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Thermal stability of mesoporous boron nitride templated with a cationic surfactant

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Abstract

The preparation of mesoporous boron nitride by using tris(monomethylamino)borazine (MAB) as boron nitride source and cetyltrimethylammonium bromide (CTAB) as structurating agent is reported. The X-ray diffraction, TEM and pore size analysis show that highly porous boron nitride (specific surface area of 800 m^2/g and mesoporous volume of 0.5 cm^3/g) is synthesized with mesopores of 6 nm in diameter. Moreover, the mesoporosity is conserved up to 1600 °C under an inert atmosphere.

Keywords: Nitrides; Porosity; Surfactant; BN

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1. Introduction

Mesoporous materials have high specific surface area and narrow pore size distribution.[1] They are useful in applications such as adsorption, separation and catalysis.[2] A soft template route is generally involved in the synthesis of mesoporous materials: a molecular precursor is polymerized in a solution containing amphiphilic molecules. The famous example is the ordered mesoporous silica family, synthesized for instance, by hydrolysis-condensation of $Si(OEt)_4$ in a cationic surfactant solution in water.[1] For specific applications, which need higher temperatures stabilities and higher chemical inertness, it is interesting to develop carbide[3–8] and nitride[9–20] mesoporous materials. There are some reports concerning nanostructured nitride ceramics: a template assisted method has been described to prepare a silicon imido nitride by ammonolysis tris(dimethylamino)silylamine $[(CH_3)_2N]_3SiNH_2$ in presence of amine.[9,10] Mesoporous silicon nitride has been also synthesized from silicon halides and ammonia.[11] Microporous GaN was elaborated by ammonolysis of $Ga_2(NMe_2)_6$ in presence of aliphatic amines.[13] Ordered mesostructured mesophases of SiCN materials have been prepared by Wiesner and co-workers.[20] by using a copolymer polyisoprene–polyethylene–oxide and a polysilazane as inorganic precursor.

Boron nitride has interesting physical and chemical properties (high thermal and chemical stabilities).[21] Porous boron nitride has been already synthesized and used in catalytic applications.[22,23] In our laboratory, porous boron nitride has been prepared by hard-template methods, involving mesoporous carbon template.[24,25] Others studies deal with porous boron nitride by hard-template methods.[26–28]

In this work, mesoporous boron nitride is synthesized by polymerizing a molecular boron nitride precursor in a solution containing a cationic surfactant. The tris(monomethylamino)borazine (MAB) was used as BN precursor and prepared from 2,4,6,-trichloroborazine $(HNBCl)_3$, (TCB), and methylamine.[29,30]

2. Experimental

2.1. Synthesis of precursor

All experiments involving boron compounds are carried out under a protective argon atmosphere using standard Schlenk techniques. Solvents are distilled over appropriate drying agents.

2,4,6,-Trichloroborazine $(HNBCl)_3$, (TCB) is prepared from the reaction of BCl_3 with NH_4Cl.[31] TCB is characterized by ^1H NMR ($\delta_{NH\,\text{borazinic}} = 5.30$ ppm) in $CDCl_3$ and ^{11}B

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NMR ($\delta = 29.29$ ppm). Tris(monomethylamino)borazine ($HN\text{-}B\text{-}NHCH_3)_3$, MAB is elaborated from the reaction of trichloroborazine with methylamine. MAB is characterized by ^1H NMR ($\delta_{NH\ \text{borazinic}} = 2.9$ ppm; $\delta_{CH_3} = 2.7$ ppm , $\delta_{NH} = 1.9$ ppm) in $CDCl_3$ and ^{11}B NMR ($\delta = 25.72$ ppm).

2.2. Synthesis of mesoporous BN

The synthesis of BN is realized using 1 g of MAB per 3.2 g of CTAB, with 50 mL of toluene. MAB is introduced in the CTAB solution. Polycondensation reactions of MAB are performed by heating the solution at 120 °C during 7 days, giving a translucent gel.[29,30] The solvent is then eliminated under vacuum for 8 h and ceramization is carried out under ammonia at 1000 °C (50 °C/h). The ceramization of polycondensed MAB leads to boron nitride, while the organic phase is eliminated which will generate porosity. Thermal behaviour is studied by using thermal treatment under nitrogen performed at 1400 °C, at 1600 °C and up to 1700 °C (for 2 h).

2.3. Characterization

The porous boron nitride is characterized by Nitrogen adsorption/desorption isotherms, X-ray diffraction, FT-IR and transmission electronic microscopy. Powder X-ray diffraction (XRD) patterns are recorded on a Philips PW 3710/3020 diffractometer equipped with a monochromator, using Cu Kα radiation. FT-IR spectra are recorded on a Nicolet Magna-IR 550 spectrophotometer between 400 and 4000 cm^{-1}, using KBr pellets. Nitrogen adsorption/desorption isotherms are measured on a Sorptomatic 1900 analyser (Fisons). Before the adsorption measurements, the samples are outgased for 4 h at 150 °C in the degas port of the adsorption analyser. The BET specific surface area is calculated from the nitrogen adsorption data in the relative pressure range from 0.05 to 0.3. The pore size distribution is analysed with N_2 adsorption branch, following the BJH (Barret–Joyner–Halenda) algorithm. The mesoporous volume is calculated between a relative pressure of 0.42 and 0.95. The TEM images are taken with a TOPCON EM002B transmission electron microscope operated at 200 kV. Samples for the TEM measurement are supported on a carbon-coated grid.

3. Results and discussion

X-ray diffractogram of the boron nitride BN prepared at 1000 °C is presented in Fig. 1. Two peaks are present at $2\theta = 26°$ and 43° demonstrating the formation of a turbostratic phase of BN (Fig. 1).[21,29]

FT-IR spectrum of boron nitride BN prepared at 1000 °C is presented in Fig. 2a. The boron nitride formation is confirmed since the ν(B–N) and δ(B–N) vibrations are observed at 1400 and 800 cm^{-1}.[21,29] Two broad bands around 3430 and 3250 cm^{-1} are also present and can be attributed to a ν(N–H) and ν(BO–H) vibrations.[21] Weak bands between 3000 and 2800 cm^{-1} can be identified as C–H bands. Their presences reveal that ceramization of boron nitride is uncomplete at this temperature.

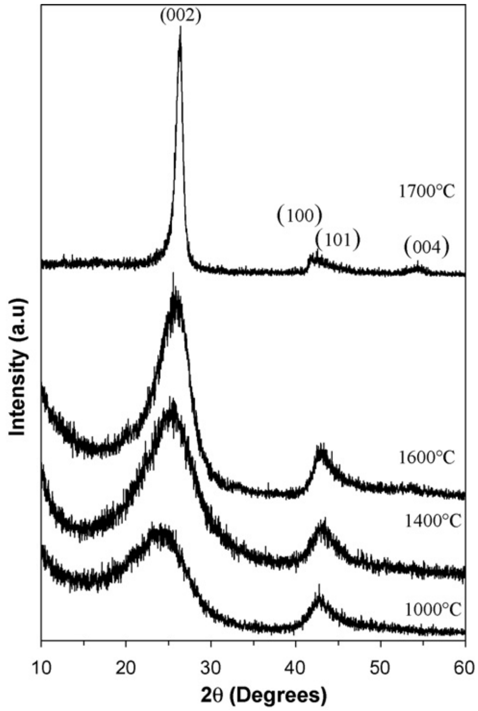

Fig. 1. XRD patterns of boron nitride BN after ceramization at 1000 °C, after thermal treatment at 1400, 1600 and 1700 °C.

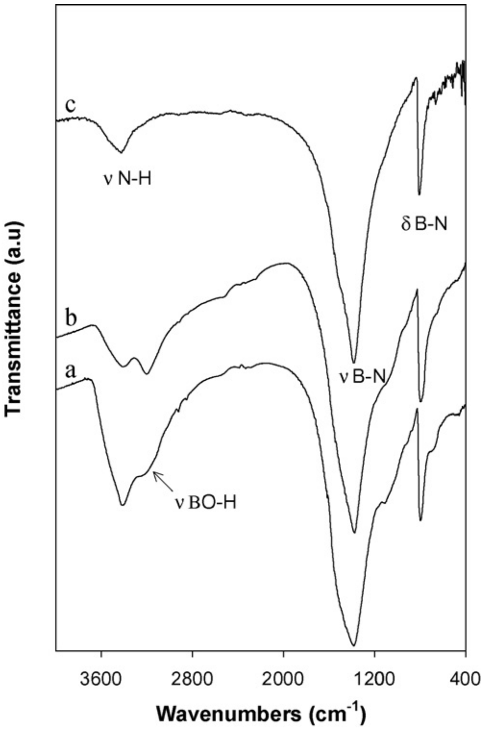

Fig. 2. FT-IR spectra of boron nitride BN after ceramization at 1000 °C (a), after thermal treatment at 1400 °C (b) and 1600 °C (c).

The transmission electron micrographs reveal that the texture is porous (Fig. 3). Mesoporosity is observed with pores of a diameter about 4 nm (Fig. 3A), equally localized on the all surface of solid. The pore size distribution seems to be monodis-

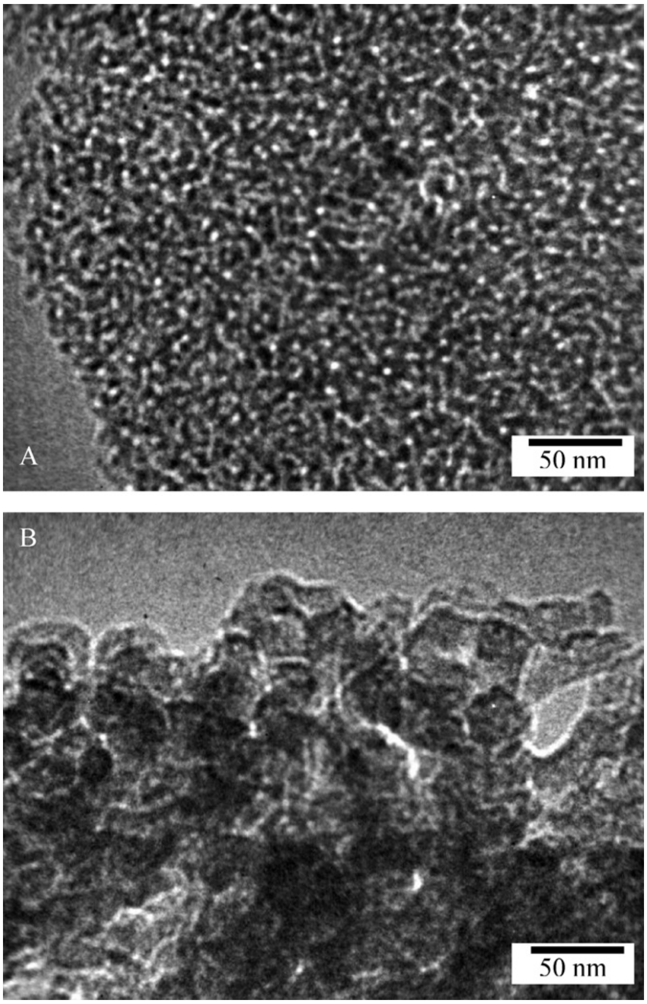

Fig. 3. Representative transmission electron micrographs of the boron nitride BN (at 1000 °C).

perse. Moreover, non-porous polycrystalline grains of approximatively 30 nm in diameter are noted. They can be responsible for a large intergranular mesoporosity (Fig. 3B).

Figs. 4 and 5 show nitrogen adsorption–desorption isotherms and corresponding pore size distribution of boron nitride. The desorption branch of the nitrogen isotherms of the BN sample reveal steps at relative pressures of about 0.45 (Fig. 4), which must be attributed to capillary evaporation in a mesoporous structure. This observed step at P/P_0 0.45, on all desorption branches, results from the meniscus instability.[32] Isotherm is between types II and IV and the hysteresis loop is of type H_2. Specific surface area of BN is 820 m^2/g and the mesoporous volume is 0.44 cm^3/g. The pore size distribution is very broad (Fig. 5). The mean value is 6.0 nm in diameter, in agreement with the TEM analysis. The pore size may be related to the size of micelles formed by CTAB in toluene.

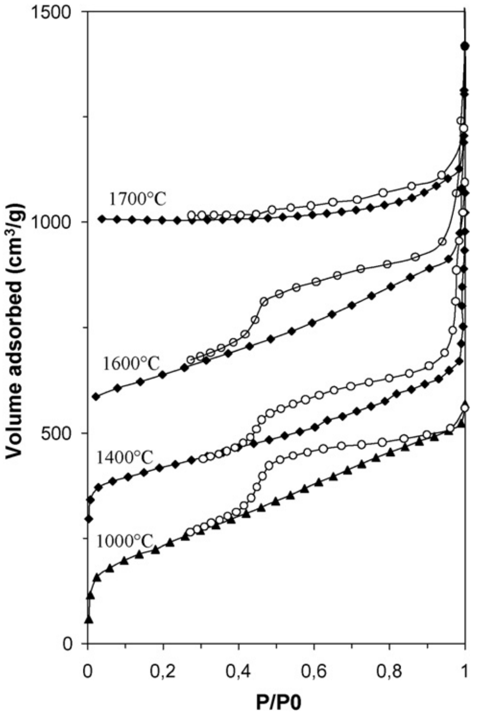

Fig. 4. Nitrogen adsorption/desorption isotherms of boron nitride (BN), after ceramization at 1000 °C, after thermal treatment at 1400, 1600 and 1700 °C (shifted from 250, 500 and 1000 cm^3/g).

Thermal treatments at 1400, 1600 and 1700 °C under nitrogen have been performed to evaluate the mesoporosity stability. On the XRD pattern, hexagonal boron nitride crystallisation is noted at 1600 °C (Fig. 1). Reflections (0 2) and (1 0) are sharper. The (0 0 4) reflection appears at 1700 °C (at $2\theta = 54°$). The crystallites size L_c is increased from 1.7 nm at 1000 °C to 9.2 nm at 1700 °C (Table 1). The *c* parameter is decreased from 7.3 Å at 1000 °C to 6.7 Å at 1700 °C while the c parameter of h-BN is of 6.66 Å.

Hexagonal boron nitride crystallisation is confirmed by FT-IR analyses (Fig. 2c) since the boron-nitrogen vibration bands become sharper. The presence of the N–H vibration band at 3430 cm^{-1} can be explained by the uncomplete mineralization of the boron nitride at 1600 °C.

Nitrogen adsorption/desorption isotherms of samples treated at 1400 and 1600 °C exhibits an hysteresis loop of H_2 type. But, isotherm of the sample treated at 1700 °C is flat, which reveals the loss of porosity. Thermal treatments at 1400 and 1600 °C induce a decrease of the specific surface area and a conservation of both the mesoporous volume and the pore size (Table 1).

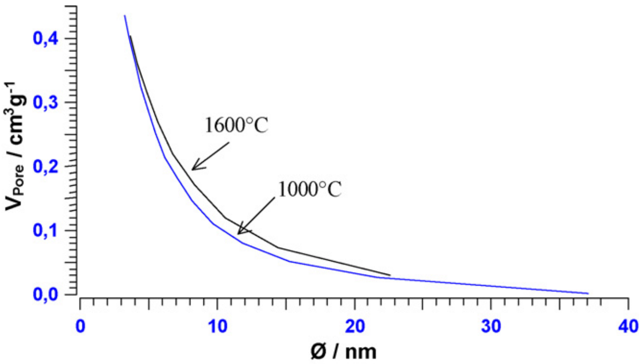

Fig. 5. Pore size distribution of boron nitride (BN), after ceramization at 1000 °C, after thermal treatment at 1600 °C.

Table 1
Textural properties of boron nitride (BN) after ceramization at 1000 °C, after thermal treatment at 1400, 1600 and 1700 °C

Temperature (°C)	Surface area (m^2/g)	Area from mesopores (m^2/g)	Pore volume (cm^3/g)	Mesopore volume (cm^3/g)	Pore size (nm)	c (Å)	L_c (nm)
1000	820	300	0.74	0.44	6.0	7.3	1.6
1400	600	240	0.60	0.39	7.0	6.9	1.6
1600	510	275	0.59	0.44	6.7	6.8	2.2
1700	30	65	0.15	0.10	–	6.7	7.8

Surface area: specific surface area according to BET; pore volume: total pore volume at $P/P_0 = 0.95$; mesoporous volume: calculated according to BJH (adsorption branch between $0.4 < P/P_0 < 0.95$); pore size: mean of pore diameter according to BJH (adsorption branch); c parameter from (0 0 2) reflection; L_c: crystallite size.

Hexagonal boron nitride crystallisation coincide with the disappearance of mesoporosity. Mesoporous volume and mesopores diameter evolutions may be related to the progressive disappearance of the microporosity. Before the h-BN crystallisation, some micropores diffuse into mesopores and coalesce with them. So, there is a slight increase of the mesopores diameter and a mesoporous volume conservation. When microporosity has disappeared, the crystallites growth by sintering may occur. Crystallites growth and their fast reorganization into h-BN lead to the mesoporosity abrupt disappearance.

The thermal stability of mesoporous boron nitride may be compared with others mesoporous materials such as carbon and silica. The MCM-41 mesoporous silica molecular sieve has been reported to collapse at 800 °C, while crystallization of the cristobalite phase occurs at 1000 °C.[33] In case of the SBA-15 mesoporous silica molecular sieve, mesoporosity is maintained up to 1000 °C.[34]

The mesoporosity of CMK-3 carbon is preserved up to 1600 °C under inert atmosphere, while microporosity is decreased during heating and disappeared at 1600 °C.[35]

Others surfactants have been tried for the synthesis of mesoporous boron nitride such as block copolymers or aliphatic amines, but unsuccessful results have been obtained.

Our result should be compared with previous works on porous boron nitride. In the case of aerogels synthesized by Lindquist et al.,[22] surface area between 300 and 600 m^2/g have been measured. The surface area and the pore volume of aerogels decrease with increasing temperature in the range 1200–1600 °C. A micropore coalescence followed by crystallization is supposed to occur. A supercritically drying process is needed. In the work of Bonnetot and co-workers.,[23] the use of ammonolysis of trichloroborazine leads to porous boron nitride with specific surface area of 300 m^2/g at 1800 °C. Mesopores from 2 to 20 nm and micropores (smaller than 2 nm) have been reported.

4. Conclusion

In summary, a mesoporous boron nitride with a specific surface area of 800 m^2/g, a mesoporous volume of 0.5 cm^3/g, and a pore size distribution with a mean value on 6.0 nm in diameter, has been synthesized from tris(monomethylamino)borazine as boron nitride source and cetyltrimethylammonium as template. The nitrogen adsorption/desorption isotherms and TEM analyses clearly show that the boron nitride is mesostructured. The mesoporosity is preserved up to 1600 °C under an inert atmosphere. This soft-template route is then a simple way to obtain mesoporous boron nitride.

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