

Oxidative dehydrogenation of propane over the boron-nitride catalysts

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Boron nitride (BN) has been found as a competitor for currently used catalysts employed in the oxidative dehydrogenation (ODH) of light alkanes, offering a high productivity of their transformation into olefins, low CO₂ emission, and thermal stability under the oxidative atmosphere. In this research, different BNs were synthesized by thermal treatment of different mixtures of precursors at different temperatures. For comparison, commercial BNs were tested as well. Catalytic behavior in propane ODH was investigated for the reaction mixture at atmospheric pressure. BN-based catalysts were characterized by powder XRD, SEM, EDS, XPS, Raman spectroscopy, and N₂-adsorption/desorption isotherms, in order to obtain details on crystallinity, morphology, surface chemistry, chemical analysis, textural properties, etc. The productivity obtained for the prepared catalysts reached 1.4 g_{olefins} h⁻¹ g_{cat}⁻¹, exhibiting higher values for the desired products, compared to the other studies with commercial products.

Keywords: Oxidative dehydrogenation of propane; Boron nitride; Catalyst; Propene

Introduction

Light olefins are one of the crucial feeds with high consumption in chemical industries, where global demands for these substances are rising every year due to their widespread use. Light olefins are usually produced by steam cracking of various feedstock containing a large portion of saturated hydrocarbons (such as naphtha, or LPG) that are broken down into smaller and often unsaturated,

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hydrocarbons. This petrochemical process inevitably needs a very high temperature at around 800 °C, which means tremendous energy consumption. Fluid catalytic cracking (FCC) of heavy gas oil (a portion of crude oil with boiling point above 340 °C), is the second more frequently used process to produce olefins at about 540 °C but regeneration of the spent catalysts is carried out at temperature up to 760 °C. Current conventional processes for the olefin production suffer from numerous limitations related to their high energy necessities (endothermic reactions), coke formation, selectivity control, and thermodynamic constraints [1–6]. In such a condition, the formation of other light alkanes is unavoidable, therefore, to take advantage of the produced light alkanes and convert them into olefins that are more practical, a finding of an efficient catalyst is interesting for researchers at universities and in the industry. Except for high-temperature requirements, the substitution of fossil fuels by natural gas as another abundant source is nowadays also highly desirable for the olefin production [7] as a more ecological way.

For this purpose, the oxidative dehydrogenation is one of the most promising alternatives. ODH does not suffer from the drawbacks of traditional methods, as well as its nonoxidative competitor. As an exothermic process, ODH can overcome the thermodynamic limitations of the non-oxidative dehydrogenation by the formation of water, as a stable product. Moreover, ODH displays highly positive equilibrium constant, decreasing at higher temperatures. Furthermore, the presence of oxygen minimizes undesirable coking, thus extending the catalyst usage. Moreover, light paraffins ODH can be operated at lower temperatures than those of either the thermal or the non-oxidative catalytic dehydrogenation. Then, ODH can thus offer a potential increase in the yield and energy savings while producing the desired olefins, even though a valuable product — hydrogen — is burned [6,8,9]. Approximately, up to 45 % of energy can be saved if the dehydrogenation (DH) process is substituted by ODH, for propane [10,11]. The reaction of the ODH type has been extensively studied by metal oxide-based catalysts [7,12–14]. But there remains left the most difficult challenge, which is an over-oxidation to CO_x because this reaction is more thermodynamically favorable, olefins are more reactive and as a consequence, the over-oxidation by metal oxide-based catalysts decreases the olefin selectivity [11,15]. For example, in the case of propane, the reaction enthalpies of ODH and most frequent accompanying reactions are [16]:



Vanadium and molybdenum-based catalysts were frequently studied for ODH, but they suffer from poor selectivity at conversion higher than 20 % [17]. Moreover, the catalysts based on alkali chlorides, another group of catalysts investigated for ODH reactions, have shown a high tendency to deactivate [18]. Yet another choice is a carbon material as a metal-free catalyst.

But it shows a very low reaction rate for ethane and propane conversion at the temperature lower than 500 °C, and at higher temperatures, carbon materials are not stable due to oxidation [1]. Carbon nanotubes have also been tested for this reaction, exhibiting a very low degree of propane conversion of about 5 %, while it is not appropriate to be used at a higher temperature in presence of oxygen [17].

Boron nitride (BN) is an analogue of graphene predominantly used for its electronic, thermoelectric, and mechanical properties and applicable also as special final products (so far, for instance, fillers, insulators, or lubricants [19]). Recently, BN has been showing significant catalytic activity in the ODH reaction [1,11,15]. The BN-based catalyst produces propene as the main product and ethylene as a by-product which is more desired than CO_x . Recently, a couple of research groups reported their work on this catalyst [11,16,17,20,21], among others, Herman's group proposed it for a 14% propane conversion over a hexagonal BN catalyst with 79% selectivity to propylene and 12% to ethylene. It is supposed that oxygen bonded to boron and nitrogen in an armchair edge, behaves as an active site in ODH.

It has been suggested that dehydrogenation starts with the withdrawal of the hydrogen atom from the secondary carbon of propane by the active sites, followed by breaking the O-O bond and the subsequent formation of B-OH and one nitroxyl radical. In a subsequent step, water desorption regenerates the active site (B-O-O-N). Apparently, this behavior distinguishes BN from traditional metal oxide-supported catalysts with Mars-van Krevelen mechanism [11]. Also, the hydroxylated h-BN, prepared by targeted modification of h-BN by treatment in the sodium-assisted high-temperature steam activation process, has been reported as an efficient catalyst for propane ODH, with high selectivity of around 80 % at 20% conversion and releasing a negligible amount of CO_2 [1].

It is another proof about BN's ability to suppress over-oxidation to CO_2 which has always been a negative aspect of this reaction. Later, Grant et al. have reported that the boron-containing materials, namely (B_4C), (TiB_2), (NiB), ($\text{Co}_2\text{B}/\text{Co}_3\text{B}$), (HfB_2), (WB), and the elemental boron itself, are active for the ODH of propane when showing the same product trends as boron nitride [22]. Therefore, it was concluded that boron was the necessary element to achieve the high olefin selectivity. Based on the results from X-ray photoelectron and IR-spectroscopy, they suggested the formation of an analogous surface-stabilized BO_x active site for all the boride catalysts tested. This observation contradicts the previous mechanistic hypotheses postulating that edge sites on the boron nitride would be the active ones [17].

In this paper, attention was focused on the study of physicochemical changes in the BN structure during the catalytic reaction. For this purpose, selected samples of both commercial h-BN and laboratory-prepared boron-based materials were subjected to chemical, structural, and textural characterization both before application in ODH propane and after 4 hours under reaction conditions (at 490 °C in a reaction mixture stream containing C₃H₈/O₂/He = 30/15/55 vol. %). Subsequent comparison of the information obtained has revealed that oxygen-containing boron species are the functional active sites and, unlike the reported data in the literature, the active sites are available not only at the edges and at the surface of BN, but chemical changes take also place inside the bulk of BN, showing that the B-O bond plays more crucial role than that of the B-N bond for ODH of propane.

Materials and methods

Catalysts

This research was focused on a set of samples, comprising two commercial BNs and three synthesized specimens; all being analyzed by different methods. h-BN was purchased from Sigma-Aldrich (purity: 98%, particle size: 1 μm), and Np-BN was acquired from Alfa Aesar (particle size: 5–20 nm). The BN (550) was prepared at 550 °C using the following procedure: 3.71 g boric acid + 3.78 g melamine were thoroughly mixed in 100 mL distilled water under stirring at 85 °C, giving rise, after evaporation, to a white solid. This product was dried at 85 °C for 12 h and, afterward, calcinated in a quartz crucible inside a furnace at the rate of 3 °C min⁻¹ up to 550 °C in the flow of N₂ (100 L h⁻¹) for 3 h and, finally, cooled down in ambient air [23]. BN (1050) and BN (1050 M) were prepared with the same method but differing in the precursors used. In typical synthesis, two mixtures of urea and boric acid were mutually mixed and ground. In BN (1050 M), melamine was also added to the boric acid and urea, as a secondary source of nitrogen. The molar ratio of urea-to-boric acid was 5 : 1, while that of melamine to boric acid remained 1 : 1. The prepared mixtures were placed in an alumina boat-shaped crucible and heated up to 1050 °C (10 °C min⁻¹) in the stream of N₂ gas with 50 mL min⁻¹ flow rate. The temperature was held at 1050 °C for 3.5 hours, and the furnace then allowed to cool naturally, again, under the atmosphere of N₂ [24]. The prepared catalysts and their labels are shown in Table 1.

Catalytic behavior of each sample in propane ODH was investigated in plug-flow fixed-bed tubular shape reactor, using 100 mg of catalyst at 490 °C under atmospheric pressure with WHSV = 7.1 h⁻¹, in a reaction mixture consisting of C₃H₈/O₂/He = 30/15/55 % (v/v). Before each test, the sample was pretreated by He (11 mL min⁻¹) at 490 °C for 2 h. The U-shape reactor used in this study had an inner diameter of 5 mm. Products were analyzed with an on-line gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled with a flame

ionization detector (GC-FID mode) and a thermal conductivity detector (GC-TCD). The Carboxen[®] 1000 column (60 m long with a diameter of 320 μm) was used for the separation of compounds. The injector and oven temperature was 150 $^{\circ}\text{C}$ and the detector temperature in the GC-TCD mode 270 $^{\circ}\text{C}$. Helium was used as carrier gas with a flow rate of 3 mL min^{-1} .

Table 1 Prepared catalysts and their specification

Sample	Label / type	Product number	Precursors, molar ratio
Hexagonal BN (Sigma Aldrich)	h-BN	255475	–
Nanopowder BN (Alfa Aesar)	Np-BN	44999	–
BN prepared at 550 $^{\circ}\text{C}$	BN (550)	–	boric acid : melamine 2 : 1
BN prepared at 1050 $^{\circ}\text{C}$	BN (1050)	–	boric acid : urea 1 : 5
BN prepared at 1050 $^{\circ}\text{C}$	BN (1050 M)	–	boric acid : urea : melamine 1 : 5 : 1

Characterization

Adsorption-desorption isotherms of nitrogen at -196 $^{\circ}\text{C}$ were measured using an ASAP 2020 instrument. Before each adsorption measurement, the sample was degassed to attain a slow removal of pre-adsorbed water at low temperatures. The temperature was slowly increased with a slope of 0.5 $^{\circ}\text{C min}^{-1}$ up to 110 $^{\circ}\text{C}$ and then 1 $^{\circ}\text{C min}^{-1}$ until 250 $^{\circ}\text{C}$. The sample was degassed at this temperature under a turbo molecular vacuum pump for 8 h. X-ray powder diffraction data were recorded on a D8 X-ray powder diffractometer (Bruker; Karlsruhe, Germany) equipped with a graphite monochromator and a position-sensitive detector (Vantec-1) using $\text{Cu K}\alpha$ radiation (at 40 kV and 30 mA) in Bragg–Brentano geometry. The surface chemical state of the samples was monitored by an X-ray photoelectron spectroscopy (XPS, model ESCA2SR; Scienta-Omicron; Uppsala, Sweden) using a monochromatic $\text{Al K}\alpha$ X-ray source (with 1486.7 eV). The binding energy scale was referred to appendant carbon (284.8 eV). The quantitative elemental composition of the surface was further evaluated using a scanning electron microscope (LYRA 3; Tescan, Brno, Czech Republic) equipped with an EDS analyzer (model AZtec X-Max 20; Oxford Instruments, High Wycombe, UK) at an acceleration voltage of 20 kV. Raman spectra were recorded by using a Nicolet DXR SmartRaman spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a 532 nm laser and 10 mW power. All the measurements were carried out at ambient conditions using finely ground samples without dilution. The spectrum was recorded by an accumulation of 300 scans with integration time 1 s, between 50–3300 cm^{-1} using the Omnic Software package.

Results and discussion

All the prepared BN-based catalysts exhibited stable catalytic activity in propane ODH for more than 200 min, without showing any deactivation tendency (Fig. 1). However, the individual catalysts had differed in the activity. After 25 min under the stream, BN (1050) and (1050 M) samples revealed a capability to convert propane from around 50 % with the highest production value for the propene and ethene, $1.4 \text{ g}_{\text{olefin}} \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$ despite low selectivities (cf. Table 2). The BN (550) demonstrated significantly lower efficiency, reaching approx. 31% conversion, besides similar propene and olefin productivity with h-BN. Even though the propene productivity of all the catalysts was comparable (except Np-BN), but the olefin productivity of BN (1050) and (1050 M) had reached higher values than those for commercial BNs.

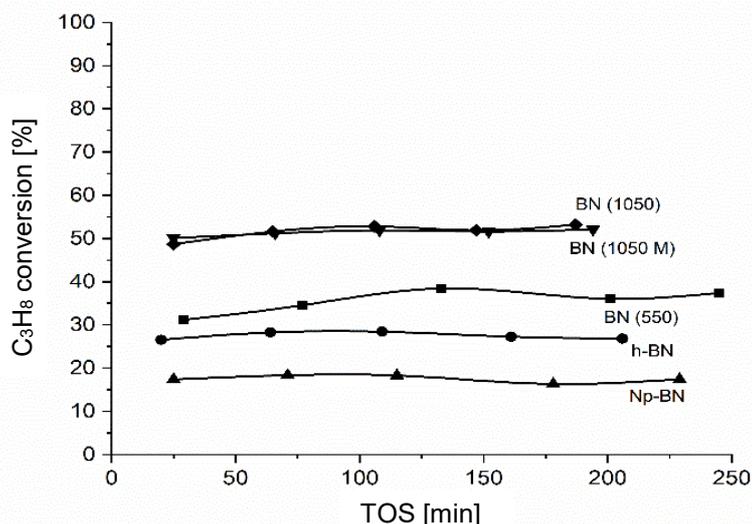


Fig. 1 Propane conversion as a function of time on stream (TOS) in ODH reaction at $490 \text{ }^\circ\text{C}$ in the flow of 20 mL min^{-1} of the mixture consisting of $\text{C}_3\text{H}_8/\text{O}_2/\text{He} = 30/15/55 \%$ (v/v)

Table 2 Propane conversion, selectivity, and productivity of the catalysts at TOS = 25 min

Sample	Propane conversion [%]	Productivity		Selectivity [%]					
		$[\text{g}^{\text{a}} \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}]$	$[\text{g}^{\text{b}} \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}]$	C_3H_6	C_2H_4	C_2H_6	CH_4	CO_2	CO
h-BN	26.6	0.9	1.1	51.2	11.8	0.4	1.8	1.1	14.5
Np-BN	17.4	0.7	0.8	63.1	10	0.4	1.4	0.8	0
BN (550)	31.1	0.9	1.1	44.7	10.3	0.3	1.6	3.4	9.9
BN (1050)	48.7	0.9	1.4	28.4	19	1.3	8.1	0	15.2
BN (1050 M)	50.1	0.9	1.3	26.2	19.9	1.6	9.5	0	14.8

^a propene; ^b propene + ethene

The limit value below which the productivity is too low to be interesting for commercial applications is $1 \text{ g}_{\text{olefin}} \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$ [13]. The selectivity varies by time on stream for different catalysts (e.g. for different steady-state propane conversions; Fig. 2). The degree of the CO_2 selectivity was kept negligible, below 3.4 % but the CO selectivity showed a wider range from 0 to 15.2 % for a product studied (Fig. 3). The methane and ethane selectivity changed between 1.4–9.5 % and 0.3–1.6 %, respectively. A relatively high production of methane has indicated a non-negligible rate of cracking reaction. For simplicity, in Table 2, the number of unknown by-products is not mentioned.

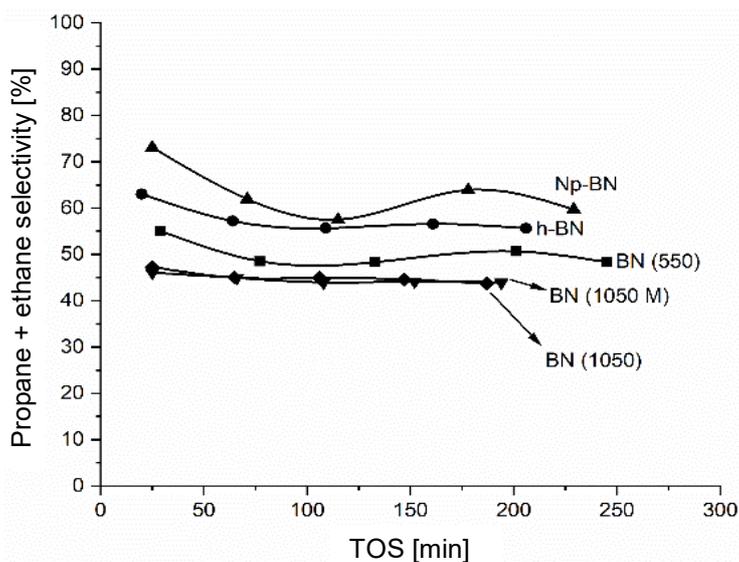


Fig. 2 Propene and ethene selectivity as a function of TOS at $490 \text{ }^\circ\text{C}$ in the flow of 20 mL min^{-1} of the mixture consisting of $\text{C}_3\text{H}_8/\text{O}_2/\text{He} = 30/15/55 \%$ (v/v)

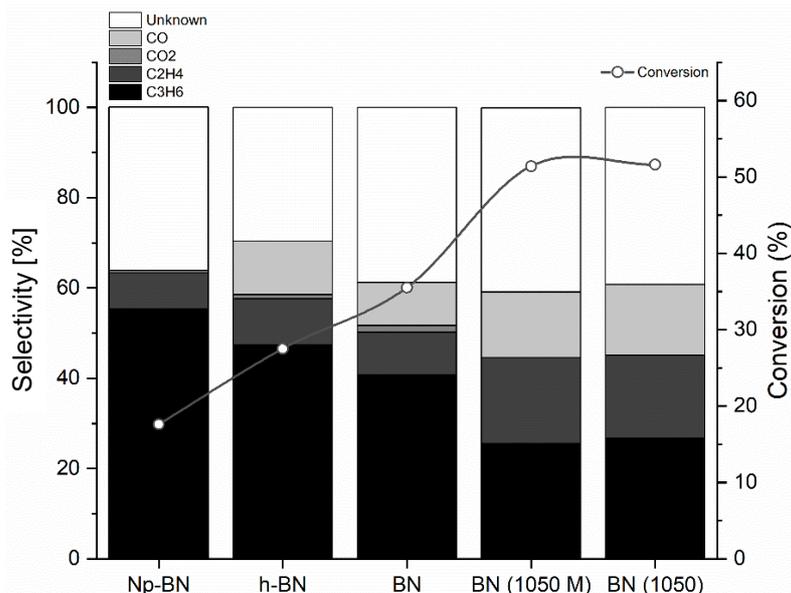


Fig. 3 Average conversion and selectivity for all the products after propane ODH at $490 \text{ }^\circ\text{C}$ in the flow of 20 mL min^{-1} of the mixture consisting of $\text{C}_3\text{H}_8/\text{O}_2/\text{He} = 30/15/55 \%$ (v/v)

Textural properties of the samples were studied to obtain the BET surface area and porosity of the catalysts. The surface area varied widely from 3, 8, 34, 46 for BN (550), BN (1050 M), BN (1050), h-BN up to 200 m² g⁻¹ for Np-BN. Followed by N₂ adsorption-desorption isotherms depicting the macroporosity for Np-BN based on the IUPAC isotherms of the type II (Fig. 4), h-BN also showed macro/mesopore structure. In contrast, non-commercial samples exhibited almost non-porous textural properties. After the ODH reaction, catalysts have revealed a high decrease in surface area (Fig. 5), for instance, h-BN, Np-BN, and BN (1050M) exhibited 17, 2, and 2 m² g⁻¹ correspondingly. Clearly, all the catalysts showed similarly a very low surface area for the spent samples, indicating quite distinct changes in the structure and morphology. It should be mentioned that catalytic activity did not change during the time of reaction, thus, it can be suggested that the change in surface area is very fast and has happened entirely immediately after starting the reaction or the surface area is not a determinative factor being able of controlling the activity and productivity of the catalysts.

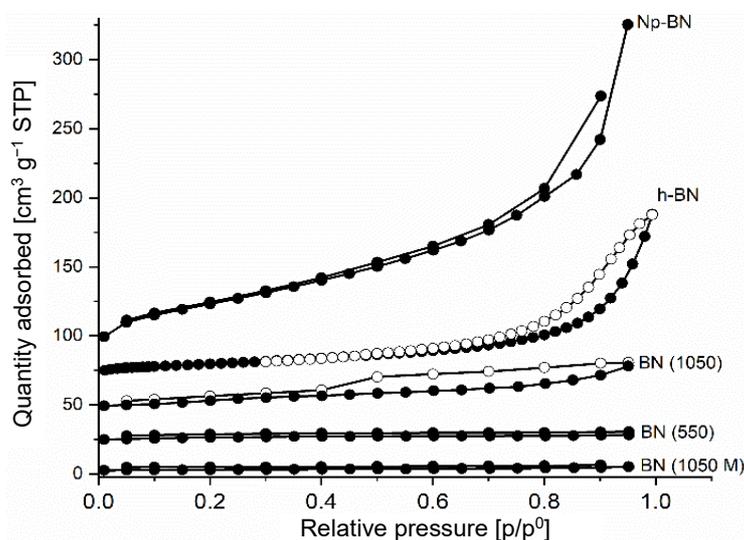


Fig. 4 N₂ adsorption-desorption isotherms of BN samples

Isotherms are shifted along the y -axis by an increment of 25 cm³ g⁻¹

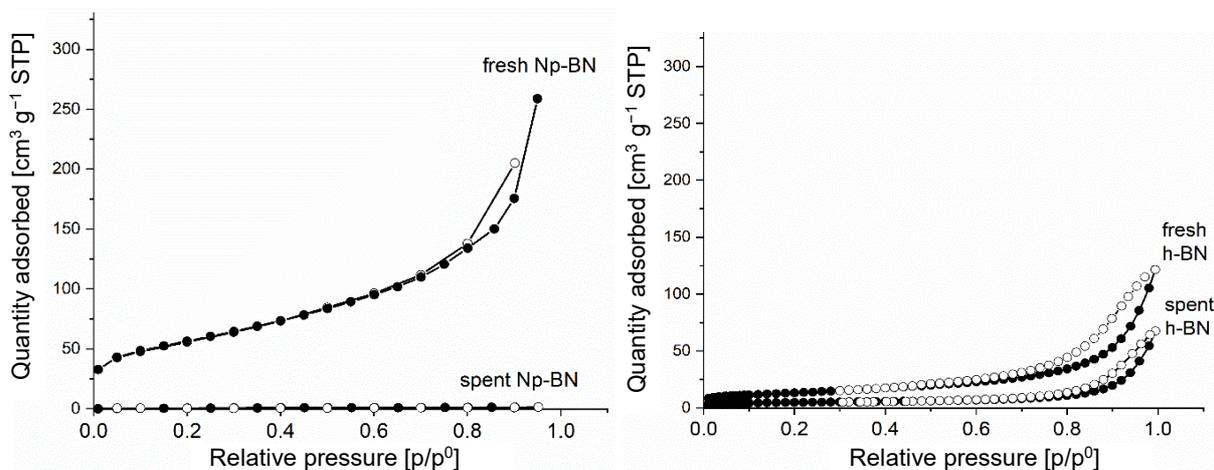


Fig. 5 Comparison of N₂ adsorption-desorption isotherms of Np-BN and h-BN samples before and after the reaction

The crystallinity and structure of BNs were investigated by the X-ray diffraction (see Fig. 6). Commercial h-BN, as expected, had shown typical hexagonal structure, whereas Np-BN and BN (550) were of amorphous structure. BNs (1050) and (1050 M) exhibited both a similar structure with broad peaks showing smaller crystallite size compared to h-BN, as the peak width is inversely proportional to crystallite size. The difference in the structure after the ODH reaction is well illustrated in Fig. 7. An appearance of few new peaks, related to the BOx compound after ODH reaction was a sign of such a difference.

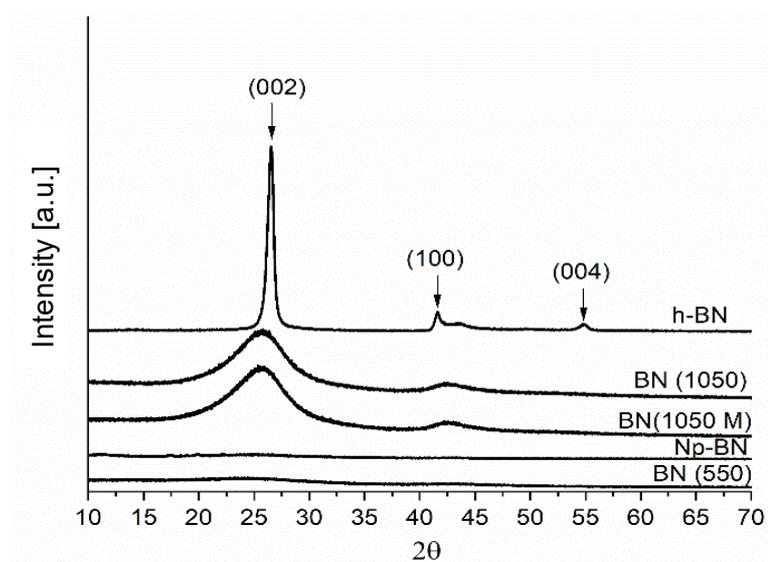


Fig. 6 X-ray diffraction pattern of BN catalysts

Diffraction patterns are shifted along the y-axis by an increment of 2000 a.u.

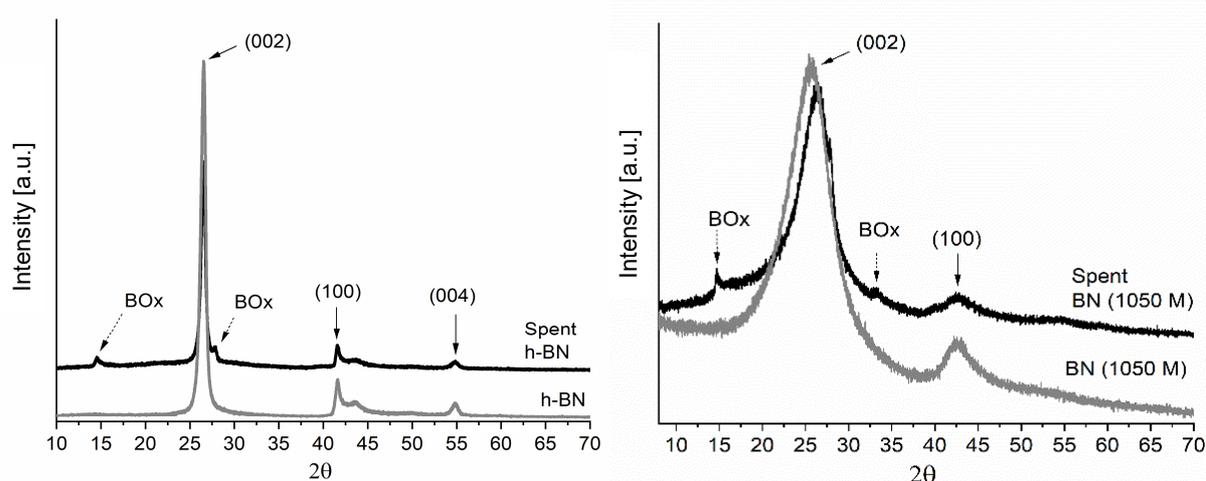


Fig. 7 X-ray diffraction pattern of h-BN (top panel) and BN (1050 M) (bottom panel), before and after ODH of propane

Diffraction pattern of h-BN is shifted along the y-axis by an increment of 1500 a.u.

The most convincing evidence of chemical changes in BN is the result of EDS analysis (Table 3). The data measured for chemical composition present a big difference in the atomic percentage of the oxygen content for the samples studied. h-BN exhibited almost stable atomic ratio of boron and nitrogen, with an increase in the post-reaction oxygen content. Np-BN was not as stable as the other commercial sample. Fresh Np-BN has already gotten a lower amount of nitrogen and a higher content of oxygen; nevertheless, the spent sample showed a large rise in the oxygen content besides removing a large amount of nitrogen. In the other hand, fresh BN (1050 M) gaining a ratio of B : N almost 1 : 1 and, in addition, 20 at. % of oxygen ($O/B = 0.5$), as the corresponding catalyst had reached one of the highest productivity for propene and ethene, and it was therefore considered as a representative for synthesized catalysts.

Table 3 The ratio between the atomic percentage of the elements by EDX

Sample	Fresh				Spent			
	B	N	O	C	B	N	O	C
h-BN	1	1	0	0	1	0.9	0.3	0
Np-BN	1	0.5	0.4	0.1	1	0.1	0.9	0.1
BN (550)*	1	1	1.1	0.4	–	–	–	–
BN (1050)*	1	0.9	0.4	0.2	–	–	–	–
BN (1050 M)	1	0.9	0.5	0.3	1	0.5	1.1	0.4

* no available data for spent samples

Mostly, the amount of carbon was preserved for the spent samples. It seems that the role of oxygen in the enhancement of productivity is about to form BO_x species, but not always via the increase of its amount because, in the case of BN (550), a very high amount of oxygen (31 at. %) was detected whereas its activity was lower than those for BN (1050) and (1050 M), and this phenomenon needs to be more investigated.

The results obtained by X-ray photoelectron spectroscopy analysis of the samples illustrate the different oxygen content, for example in case of fresh h-BN (Fig. 9), the ratio between the elements was found to be $B/N/O = 1/1/0.1$, which means that oxygen was acting at the surface of the fresh sample from the beginning, compared to the EDX results without oxygen detection in the bulk, due to differences in the depth of the surface of the material from which the information about composition could be obtained. The XPS data for the spent h-BN sample showed a lower oxygen content in the surface than bulk measured by EDX, $B/N/O = 1/0.9/0.2$. As a result, the B-O active sites were not formed only in the edges of the layers, and they also existed inside the bulk. This was a finding that did not correspond to the previous works reported in the literature.

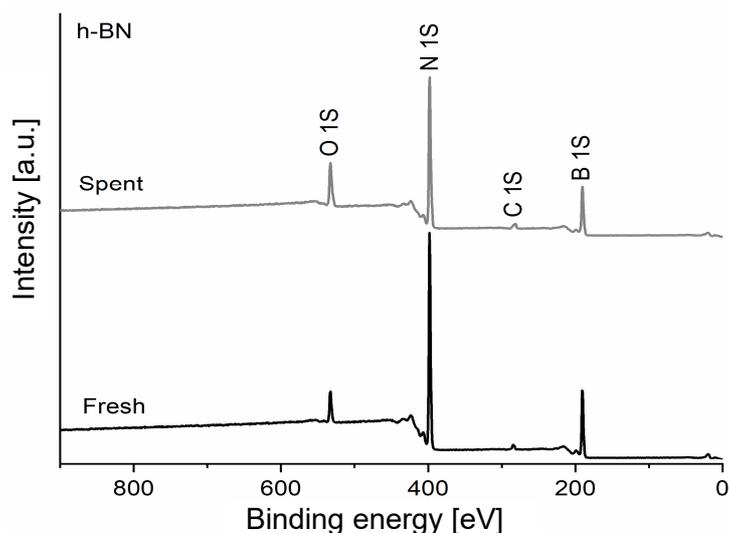


Fig. 9 XPS results for fresh and spent h-BN
Shifted along the y-axis by an increment of 124000 a.u.

Accordingly to the literature [1,11,20–21,26], it has been observed in this research that the oxygen-containing boron species on the surface of boron nitride and also inside the layers, seem to be one of the hot candidates for the active sites of BN-based materials in the ODH reaction of light alkanes. A new and a relatively simple reaction pathway proposing a redox reaction cycle based on B-OH sites [21], can be applied here as well, for the ODH of propane. The B-OH sites initially react with molecular oxygen, leading to the B–O–O–B intermediates (oxidation step) that further withdraw the hydrogen atoms from the alkane, then forming an olefin and water (reduction step), and finally rearranging into the B–OH sites with the participation of water. This mechanism can meet a majority of the experimental facts reported by different research groups [11,20,21]. Thus, maximization of the number of OH-containing boron sites is considered to be the most effective pathway to improve the catalytic activity of the ODH reaction. In one hand, a combination of X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS) measurements showed the emergence of the B–O functional groups for the increased activity of BN material in the ODHP reaction, but in second hand, the incorporation of oxygen takes place also in the bulk and not only in the surface layer.

In order to complete the picture of changes in catalysts during the reaction, micrographs of catalyst surfaces before and after the reaction, the SEM imaging was performed and the results presented here in Fig. 10. The morphology of all the catalysts changed after the ODH reaction compared to the fresh ones. A molten layer was formed on the surface of the spent catalyst, which is in accordance with N_2 adsorption-desorption isotherms and a low BET surface area for spent catalysts.

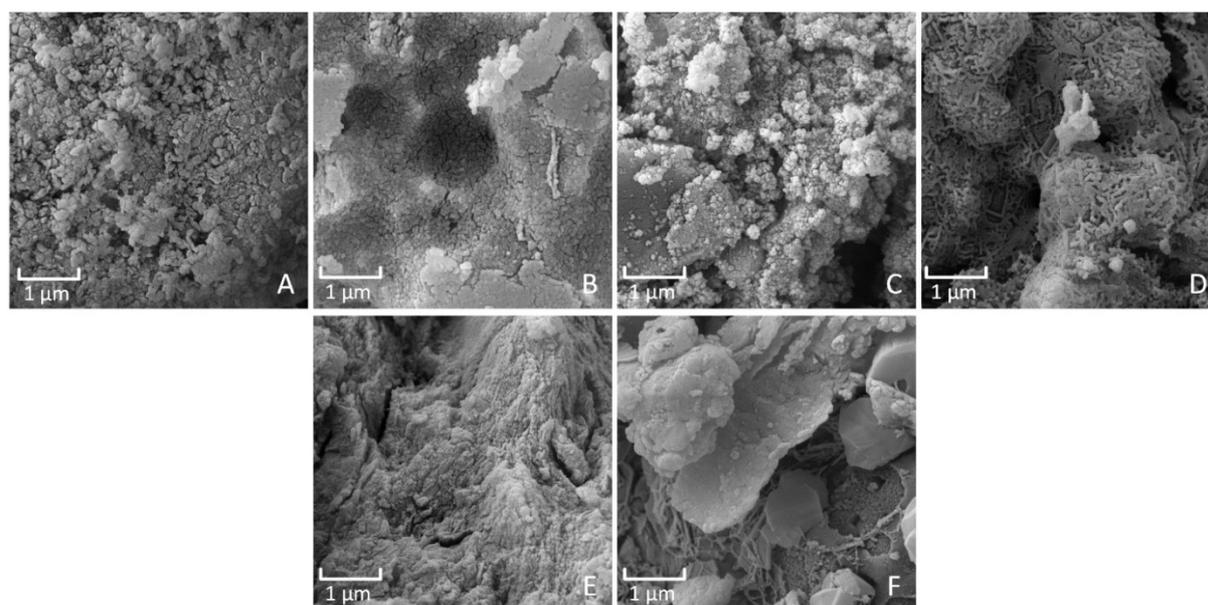


Fig. 10 SEM images of A. fresh h-BN, B. spent h-BN, C. fresh Np-BN, D. spent Np-BN, E. fresh BN (1050 M), F. spent BN (1050 M)

It seems that the formation of new compounds, i.e. boron oxide (BOx) species on the surface just after started reaction, has changed the morphology and the catalysts then work differently based on available active sites. This interpretation is also in agreement with XRD patterns about the formation of BOx species and the EDS results for different compositions after the propane ODH.

A comparison between the productivity of different boron nitride- and boron-based catalysts with traditional ODH catalysts reported in the literature [11,18,22,25–28], could be useful to build a new mindset about this type of catalyst (see Table 4).

Table 4 The productivity of BNs and other types of known catalysts used for propane ODH

Catalyst	Productivity [g _{propene} h ⁻¹ g _{cat} ⁻¹]	Ref.	Catalyst	Productivity [g _{propene} h ⁻¹ g _{cat} ⁻¹]	Ref.
h-BN	0.92	This work	BNOH *	5.9	[26]
Np-BN	0.74	This work	hBN	0.4	[22]
BN (550)	0.94	This work	NiB	0.5	[22]
BN (1050)	0.93	This work	TiB ₂	0.6	[22]
BN (1050 M)	0.89	This work	B ₄ C	0.65	[22]
hBN	0.75	[11]	(V ₂ O ₅ /ZrO ₂)	0.29	[27]
BNNT	0.6	[11]	(V ₂ O ₅ /TiO ₂)	0.21	[27]
BN	0.06	[17]	(Mg-Dy-Li)	0.14	[18]
B/SiO ₂	1.04	[28]	(Mg-Dy-Li-Cl)	0.12	[18]
B ₂ O ₃ /SBA-15	1.82	[25]			

* Measured at 530 °C

The propene productivity of different BNs in this work had varied between 0.89 to 0.94 $\text{g}_{\text{propene}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$, which was at least three times higher than the well-known transition metal supported and alkali chloride catalysts. A report on the $\text{B}_2\text{O}_3/\text{SBA-15}$ [25] quotes a propene productivity at 500 °C being higher than the others, around 1.8 $\text{g}_{\text{propene}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$, which has verified data in this research showing on the importance of BOx compared to the B-N bond.

Conclusions

In this research, an investigation on different BNs for the ODH reaction of propane has been reported. The BNs prepared showed productivity as high as 1.4 $\text{g}_{\text{olefin}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$ through propene and ethene, even higher than that of commercial BN. In general, BN's productivity is more promising in the industrial scale compared to the conventional transition metal oxide-based catalysts.

The study has revealed that the O-containing boron sites generated in the catalysts during the reaction are decisive for the unique catalytic function in the ODH reaction. A deeper characterization of the spent catalysts has revealed that boron nitride is subject to significant chemical and morphological changes which are not limited to the surface layer, but also indicate a deep penetration into the volume of the particles. These changes have led to a significant increase in the oxygen content and a decrease in the nitrogen content. It is hypothesized that some boron oxide-like phase or species are being formed. Thus, the findings reported here indicate that BOx moieties could be responsible for the catalytic activity. It is suggested to obtain more experimental material on the BOx species formed on the surface and inside the bulk, which controls the activity. In overall, from the viewpoints of activity, selectivity, and stability, there is still a lot to improve in the catalytic efficiency of boron-based catalyst in the ODH reaction. This newly developed catalyst system not only opens up a research direction of metal-free catalysts in selective cleavage of C-H bonds of alkanes, but it can also enrich our fundamental understanding of active sites of this type of non-metallic catalysts.

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