\ g^{-1}$, the crystallisation was very different and Lc decreased down to 16 Å. Moreover, as shown in Fig. 3, the TGA performed under the same conditions than the preceramisation protocol A led to important differences in the ability of the precursor to react with reductive atmosphere used to strip off the carbon moieties bound to the amino group of the aminoborazine. After the preceramisation treatment performed using the TGA apparatus the residue corresponding to the sample 20 was deeply black showing the presence of an important amount of carbon coming from the pyrolysis of the hydrocarbon amino parts.

MAB reacted very rapidly with ammonia whereas BAB was very stable up to 200 °C. Aniline described as a good 'living group' did not react very rapidly if the temperature was lower than 100 °C. However, the thermolyse residues for MAB and AAB after TGA were white, without carbon while the sample issued from BAB was black consistent with the theoretical weight loss of 81 for 75% experimental.

The crystallinity of the samples obtained from the different precursors was very different and always the ceramics obtained from ammonia borane or polyborazylene were more crystallised as reported [29].

2.2.2. *Micrographic morphology of the samples*

Prior the specific area measurements, the morphology of the different samples had been examined using SEM. From precursor (P I) no difference could be noticed between the two products. The samples were very well crystallised and the morphology of the BN powder given in Fig. 4 showed a regularly grained powder.

For samples coming from precursor (P II), important differences were observed in the crystallisation and surface. Using a slow preceramisation, the sample exhibited a glassy out side structure as shown on Fig. 5a, but if the thermolysis was faster with an important ammonia flow (protocol B), a more porous compound was obtained as shown in Fig. 5b.

On the sample 15, the specific area related to the pores repartition had been studied. The pores size was measured between 25 and 5 nm with about the same proportion. Only a macro porosity had been shown as given on Fig. 6 a and b corresponding, respectively to the sum of the specific area as a function of the pores size and the ratio of the pores versus their radii.

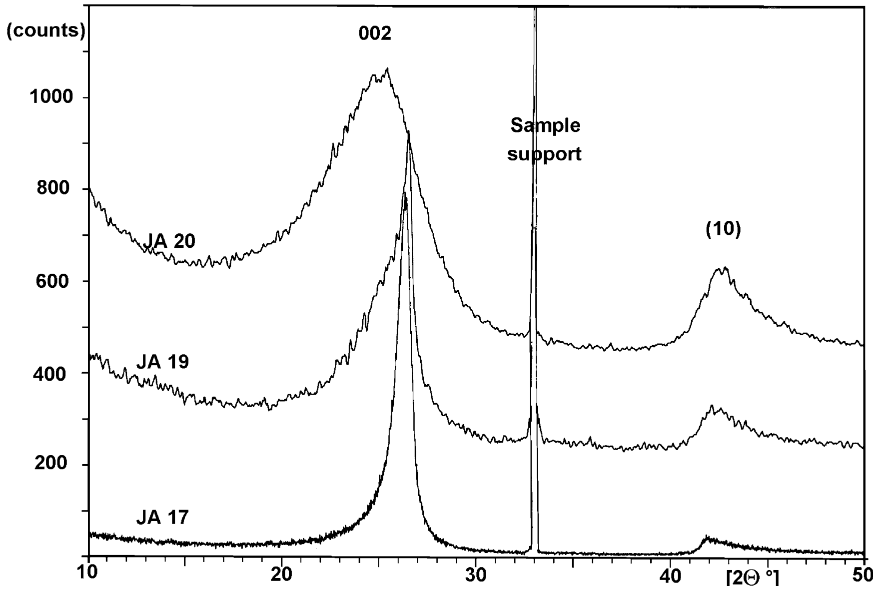


Fig. 2. DRX spectra of different samples issued from aminoborazines.

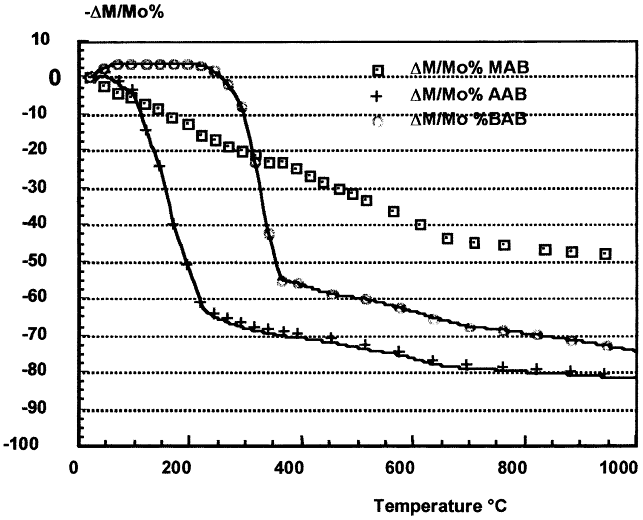


Fig. 3. TGA of aminoborazines under the preceramisation conditions.

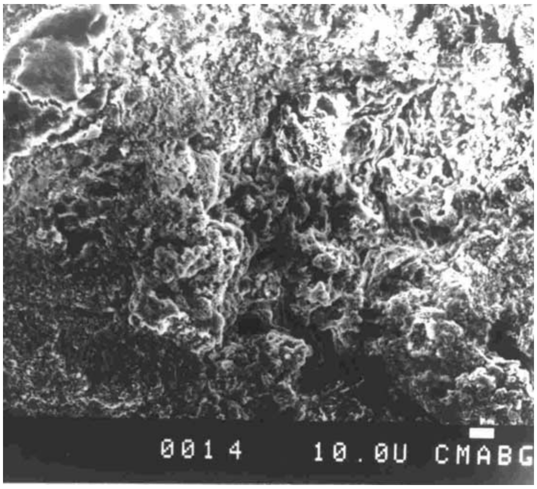


Fig. 4. Sample JA 13 issued from polymer P I.

The samples prepared from MAB (P III) presented very similar SEM morphology (Fig. 7a for JA 06, b for JA 08 and c for JA 11) whatever the thermal or physical treatment of the polymer had been before ceramisation.

All the samples seemed to be very heterogeneous with an outside skin very regular and crystallised and an inside part looking more porous and covered by the smooth BN skin. This complex structure could be observed at any scale. For instance the magnification of the SEM figures on the Fig. 7a and b was 10 times different but the same morphology was observed with a skin and an inside porous part.

The picture obtained on the sample pretreated using the flash thermolysis of precursor P III showed clearly that the molten precursor had been expanded into very large pores, more than 20 µm, in a very strong and stable glassy structure which had been ceramised without any change. It corresponds to the sample obtained from very polymerised precursor with a very low surface and a poor crystallisation as observed with the samples JA 03, 07 and 17.

From precursors P IV and P V, only powders had been obtained, looking like the sample obtained from P I.

3. Experimental

3.1. Starting materials

All experiments were performed under an atmosphere of pure Ar using standard vacuum-line, Schlenk techniques and an efficient dry box with solvents purified

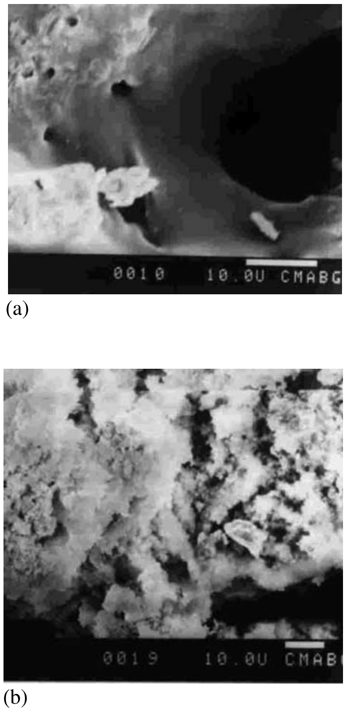


Fig. 5. Samples JA 12 (a) and 15 (b) issues from polymer P II.

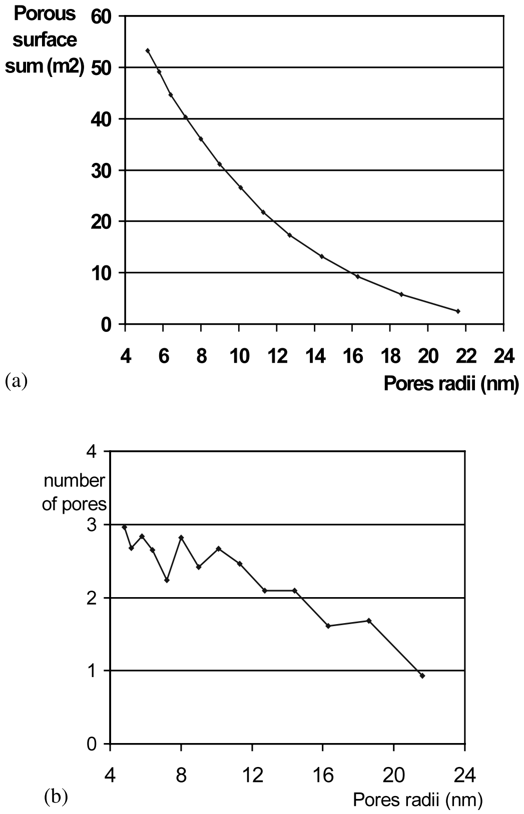


Fig. 6. (a and b) Sum of the specific area and pores number as a function of the size of the pores.

using standard methods [32]. The starting materials, NH_4CO_3 and KBH_4 (Aldrich ACS) for the synthesis of NH_3BH_3 and polyborazylene were used as received. The trichloroborazine (TCB) was prepared from BCl_3 (Alphagaz) and NH_4Cl (Aldrich, ACS reagent). Ammonium chloride was dried under vacuum at 130 °C for 12 h before the synthesis. Methylamine (Fluka, 97%), aniline and $C_6H_5NH_2$ (Aldrich, ACS reagent) were used as supplied without further purification.

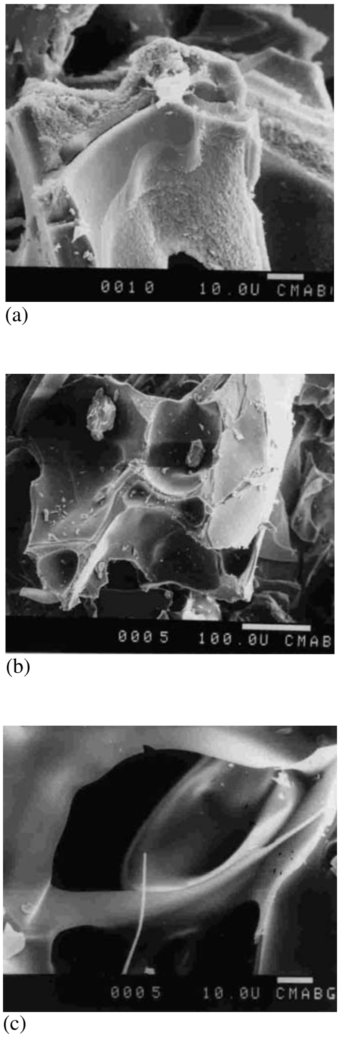


Fig. 7. SEM pictures of the samples JA 06 and 08 obtained from precursor P III. (c) Sample JA 11 issued from precursor P III.

3.2. Characterisation

^{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 non decoupled), with positive value down field), 300 MHz (reference Me_4Si) and at 75 MHz (reference Me_4Si, total decoupling). The chemical shifts were explained in ppm and proton and carbon spectra were obtained from CH_2Cl_2 solutions. The following abbreviations are used: d, doublet; s, singlet; t, triplet; q, quadruplet; m, unresolved multiplet; br, broad. The IR spectra were recorded on a FTIR Nicolet Magna 550 spectrophotometer in KBr pellets. The ceramic yield was determined using a TGA B70 apparatus and the study was performed under ammonia up to 600 °C and then under nitrogen up to 1000 °C with a 2 °C min^{-1} heating rate. DCS analysis were ran on a TA 8000 Mettler-Toledo under an Ar atmosphere. SEM images were obtained from a JEOL 55 CF (CMEABG Lyon). X-ray powder diffraction (XRD) 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 using a apparatus build in the Institute of Catalysis. All the samples were outgassed at 673 K for 4 h prior to the absorption measurements.

3.3. Preparation of the studied compounds

3.3.1. Synthesis and characterisation of ammonia–borane, NH_3BH_3 (P I)

Ammonia–borane (NH_3BH_3) was prepared from NH_4CO_3 and KBH_4 through an exchange reaction performed in THF [32,33]. IR (cm^{-1}): ν 3320 (NH); 2355 (BH); 1380 (BN stretch.); 789 (BN bend); ^{1}H-NMR: (ppm): δ 1.49 (q, 3H, $^1J_{HB} = 93$ Hz (BH_3); 4.1 (br t, 3H, $^1J_H 14_N = 35$ Hz (NH_3); ^{11}B-NMR: (ppm): δ −22.6 (q, $^1J_{BH} = 94$ Hz). The ceramic yield measured by TGA is a function of the ceramisation atmosphere. Up to 1000 °C with a heating rate of 2° min^{-1} under nitrogen flow (0.2 l min^{-1}), the ceramic yield was 49% however, under NH_3 (0.2 l min^{-1}) it was only 25%. This was interpreted by the formation of volatile borazine favoured by NH_3 [31] which was stripped off of the crucible lowering the ceramic yield.

3.3.2. Synthesis and characterisation of polyborazylene (P II)

The borazine was prepared using a two steps classical method from ammonia borane, NH_3BH_3, which was pyrolysed in glyme as described in literature [17]. However, the borazine was not distilled but polymerised in situ yielding directly a polymer. The solvent was removed by fitration under an Ar atmosphere and the remaining borazine and the volatiles were removed as recommend in the preparation of poly(aminoborane) [20,21,33]. A white waxy polymer is isolated which is a mixture of polyborazylene and poly(aminoborane) whose dissolution is very difficult without decomposition. IR (cm^{-1}) ν: 3400 (NH); 2875 (CH); 2478 (BH); 1465 (BN stretch.); 1105 (CN); ^{1}H-NMR (ppm): δ 4.3 (m, br), 3.5 (s, br CH); ^{11}B-NMR (ppm): δ 27.6, 21.1 (N_3B groups), −17.9 (m, br, N_2BH_2), −22.7 (m, br NBH_3). The presence of organic moieties in the polymer is confirmed by the elemental analysis (given in % weight): B = 23.0; N = 45.8; H = 7.1; C = 18.0; oxygen could not be measured in presence of boron and its amount can be calculated at about 6%. The presence of oxygen and carbon can be related to a partial reaction of borazine with glyme, leading through 〉BOR bridges to the incorporation of alkoxide into the precursor.

3.3.3. Synthesis and characterisation of the triaminoborazine (P III, IV and V)

The aminoborazines were prepared from trichoroborazine (TCB) and the corresponding amine. TCB was not commercially available so it was prepared in the Laboratory using the standard method using the reaction between BCl_3 and NH_4Cl in $C_6H_5CH_3$ [34]. To a suspension of NH_4Cl in refluxing $C_6H_5CH_3$, BCl_3 was slowly added, the addition rate was regulated by the reflux of BCl_3. After the reaction, TCB was recovered from $C_6H_5CH_3$ with a 80% yield from BCl_3. IR (cm^{-1}): ν 3450, 3416 (NH); 1438 (BN stretch.); 1031 (NH); 743 (BCl); 704 (BN bend); ^{1}H-NMR: (ppm): δ 5.29 (t, br, (NH); ^{11}B-NMR: (ppm): δ 29.7 (s). In a second step, TCB was reacted with the required amine at low temperature in a ratio 1/8 leading to the formation of aminoborazine and amine-chlorhydrate which was separated by filtration. The triaminoborazine was recovered after the evaporation of $C_6H_5CH_3$ under low pressure at room temperature (r.t.) [26–35].

Precursor (P III): it was prepared from MAB, however, the synthesis of pure MAB was difficult because of its ability to polymerise. Usually a mixture of 6% molar of dimer is isolated while the remaining $C_6H_5CH_3$ is about 15% molar. The precursor looks like a very viscous oil and the removal of $C_6H_5CH_3$ is difficult and leads to an important polymerisation progression. The MAB is characterised in situ and the amount of $C_6H_5CH_3$ can be measured using ^{1}H-NMR. IR (cm^{-1}): ν 3446, 3250 (NH); 2922, 2830 (CH); 1514 (CH); 1420 (BN stretch.); 1194 (NC); 1029 (NH); 715 (BN bend); ^{1}H-NMR (ppm): δ 1.50 (s, br, 1H, (BN*H*CH$_3$); 2.5 (s, br, 3H, (NHC*H*$_3$)), 2.66 (s, br, 3H(NH cycle)); ^{11}B-NMR (ppm): δ 25.9 (s, br); ^{13}C-NMR (ppm): δ 27.5 (s, br (NH*C*H$_3$). This 'monomer' will be transformed into polymer using a thermal polymerisation conducted under an Ar stream. As shown on Fig. 2, the polymerisation of MAB evolved methylamine and each methylamine molecule evolved corresponds to an intercyclic bonding. The reaction can be monitored by the determination of the quantity of amine evolved. The polymerisation was carried following the standard process described [24]. For the precursor (P III), the ratio of the amine evolved versus the monomer quantity was 0.5, which led to a polymer with glass transition Tg = 85.5 °C and a ceramic yield of 55% at 1000 °C. The elemental analysis (given in % weight): B = 23.5; N = 47.8; H = 7.2; C = 18.8; oxygen, not measured in presence of boron can be estimated at less than 2.8%. I.R. ν cm^{-1}: 3441 (NH); 2929, 2886 (CH); 1420 (BN stretch.); 1108 (NH); 736 (BN bend); NMR ^{1}H, δ: 1.80 (m, br, BN*H*CH$_3$); 2.53 (s, br, NHCH_3), 3.3–2.66 (m, br, NH cycle); ^{11}B, $\delta = 25.77$ (s, br); ^{13}C, $\delta = 27.9$ (s, br, NHCH_3).

The precursor P IV was obtained reacting TCB with aniline as reported in the literature [26]. The tri anilino aminoborazine $(C_6H_5NHBNH)_3$ was prepared with a 45% yield due to its poor solubility in $C_6H_5CH_3$. The AAB was characterised using ^{1}H-NMR. IR (cm^{-1}): ν 3421, 3278 (NH); 2922, 3032 (CH); 1501 (CH); 1429 (BN stretch.); 1231 (NC); 1028 (NH); 696 (BN bend); ^{1}H-NMR (ppm): δ 3.80 (s, br, 1H, (BNHC$_6$H$_5$); 6.77, 6.94, 7.24 (m, br, 5H, (NHC$_6H_5$)), 3.67 (m, br ,3H (NH cycle)); ^{11}B-NMR (ppm): δ 25.2 (s, br). The ceramic yield was 19.4% up to 1000 °C; it was consistent with the theoretical weight loss of 21% when AAB was converted into BN.

The precursor P V was obtained using the same method [26]. The tribenzylaminoborazine $(C_6H_5CH_2NHBNH)_3$ was prepared with a 30% yield. It was purified by recrystallisation from a chlorobenzene solution. The BAB was characterised using ^{1}H-NMR. IR (cm^{-1}): ν 3440, 3240 (NH); 2910, 3025 (CH); 1495 (CH); 1443 (BN stretch.); 1028 (NH); 713 (BN bend); ^{1}H-NMR (ppm): δ 2.73 (s, br, 1H, ($C_6H_5CH_2NHB$); 3.12, 3.15 (m, br, 2H, (BNHCH_2C$_6$H$_5$); 7.19, 7.27, 7.37 (m, br, 5H, (NHCH$_2$C$_6H_5$)), 4.2, 4.32 (m, br, 3H(NH cycle)); ^{11}B-NMR (ppm): δ 30.10 (s, br). The ceramic yield determined using TGA was 25.6% which was very high but the residue was black and carbon containing, so this value was not taken into account and confirmed the poor ‘living group’ character of the benzyl group.

3.4. Preceramisation and ceramisation conditions

The crude foams after the expanding treatment were transformed into ceramic by a two steps thermal and chemical treatment using two different apparatus. First, a preceramisation was performed from r.t. up to 1000 °C in classic ovens fitted with a silica tube, this operation was run under reactive ammonia flow (1 L h^{-1}) up to 600 °C and then under nitrogen flow. Ammonia was used to strip the organic parts of the copolymer, as shown in previously [25]. Two heating rates were used, the standard heating used for ceramic fibres production Protocol A: 1° min^{-1} up to 600 °C and then 5° min^{-1} up to 1000 °C and a more rapid preceramisation protocol B: heating rate of 200 °C h^{-1} under a 6 l h^{-1} ammonia flow up to 600 °C and then under nitrogen. Then the fibres were transferred into a high temperature oven where they were heated up to 1800 °C with a heating rate of 10° min^{-1} under a nitrogen atmosphere. The ammonia gas used was from Alfagaz Electronic grade N_{36} (99.96%; $H_2O < 100$ ppm, $C_nH_{2n} < 1$ ppm) used without further purification and nitrogen was from ‘air liquid’ N_21 grade (99.999%, $H_2O < 3$ ppm, $O_2 < 0.2$ ppm).

4. Conclusion

Porous boron nitride could be prepared from polymeric precursors and the physical properties of the obtained ceramic supports could be adapted to the required utilisation conditions. Higher specific areas were obtained from polyborazylene derived precursor. The preceramisation conditions were shown to be very independent of the obtained sample and, using the same precursor, the surface of the porous BN could be two times higher following different ceramisation protocols. No microporous structure could be obtained as described in the literature. The porous substrates were composed of broad pores, widely open to the surface of the sample that could be interesting to depose an active part of noble metal to prepare a catalyst. The commonly obtained specific area of about 30 m^2 g^{-1} could be related to the surface of the powder used in literature and attempts would be made to prepare noble metal deposed on the new BN porous supports. The behaviour of aminoborazine derived precursors showed that the better results were obtained from the compounds exhibiting the lower ceramic yield. However, this lowering was shown to be difficult to be obtained using very broad amino group which were known to be hard to strip from the polymer. A future study would be to prepare some catalyst samples using first BN foam and an impregnation technique with Pt or Pd precursor and other attempts would be made to incorporate the noble metal precursor into the polymer before the expansion and the ceramisation of the samples.

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