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Boron nitride: A high potential support for combustion catalysts

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Abstract

High surface area BN powders have been prepared from different precursors to be used as supports for noble metal catalysts. The more suitable boron nitride powders were obtained using polytrichoroborazine, pTCB, as precursor, leading to a surface area higher than 150 m^2/g. The BN powders were characterized by XRD, XPS, TG, SEM and adsorption microcalorimetry measurements (aniline and ammonia). The preliminary results showed a remarkable stability of the BN supports, even in the presence of moisture. Palladium impregnation of the BN powders was performed using a classical method and the obtained catalysts exhibited a high dispersion with Pd particles of about 4 nm.

Keywords: Boron nitride; Catalyst; Support; Palladium; Acidity

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1. Introduction

Catalyst supports are usually high surface area oxides on which an active phase (e.g. a noble metal) is dispersed. However, the metal oxides traditionally used as supports (such as alumina or silica) possess a low thermal conductivity and a high sensibility to moisture [1–4]. Moreover, particularly for oxide supported metal catalysts, the metal–support interaction has very often a negative influence on the catalytic activity. Consequently, for such case a non-oxide support has been considered [5,6].

Boron nitride (BN), a non-oxide ceramic, can be an interesting support. The hexagonal boron nitride phase, h-BN, is the most common crystallographic form of BN [7]. Due to its thermal properties and chemical inertness, h-BN is very promising for applications under hard operating conditions. The high thermal conductivity (125 W/m K for BN versus 23 W/m K for Al_2O_3) could be a solution to dissipate the important energy of the metal active sites during the oxidation of hydrocarbon moieties and to preserve the catalyst efficiency for a longer life time. When a catalyst is used in a combustion reaction, partial oxidation of hydrocarbons or catalytic oxidation of volatile compounds, small amounts of carbon residues (coke) may occur on the catalyst surface and the efficiency of the catalysts progressively decreases. Boron nitride presents a higher stability towards oxidation than carbon, so carbon deposits can be successfully burned on the surface of the support and consequently the catalyst regenerated and suitable for a new run. Moreover, boron nitride is hydrophobic, which prevents moisture condensation on its surface [7–9]. Crystallized h-BN is not attacked by water or any mineral acids except hydrogen fluoride, and is very resistant to any chemical attack [10,11].

Volter et al. [12] and Aryafar and Zaera [13] both concluded that hydrocarbon oxidation reaction over noble metal (Pt) occurs more easily on the reduced sites than on oxidized sites. Lin et al. [7] who compared the activity for oxidation of benzene of Pt/h-BN and Pt/Al_2O_3 have found that the difference between the activities of these catalysts (lower for Pt/Al_2O_3) is due to the fact that platinum particles are more easily maintained in their reduced state on boron

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nitride support. Platinum binds generally more weakly on boron nitride than on γ-alumina; this weaker bonding allows Pt particles to remain in the reduced state. A weaker bonding between BN and supported reduced states of Pt or Pd particles facilitates a higher mobility of surface oxygen, thus promoting hydrocarbon oxidation [3].

In this paper we report about characterization of some high surface area boron nitride, with the aim of finding an appropriate support for noble metal (Pt, Pd) catalysts for C_1–C_3 hydrocarbon combustion.

2. Experimental

Three high surface area boron nitride powders have been prepared from three different precursors, namely: (a) trichloroborazine (TCB), containing a large amount of TCB polymers (precursor P_I) [9], (b) polytrimethylaminoborazines ($-(NMe)_3-[BNH]_3$) obtained through the polymerization of trimethylaminoborazines $(MeNH[BNH])_3$ (precursor P_{II}) and (c) polyborazylenic polymer obtained from the thermolysis of borazine $[HBNH]_3$ (precursor P_{III}). The boron nitride powders were prepared from these precursors by using appropriate thermolysis conditions (ceramisation under ammonia flow). Details of the procedures of preparation have been published previously [9].

The impregnations of the obtained powders were realized using a classical wet process. The palladium precursor was $Pd(NO_3)_2$ hydrate from Strem Chemicals (40 wt.% Pd). In a typical experiment, required quantities of the precursor and support were dissolved in a minimum volume of water and mixed together by stirring at room temperature for 7 h. After drying overnight at 110 °C the samples were calcinated in air flow at 500 °C for 12 h, and then cooled down under the same gas flow.

The concentrations of the supported palladium were determined by chemical analysis using inductively coupled plasma emission spectroscopy (ICP). For that purpose, the samples were treated with a mixture of $HCl + HF + HNO_3$ in order to dissolve them completely. In addition we also performed XPS analysis.

The physicochemical characteristics of the powders and the catalysts were determined using several techniques:

- the specific surface area of the samples which was calculated from N_2 adsorption, by using BET equation. Prior to surface area determination, the powders were outgazed at 100 °C overnight and then 6 h at 400 °C.
- the pore size distribution of each sample was determined by desorption isotherm measurements, using an ASAP 2010 M apparatus, from Micromeritics.
- the crystalline structure of h-BN phase was examined by X-ray diffraction in a Bruker (Siemens) D5005 apparatus (Cu Kα radiation, 0.154 nm).
- the XPS analysis were performed with an SSI (Surface Science Instruments) 301 spectrophotometer using a monochromatic Al Kα radiation. The 1s binding energy of boron was considered to survey the surface chemical species of the h-BN samples.
- the morphology of the different samples has been examined using SEM and the palladium dispersion and particles size measured by TEM. SEM images were obtained from a Jeol 55 CF (CMEABG Lyon) and TEM pictures were recorded using a Jeol 2010 (IRC Lyon).
- TG experiments were performed in a TG-DSC 111 apparatus from Setaram.
- the acidic properties of the samples were determined using calorimetry both in gas phase (NH_3) and liquid phase (aniline titration). The microcalorimetric studies of ammonia adsorption were performed at 80 °C in a heat flow calorimeter (C80 from Setaram) linked to a conventional volumetric apparatus and equipped with a Barocel capacitance manometer for pressure measurements. The samples were pretreated in a quartz cell by heating overnight under vacuum at 400 °C. The differential heats of adsorption were measured as a function of coverage by repeatedly sending small doses of ammonia gas onto the catalysts until an equilibrium pressure of about 67 Pa was reached [14]. The sample was then outgassed for 30 min at the same temperature and a second adsorption was performed at 80 °C until an equilibrium pressure of about 27 Pa was attained in order to calculate the amount of irreversibly chemisorbed ammonia at this pressure.

  For the calorimetric studies in liquid phase (*n*-decane) a Setaram "Titrys" microcalorimeter was used. The samples were activated under vacuum overnight at 100 °C and then 4 h at 400 °C; this was followed by a swelling in 1.5 mL decane in the calorimetric cell, with the same volume of decane in the reference cell. The experiments were performed at 40 °C. The titrant—a solution of aniline in decane, 0.03 M—was added to the cell using 0.2 mL doses at 2 h intervals, until no adsorption was observed. The heat evolved from aniline adsorption on the acidic sites of BN samples was measured for each addition and the cumulative heats plotted versus the amount of added base.
- *TPR measurements*. The samples were placed in a quartz tube reactor and heated up to 600 °C with a heating rate of 5 °C/min in different atmosphere (1% H_2/Ar or 1% O_2/He). The hydrogen/oxygen concentration at the outlet of the reactor was measured by a catharometer connected with a recorder. The total gas flow rate was 20 cm^3/min and the samples weight around 0.05 g.

3. Results and discussion

Table 1 lists the specific surface areas, the XRD data and the XPS results for the BN samples and Pd/BN-P_I catalyst.

As shown, all BN powders exhibit surface areas higher than 100 m^2/g. The largest surface area (375 m^2/g) was obtained for BN-P_{II} but the XPS analysis showed the presence of oxygen as contaminant.

Table 1
Physicochemical characteristics of the samples

Sample	S_{BET} (m^2/g)	XPS results in atomic percent data							XRD	
		B (%)	Pd (%)	O (%)	C (%)	N (%)	B 1s (eV)		d_{002} (Å)	La/Lc
BN-P_I	184	49.3	–	3.6	4.2	42.9	BN: 190.5, 100%		3.361	2.61
BN-P_{II}	375	48.3	–	6.6	2.1	42.9	BN:190.5, 95%	B_2O_3: 192.9, 5%	3.380	2.88
BN-P_{III}	115	48.3	–	7.2	4.7	39.8	BN:190.5, 97%	B_2O_3: 193, 3%	3.349	3.22
Pd/BN-P_I	233	49.2	2.2	5.3	2.5	40.8	BN:190.5, 100%			

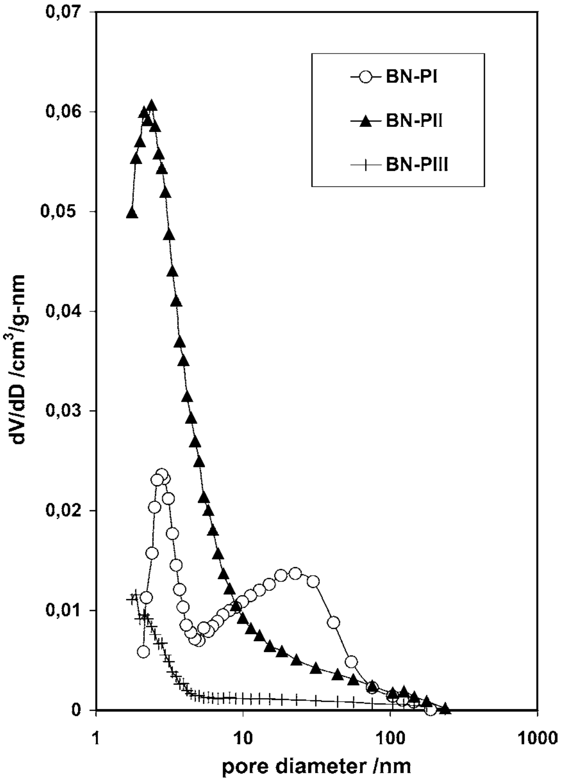

Fig. 1. Pore repartition in the BN samples.

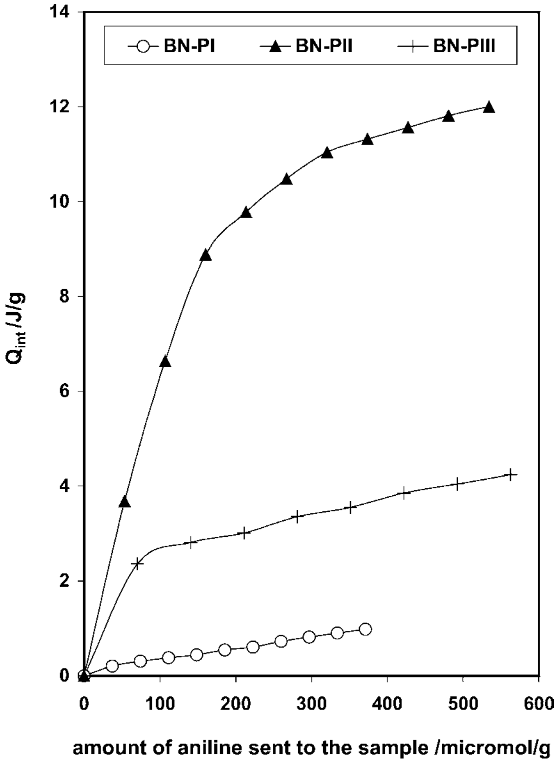

Fig. 2. Integral heats (J/g) during adsorption of aniline at 40 °C for BN samples.

The crystallisation of boron nitride phases was low, in spite of the high temperature used for annealing (1800 °C). The XRD diffraction patterns obtained using the samples showed a very low crystallisation of h-BN. Only the 0 0 2 line appeared clearly and the 1 0 0 and 0 1 0 diffraction lines remained unresolved. As described in the literature [15] the characteristics of the turbostratic form of lamellar compound such as graphite and h-BN, can be determined by the crystallites size specially along the *a* axis, La (using the 1 0 0 and 0 1 0 diffractions) and the *c* axis, Lc, 0 0 2 line. The La/Lc value is a characteristic of the crystallisation of the compound. In fact the crystallisation of the BN supports decreased from precursor P_{III} to P_I as already described in Table 1, and the values obtained are consistent with a low organised turbostratic h-BN. No diffraction lines corresponding to boron oxide can be seen.

As shown in Table 1 from the XPS results of the BN samples compared to a standard highly crystalline hexagonal BN (B 1s: 190.3 eV [7] or B 1s: 190.1 eV [10]), the binding energy of B 1s (eV) indicate a positive shift. It means that in

Table 2
Calorimetric data of NH_3 adsorption at 80 °C

Sample	V_t (μmol/g)	V_{reads} (μmol/g)	V_{irrev}		Number of acid sites micromol NH_3/g sample		
			μmol/g	%	$50 < Q < 100$	$100 < Q < 120$	$120 < Q < 150$
BN-P_I	83	35	48	58	33	5	4
BN-P_{II}	528	231	296	56	276	95	53
BN-P_{III}	474	160	314	66	226	73	82

Acidic sites strength distribution of the supports.

Table 3
Weight loss of BN samples during heating up to 600 °C

Sample	Mass loss (%)
BN-P_I	0.45
BN-P_{II}	5.44
BN-P_{III}	9.12
BN-P_{III} (after 3 days in air)	10.86

spite of higher temperature of calcination the samples display residual B–O bonds which induce a positive binding energy shift. For BN-P_{II} and BN-P_{III} samples, the B 1s binding energies of two kinds of boron bonds are observed. Signals at 190.5 eV are specific of pure BN while 193 eV correspond to B–O.

Two types of pores were observed: large mesopores from 4 to 30 nm and a small microporosity with pores about 2 nm enhancing the surface area. Although the surface area of samples was different, the pores repartitions appear to be comparable with a constant meso to microporosity. This remark is illustrated in Fig. 1 where the microporosity of the BN-P_I sample is more important than for the other samples.

Calorimetric experiments with adsorption of basic probe molecules (aniline in liquid phase or ammonia in gas phase) were performed in order to obtain information about the acidic strength and distribution by strengths of surface sites for the three supports. Aniline is less basic than ammonia, due to the electron withdrawing effect of the benzene ring on the electron density of the –NH_2 group. The differences

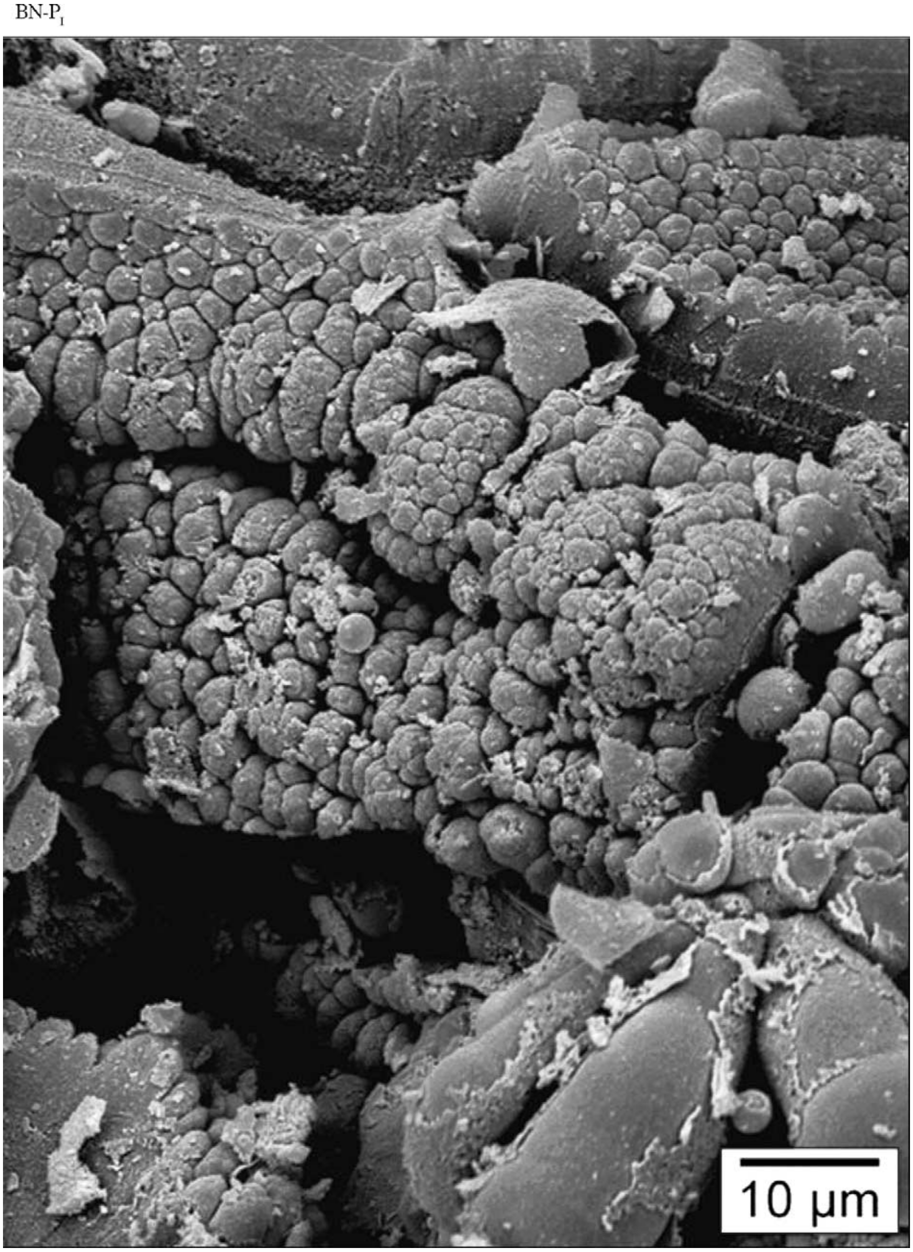

Fig. 3. SEM for BN-P_I and BN-P_{II} samples.

BN-P_{II}

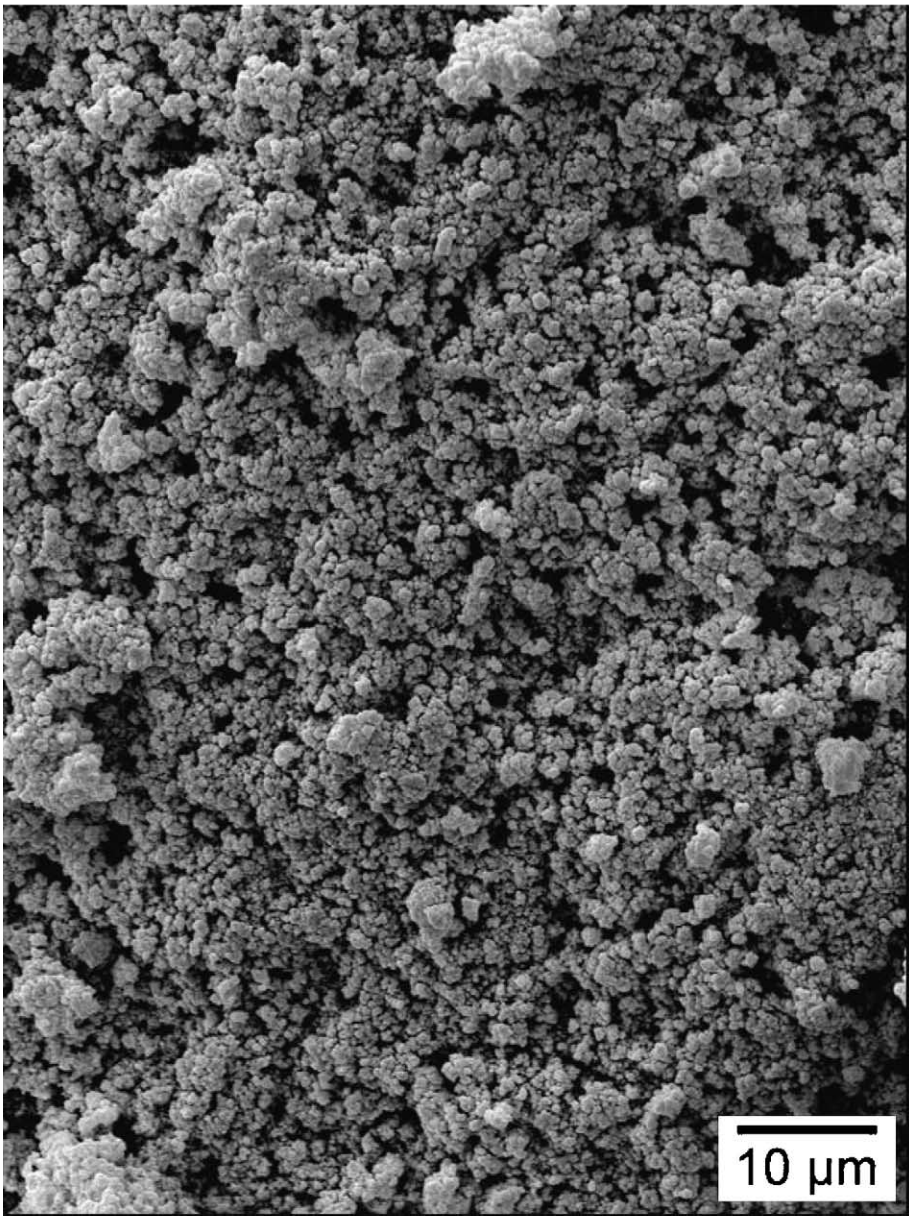

Fig. 3. (*Continued*).

between powders consist in the strengths of acidic sites which differ as a function of preparation methods as it is shown in Fig. 2.

Calorimetric measurements using ammonia as a probe molecule (gas–solid interaction) were also performed. It is generally recognized that ammonia is an excellent probe molecule for testing the acidic properties of solid catalysts as its strong basicity and small molecular size allow for detection of acidic sites located also in very narrow pores.

In spite of the relative similarity between values of the initial heats of NH_3 adsorption on the three samples (124 kJ/mol for BN-P_I, 125 kJ/mol for BN-P_{II} and 148 kJ/mol for BN-P_{III}) the amount of irreversibly adsorbed ammonia, calculated at equilibrium pressure of 27 Pa (which evaluates the number of strong chemisorption sites), decreases as in the sequence BN-P_{III} > BN-P_{II} > BN-P_I. However, although the volume of total acidic sites is different for each sample, the percentage of volume of ammonia irreversibly adsorbed is approximately the same, as it can be seen in Table 2. The acidic site strength distributions are also presented in Table 2. It is obvious that no discrimination between Bronsted and Lewis acid sites can be made based of these results. When XPS of N 1s measurements were performed after ammonia adsorption, only Lewis acid sites were found for all BN samples.

TG experiments were also performed in order to compare the level of hydration of the samples. The results are shown in Table 3. The biggest weight loss was obtained for the BN-P_{III} sample (which has the smallest surface area) and the endothermic effect was smaller than it was observed for BN-P_{II} (with the highest surface area). So, the water species are weakly bonded on the BN-P_{III} sample. The same experiments for the same batch of BN-P_{III} sample were repeated (i.e. previously submitted to TG experiment) after 3 days of stay in laboratory air in order to see if it was sensible to atmospheric humidity, and if the amount of weight loss was reproducible. The percentage of weight loss was found to be comparable (a little higher in this case).

These TG-DSC measurements under air flow up to 600 °C showed also the remarkable thermal stability of all BN samples and especially for BN-P_I powder.

Moreover, the XRD spectra performed for all samples after repeated cycles of heating (up to 400 °C)-cooling in different atmospheres (inert, dry and humid oxygen flows) showed that the structure of BN powders remains unchanged without oxide diffraction lines apparition.

The morphology of the different samples can also be related to the precursor. Fig. 3 exhibits typical SEM micrographs of BN-P_I and BN-P_{II} (due to similarity between BN-P_{II} and BN-P_{III} samples, only SEM pictures for BN-P_I and BN-P_{II} are represented), showing the structure of the different powders. It can be easily seen that the BN sample obtained from P_{II} precursor has a granules aspect, while BN-P_I seems to be formed of ball shaped powders.

It is likely that the presence of boron oxide is responsible of the different behaviour of the samples obtained from P_{II} and P_{III} precursors compared to BN-P_I (which has the smallest acidity and the highest stability under oxidative atmosphere).

The BN powders were impregnated using a classical aqueous method, leading to BN-supported Pd (1 wt.%) catalysts.

The supported catalysts were also characterized using the classical methods: BET, XRD, XPS, SEM, TEM, TPR-TPO and ammonia adsorption microcalorimetry measurements.

Catalysts were prepared from the three supports even with those obtained from P_{II} and P_{III} in spite of the presence of oxide. As boron oxide is known to be soluble in water, the amount of oxygen in the catalyst should decrease after Pd impregnation. The XPS results obtained on the catalysts showed a small increasing of the oxygen amount. The presence of oxygen on the surface of these two powders and on the Pd catalysts obtained from these supports could be related to the incorporation of oxygen in place of nitrogen in the framework of the boron nitride hexagons, leading to a $B_3N_{3-x}O_x$ structure, in which the oxyde part could not be dissolved and removed from the oxi-nitride which it is not a mixture of BN and B_2O_3.

The properties of samples are not affected by impregnation (e.g. porosity, acidity, etc.). It is evidenced by the comparison of acidity of supports and catalysts as shown in Fig. 4 and Tables 2 and 4.

Transmission electron microscopy (TEM) was employed to determine the dispersion and the size of palladium particles deposited on BN. The picture obtained shows a very good dispersion of the palladium particles on the surface of the boron nitride (Fig. 5A). The nano-crystalline parts of the support clearly appear as described in a previous paper [9]. The small 1–5 μm BN powder grains observed using SEM are effectively surrounded by a crystalline nano-coating of about 10 BN layers. The size distribution of the palladium catalyst particles has been determined. An automatic measurement using a commercial program has not led to convenient results because the automatic choice of the measured particles was focused on the more contrasted grains and was not representative of the sample. A manual measurement of 100 particles has been done including all the particles. The histogram is given in Fig. 5B. A very homogeneous size repartition can be noted with an average value of 3.8 nm and a standard deviation of ±0.9 nm.

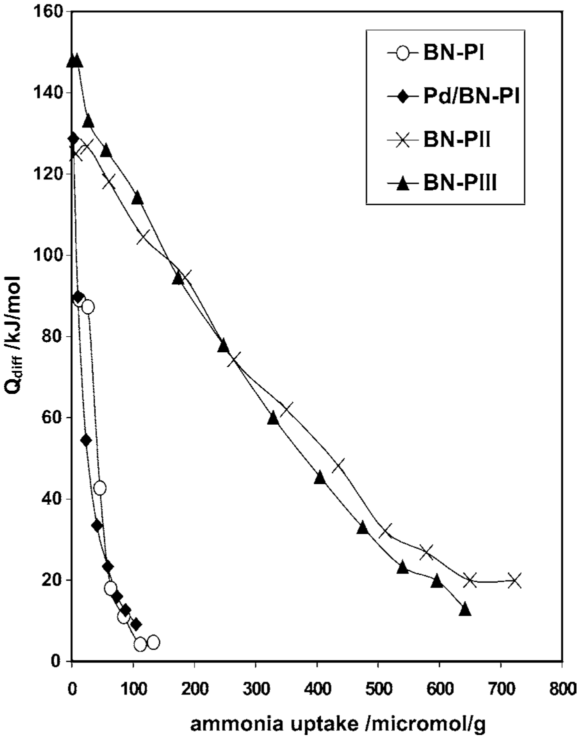

Fig. 4. Differential heats of NH_3 adsorption at 80 °C vs. adsorbed amount on BN supports and Pd/BN-P_I catalyst.

The total amount of palladium was determined using chemical analysis and XPS. The results yielding from XPS technique (2.2 at.% or 16.1 wt.%, Table 1) were very different of the averaged values obtained from chemical determination, 0.97 wt.%. These results confirm that the palladium

Table 4
Calorimetric data of NH_3 adsorption at 80 °C for the Pd/BN samples

Sample	V_t (μmol/g)	V_{reads} (μmol/g)	V_{irrev}	
			μmol/g	%
Pd/BN-P_I	74	38	36	49
Pd/BN-P_{II}	642	219	423	66
Pd/BN-P_{III}	589	161	428	73

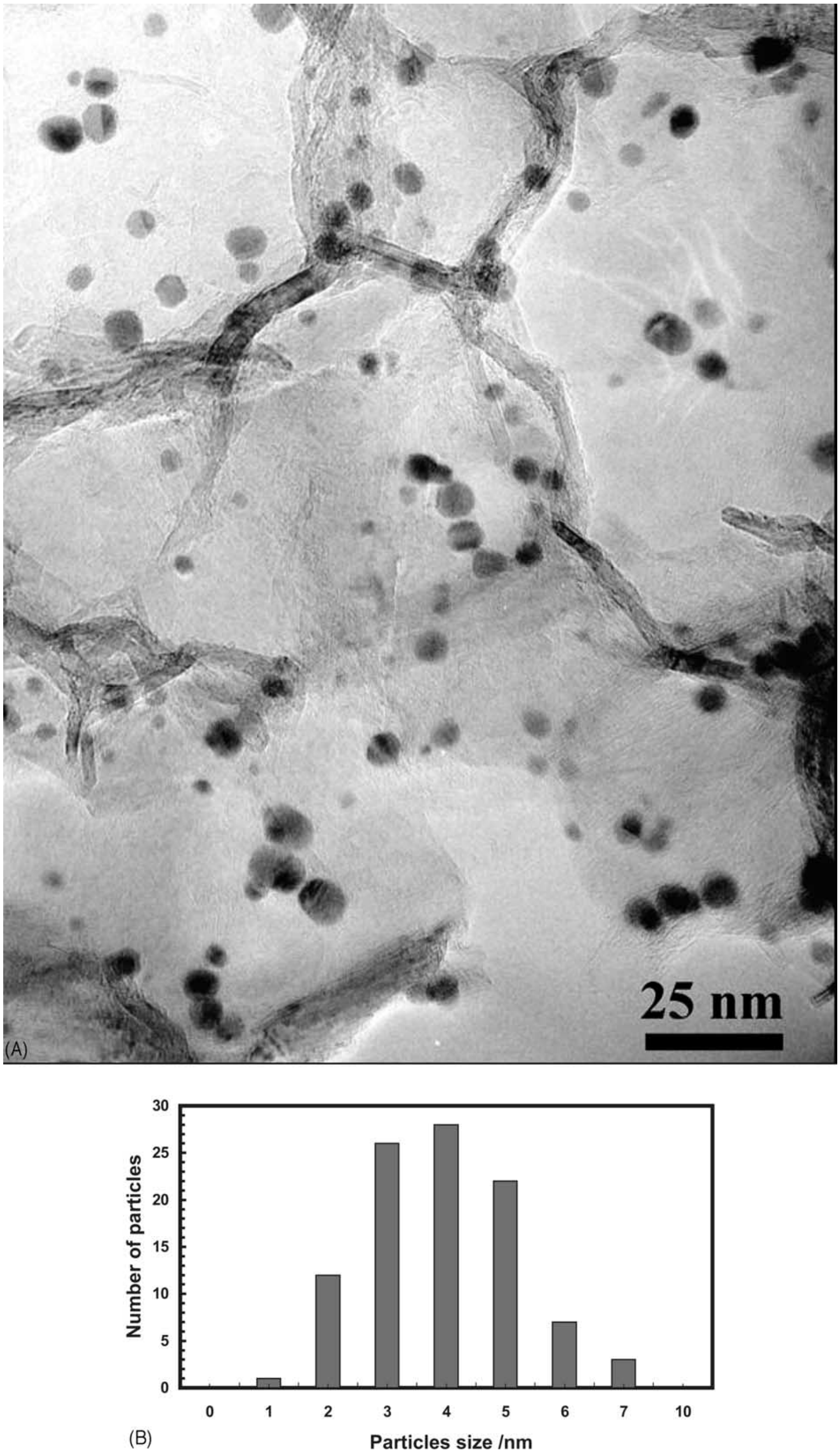

Fig. 5. (A) TEM for Pd/BN-P_I. (B) Size distribution of palladium particles as deduced from TEM measurements.

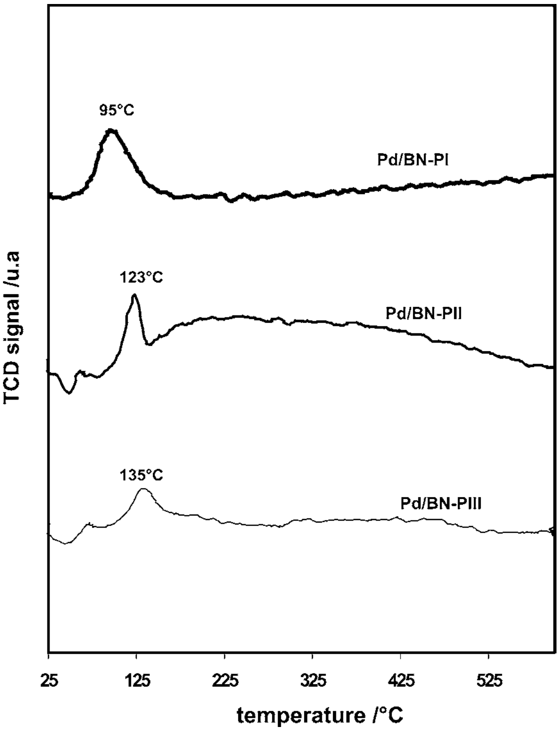

Fig. 6. TPR profiles for Pd/BN samples.

deposited on BN-P_I remains on the support surface that is of interest for enhanced catalytic activity.

Temperature programmed reduction (TPR) was performed on Pd/BN samples. Fresh catalyst (about 0.05 g) was reduced under 1% H_2/Ar flow during increasing temperature up to 600 °C (with a heating rate of 5 °C/min). After cooling to near 50 °C, the sample was purged under argon, and then submitted to a 1% O_2/He flow while the temperature was increased up to 600 °C with a heating rate of 5 °C/min. The H/Pd ratio were calculated for the various samples (using the hydrogen uptake) leading to 0.74, 0.37 and 0.43 for Pd/BN-P_I, Pd/BN-P_{II} and Pd/BN-P_{III} respectively. These values confirm the results obtained by XPS and TEM: palladium is highly dispersed on Pd/BN-P_I. Fig. 6 displays the TPR profiles. For Pd/BN-P_I, only one reduction peak was observed near 95 °C due to the reduction of PdO. For the other two catalysts, the maximum of temperature corresponding to the reduction peaks are slightly shifted to higher temperature.

4. Conclusion

Thermal conducting high surface area boron nitride powders have been prepared and characterized from various molecular precursors. The more pure and stable powders were obtained from poly-haloborazine precursors with a 184 m^2/g surface area and a high resistance to oxidation up to 600 °C. These powders transformed in palladium supported catalysts showed a great metal dispersion with a Pd particles size of about 3.8 nm.

The thermal stability of the BN supports and the weak chemical support–active species interaction lead to a catalyst which could be used under very hard working conditions like methane oxidation or hydrocarbon cracking without any decreasing activity.

The very high palladium dispersion on the support surface coupled to a very small and homogeneous particles size should yield to a very active catalyst as the preliminary catalytic test have revealed. For methane cracking, a by-pass system involving cracking of hydrocarbon compounds yielding to hydrogen and stacked carbon on the catalyst, followed by a carbon oxidation leading to the catalyst activity recovering without performance lowering, followed by a carbon dioxide sequestration seems to be easily obtained from this new generation of catalysts.

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