**Carbon nanofibers modified with boron, phosphorous and nitrogen as metal-free catalyst
for propane oxidative dehydrogenation**

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Abstract

Carbon nanofibers (CNFs) were modified with B and P by an *ex-situ* approach. In addition, CNFs doped with nitrogen were prepared *in-situ* using ethylenediamine as N and C source. After calcination, the doped CNFs were used as catalyst for the oxidative dehydrogenation of propane. For B-doped CNFs, the effects of boron loading and calcination temperature on boron speciation and catalytic conversion were studied. For the same reaction temperatures and conversions, B and P doped CNFs exhibited higher selectivities to propene than pristine CNFs. The N-doped CNFs were the most active but the least selective. Our results also show that the type of phosphorous precursor affects the selectivity to propene and that CNFs modified using triphenylphosphine as precursor exhibited the highest selectivity at isoconversion.

Keywords: metal-free catalysis, carbon nanofibers, heteroatom doping, hydrocarbon dehydrogenation

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1. Introduction

The chemical industry is largely based on the conversion of alkenes that may be easily and economically obtained from petroleum. As the demand for propene is growing faster than the demand for either ethylene or gasoline, there is a widening gap between propene demand and that which can be supplied via conventional routes, i.e. catalytic (FCC) and steam cracking or direct dehydrogenation of propane. Oxidative dehydrogenation of propane (ODH) offers an attractive alternative route to propene production, since the reaction is exothermic and avoids the thermodynamic constraints of nonoxidative routes by forming water as by-product. However, the yield of propene obtained by ODH on most catalysts is limited by alkene oxidation to CO and CO₂. The poor selectivity and safety issues like risk of explosion and formation of hot-spots in the catalyst bed due to the highly exothermic nature of this type of reaction have impeded the industrial implementation of ODH yet.^[1]

In order to increase selectivity to alkene, several catalysts have been used in ODH, including carbon catalysts.^[2] Even for some non-carbon catalysts, it has been reported that ODH activity is due to coke deposited at the beginning of reaction.^[3] It has been reported that boron or phosphorous modified carbon nanotubes (CNTs) increase selectivity in ODH of n-butane.^[4] The fact that the surface modification of CNTs can increase the selectivity to alkene has also been reported for the oxidative dehydrogenation of propane to propene.^[5] CNT doped with boron or phosphorus exhibited selectivities to propene higher than the pristine or oxidised CNTs. B-doped CNT afforded a high selectivity to propene, *i.e.* 60% selectivity at 5% conversion. Other authors performed the same reaction using P-doped CNFs.^[6] The P-doped CNFs exhibited 39% selectivity to propene at 42% conversion, along with enhanced stability to oxidation compared to that of the undoped CNFs. The higher selectivity using P or B doped CNTs has been explained

because the addition of phosphorous or boron reacts with defects of carbon suppressing the formation of electrophilic oxygen species, which are the cause of the decrease in selectivity.^[5]

Recently, N-doped CNTs have shown enhanced performance in the ODH of propane.^[7]

Unlike CNTs, which expose graphitic planes to the gas reactants, CNFs expose the basal plane edges. Therefore, CNFs can potentially have more density of defects located on the outer surface, which are very accessible to reactants in turn. These defects at the edges are where oxygenated surface groups can be located. The oxygenated groups on carbon are reported to be the active phase in ODH. The selective sites are reported to be quinone or dicarbonyl groups on carbon materials, while carboxylic acids are unselective to propene favouring complete oxidation of its double bond.^[5, 8, 9] CNFs have been used, as e.g., in the oxidative dehydrogenation of ethylbenzene showing that the graphitic platelet orientation has a significant effect on the catalyst activity and selectivity.^[10] In that case, the conversion was promoted by the enhanced π - π interaction of the ethylbenzene phenyl ring with the carbon basal planes.

Pursuing the challenging objective of increasing conversion and selectivity to propene, by maximizing the density of selective sites, here we have prepared CNFs doped with several heteroatoms (B,P,N). The catalysts have been characterized by multiple techniques and a critical comparison has been made between the performance of CNFs with different dopants and with similar catalysts in the literature.

2. Experimental

CNFs were grown on a 20 wt% Ni on alumina catalyst prepared by incipient wetness impregnation of nickel nitrate on alumina (Pural, Sasol) and calcined at 873 K in N₂ flow. The

powder catalyst was placed on a porous frit of a vertical reactor. After reducing the catalyst at 823 K using 100 ml/min of $\text{H}_2:\text{N}_2$ mixture during 1 h, the CNFs growth was carried out at 873 K using 100 ml/min of a $\text{C}_2\text{H}_6:\text{H}_2$ mixture (50:50). The CNFs produced were then purified from the growth catalyst under reflux of NaOH (5M) at 353 K for 4 h and later with HNO_3 (65wt%) under reflux at 353 K for 4 hours. After this purification process, the residual catalyst was less than 1 wt% as determined by oxidation in thermobalance.

B-doped CNFs with different B-loadings were prepared by incipient wetness impregnation of aqueous boric acid solutions. Subsequently, the B-doped CNFs were calcined at 773 K as standard temperature in N_2 atmosphere. CNFs were also doped with phosphorus by incipient wetness impregnation employing triphenyl phosphine and ammonium phosphate as precursors. After impregnation the samples were dried at room temperature and calcined at 773 K. The catalysts were denoted as 1.5% P_{TPP} -CNF and 1.5% $\text{P}_{\text{phosphate}}$ -CNF, respectively.

N-CNF were grown on a 20 wt% Fe on alumina catalyst prepared by incipient wetness impregnation of iron nitrate on alumina (Pural, Sasol) and calcined at 873 K in N_2 flow. The catalyst was reduced at 823 K using 100 ml/min of a $\text{H}_2:\text{N}_2$ (50:50) mixture during 1 hour. Subsequently, the reactor was heated to the growth temperature (1023 K) under Ar. After reaching the temperature, the reaction mixture was admitted. The reaction mixture consisted of 100 ml/min Ar mixed with 0.15 ml/min of ethylenediamine (10 ml in total) fed using a syringe. The ethylenediamine in argon mixture passed through an evaporator at 200 °C and a heated line to the reactor containing the growth catalyst. The N-CNFs were purified from the growth catalyst under reflux of NaOH (5M) for 4 h at 353 K and later under reflux of HCl at 373 K for another 4

h. After this purification process, the residual catalyst was less than 1 wt% as determined by oxidation in thermobalance.

The catalysts produced were characterized by X-ray photoelectron spectroscopy (XPS). The XPS system used was an ESCAPlus Omnicrom equipped with a Mg K α radiation source to excite the sample. Calibration of the instrument was performed with Ag 3d_{5/2} line at 368.27 eV. All measurements were performed under UHV, better than 10⁻¹⁰ Torr. Internal referencing of spectrometer energies was made using the C 1s signal at 284.6 eV. The curve fitting of the spectra was performed using CASA XPS software after applying a Shirley baseline. For peak deconvolution, the FWHM was fixed equal for all the peaks and with a maximum value of 2.5 eV.

The specific surface area was measured by N₂ adsorption using the BET method in the relative pressure range 0.01-0.10 following the ASTM-4365 standard on a Micromeritics ASAP 2020 at 77 K. The pore size distribution was estimated by the BJH (Barrett–Joyner–Halenda) method from the adsorption branch. Transmission electron microscopy (TEM) images of CNFs were collected with a FEI TECNAI F30 electron microscope equipped with Gatan Energy Filter and cold field emission gun (FEG) operated at 300 kV with 1.5 Å lattice resolution. Specimens for TEM characterization were prepared by ultrasonic dispersion in ethanol of powder retrieved from the monoliths. A drop of the suspension was deposited onto a holey carbon support grid.

Temperature programmed oxidation (TPO) was carried out in air using a SETARAM Setsys Evolution thermobalance under air-flow 100 ml/min from room temperature to 1073 K at a heating 10 K/min. Temperature programmed desorption (TPD) of catalyst before and after ODH was conducted in a vertical quartz tube of 6 mm diameter. Argon was used as carrier gas (50

mL/min) and was heated by rate ramp 10 K/min up to 1273 K. The gases were analysed by a Pfeiffer quadrupole mass spectrometer.

Catalytic testing in ODH was carried out in a continuous-flow 6 mm i.d. quartz reactor inside vertical furnace with a temperature controller (Eurotherm). 130 mg of catalyst diluted in SiC were placed on quartz wool inside the reactor. The reaction temperature was controlled with a thermocouple inside the catalytic bed. ODH reaction was carried out using a mixture of propane: oxygen: argon (15:5:80). Because O₂ became depleted at the highest temperatures, a composition of (15:15:70) was used for comparison of selectivities and calculation of activation energies in section 3.3. The total flow rate was varied between 20-100 ml/min. The reaction was first carried out at the highest temperature and subsequently the temperature was reduced stepwise. The conversions and selectivities reported are measured at steady state because an induction period was observed at the first temperature tested (Figure S1, supplementary information). The outlet reaction gases were analysed with an Agilent Micro GC 3000A. H₂, O₂, CO and CH₄ were analysed in a molsieve column, CO₂ in a Plot-Q column, and propane and propene in an alumina column. To ensure repeatability, 2–3 separate GC samples were taken and averaged for each experimental data point. In all ODH testing, the gases analysed closed the carbon balance to 100±3 %, ruling out either carbon products accumulated on the catalyst or gasification of carbon. As an example of typical product distribution , using CNF as catalyst at 673 K a propane conversion of 6.6% was achieved and the products were C₃H₈ (58.5%), CH₄ (0.36%), C₂H₆ (2.5%), CO (9.9%), CO₂ (26%).

3. Results and discussion

3.1. Characterization of CNFs modified with boron: effect of B-loading and calcination temperatures.

Pristine CNFs and CNF with different B-loadings were characterized texturally by N₂ physisorption. All the isotherms are of Type IV with hysteresis loops at high relative pressures indicative of mesoporous materials. The samples exhibit a broad pore size distribution with peak maximum at 58 nm for pristine CNFs and at 80 nm for CNF after B-doping (Figure S2, supplementary information). The surface area and pore volume (table 1) increase after doping with only minor amounts of boron (0.5 wt% B). Further B-doping diminishes the surface area and pore volume slightly but the values are still larger than for pristine CNF. This suggests that boron does not plug the pores of original CNFs but it is covering the pore walls. The increase of surface area and pore volume could be explained by the etching of some amorphous carbon during calcination at 773 K in the presence of boric acid.

Table 1. Textural properties of CNF with several percentages of boron doping

sample	B/C nominal at%	B/C by XPS at%	O/C by XPS at%	Position of B 1s XPS peak	Surface Area (m²/g)	Pore volume (cm³/g)
CNF	0	0	5.6	-	154	0.30
0.5%B-CNF	0.58	0.92	6.7	192.4	217	0.48
1%B-CNF	1.17	1.58	6.6	192.5	175	0.41
1.5%B-CNF	1.75	2.03	8.6	192.7	165	0.41
2%B-CNF	2.34	2.89	7.9	192.8	164	0.43

Figure 1 compares the thermal resistance in air of the original CNFs and CNFs with several percentages of boron. The thermal resistance increases about 80 K after depositing only 0.5 wt%

boron. The increase in thermal resistance is only marginal for further boron loadings. The inhibition of carbon oxidation by modification with boron has been widely studied for the preparation of oxidation resistant carbon/carbon composites used as friction materials in aircraft brakes.^[11, 12] The B-doped CNF samples seem to be stable in air until 873 K, approximately. The residue after carbon gasification increases slightly as the amount of boron on the CNF increases presumably due to the residual boron oxide.

Figure 1. Thermogravimetric analysis by temperature programmed oxidation in air of CNFs doped with different amounts of B: (·····) CNF, (- -) 0.5%B-CNF, (—) 1%B-CNF, (— ·) 2%B-CNF.

Pursuing the objective to create different boron species such as substitutional boron or boron linked to carbon atoms, several calcination temperatures were used for 1.5 wt% boron on CNF. The XPS spectra of B-doped CNF calcined at 673 K shows one peak centred at 192.7 eV (S3 of supplementary information). The increase in the B loading from 0.5 to 2 % shifted the centre of this peak to only 0.4 eV higher binding energy (table 1). Figure 2 shows the evolution of B1s peak as a function of calcination temperature. As the calcination temperature increases, the peak widens to higher binding energies when calcined above 973 K and additionally widens to lower

binding energies when calcined at a higher temperature of 1173 K. This suggests that new boron species develop as calcination temperature increases. The increase of the B/C ratio (table 2) as calcination temperature rises up to 973 K also points to a change in the type of boron species such as the formation of oxidic boron cluster on carbon surface. In parallel, as calcination temperature rises from 673 to 773 K, there is a substantial decay of O/C ratio which can be attributed to the removal of oxygenated species of CNF surface. For further increase of temperature, the O/C ratio remains almost constant.

On the basis of XPS assignments in the literature, the peaks after deconvolution of spectra in Figure 2 can be attributed to several boron species quantified in table 2 and schematically represented in Figure S4 of supplementary information. The peak at 188.5 eV, which is attributed in the literature to substitutional B with three B-C bonds, is absent for all the samples. The peak at 192.7 eV (B_1), which is the predominant in B-CNF calcined at 673 and 773 K, can be attributed to boron linked to three oxygens^[13] as isolated or $(BO_3)_n$ chain bonded to the “zig-zag” face of graphite lattice (Figure S4a supplementary information). This structure has been predicted to be the most stable due to a steric fit of the terminal oxygen atoms in BO_3 with the zig-zag edge carbon atoms.^[11, 14] The peak at 194.5 eV (B_2) that appears in sample calcined at 773 K (9%) and it is larger for that calcined at 973 K (49.6%) can be attributed to B_2O_3 clusters segregated on the CNF surface (Figure S4b supplementary information). This explains also the significant increase of B/C ratio after calcination at 973 K (table 2). This segregation is logical since the melting point of B_2O_3 is 723 K. It is reported that, above the melting point temperature, a glassy residue of polymeric oxide is formed which blocks active sites on the carbon surface.^[14] A new peak at lower binding energies of 191 eV (B_3) appears for sample calcined at 973 K (9.3%), whose intensity increases upon calcination at 1173 K (31.9 %). This peak is attributed in the literature to boron species with mixed B-C and B-O bonding such the oxycarbides depicted in Figure S4c supplementary information.

Figure 2. B 1s peak of 1.5wt%B/CNF calcined at several temperatures from 673 to 1173K.

Table 2. Quantification of XPS atomic ratios and percentage of deconvoluted peaks for 1.5 wt%B-CNF calcined at several temperatures

Calcination temperature	B/C	O/C	Abundance of deconvoluted XPS peaks		
			%		
			B ₃	B ₁	B ₂
			191.1(±0.1) eV	192.7(±0.1) eV	194.5(±0.2) eV
673	1.8	4.5	0	100	0
773	3.1	2.6	0	90.5	9.5

973	6.1	2.5	9.3	41.1	49.6
1173	5.8	2.4	31.9	33.3	34.8

3.2. Testing of boron modified CNFs for oxidative propane dehydrogenation

It is reported that the active phase in ODH of carbon materials are oxygenated surface groups.^[5] These oxygenated groups are present initially on the CNFs catalyst or are developed during reaction as demonstrated by an induction period which disappears when the catalyst is pre-treated with diluted O₂ at the reaction temperature (Figure S1, supplementary information). The ODH catalytic activity of residual growth catalyst (~1 wt%) is ruled out for several reasons explained below. The residual nickel found in TEM characterisation was always encapsulated. No Ni peak at 850 eV was found by XPS survey and 2p core level spectra, corroborating the absence of Ni at the surface. Therefore, both TEM and XPS indicated that the residual Ni metal must be buried and, hence, it is not catalytically active. In addition, we performed the experiment with the growth catalyst that contains 20% Ni (20 times more than residual Ni) and the C₃H₈ conversion was only 2% and O₂ conversion was zero at 673 K, despite containing 20 times more nickel. Therefore, if there is some residual nickel accessible, its activity would be negligible.

Figure 3 shows the conversion, selectivity and yield to propene in the oxidative dehydrogenation (ODH) of propane using 1.5%B-CNF catalyst calcined at different temperatures. For catalysts calcined at 973 K and 1173 K, the propane and oxygen conversions decrease significantly and although propene selectivity increases slightly, the resulting propene yield decreases dramatically with respect to the samples calcined at lower temperature of 773 K. The decrease of propane conversion for the two catalysts calcined at the highest temperatures can be related to the blocking of oxygenated surface sites for activation of reactants, namely O₂ and C₃H₈. This blocking can occur because boron oxide melts and aggregates forming surface polymeric overlayers for catalyst calcined at 973 K and above. Therefore, the temperature of 773 K was fixed as standard calcination temperature for the preparation of subsequent catalysts.

Figure 3. Testing in propane dehydrogenation at 698 K of 1.5%B-CNF calcined at several temperatures. Feed: 60 ml/min of a mixture of propane: oxygen: argon (15:5:80). propane conversion; oxygen conversion; propene selectivity; propene yield.

Figure 4 shows the performance in propane ODH as a function of the reaction temperature using purified CNF (panel a) and 2%B-CNF (panel b) as catalysts. For low reaction temperatures (up to ~730 K) both propane and O₂ conversion are higher for boron-free CNF. For instance, total O₂ conversion is achieved at 698 K for CNF and at 748 K for 2%B-CNF. However, selectivity is higher for 2%B-CNF in all range of temperatures. Accordingly, propene yield is higher for 2%B-CNF for temperatures above 723 K reaching around 11 % propene yield, which are quite competitive with respect to catalysts based on metal oxides.^[15-17]

Figure 4. Testing in propane ODH at several temperatures using either CNF (a) or 2%B-CNF (b) as catalyst. Left axis: (●) propane conversion, (▲) O₂ conversion, (□) propene selectivity. Right axis: (△) propene yield. Feed: 60 ml/min of a mixture of propane: oxygen: argon (15:5:80).

Figure 5 illustrates the performance for two temperatures, 698 K (a) and 748 K (b), as a function of the amount of boron on CNFs. For the low temperature testing, the conversion increases as boron loading rises up to 1.5%B-CNF and concomitantly the selectivity increases resulting in maximum propene yield for sample with 1.5 wt% boron. Since blank tests with B₂O₃ showed no activity at all, the increase of conversion when doping with boron could be explained because of the increase in surface area and the creation of new oxygenated surface groups upon heat treatment of boric acid precursor as demonstrated by the increase of the O/C ratio determined by XPS (table 1). Further amount of boron (2 wt%) results in a decrease of propane conversion, which occurs in parallel to a decay of O₂ conversion because of the blocking of reactant chemisorption sites by an excess of boron. This decay in conversion for 2%B-CNF does not occur when working at the high temperature of 748 K (panel b of Figure 5). Since 728 K is the melting point of B₂O₃, it can be argued that it becomes mobile liberating some oxygen surface groups for O₂ activation.

Figure 5. Performance in propane ODH of CNF with several boron loadings for two temperatures, 698 K (a) and 748 K (b). $\square$ propane conversion; $\blacksquare$ propene selectivity; $\square$ propene yield. Feed: 60 ml/min of a mixture of propane: oxygen: argon (15:5:80).

Since the best performance was achieved using 1.5%B-CNF and 2%B-CNF catalysts at reaction temperatures of 698 K and 748 K, respectively, the long-term stability of these catalysts was studied at the corresponding temperatures (Figure 6). While the propane conversion and propene yield remains constant when operating at 698 K for at least 20 hours (panel a), they drop after 10

hours operation at the highest temperature of 748 K (panel b). Temperature programmed oxidation in air (Figure 1) demonstrated that boron modified CNF did not lose weight by combustion until 873 K. Therefore, carbon combustion at 748 K cannot be unambiguously claimed as the reason for deactivation unless hot spots are produced in the exothermic reaction of H_2O formation. XPS of catalyst after long-term testing (Figure S5 supplementary information) revealed that the B 1s peak of catalyst after reaction at 698 K was similar to that before reaction while new peaks at higher binding energies were developed after reaction at 748 K. As pointed above, B_2O_3 melts at 723 K becoming mobile and forming clusters, which can account for the loss of activity during long testing at the highest reaction temperature. In any case, reaction temperatures above 698 K should be avoided to guarantee the long-term stability of these catalysts. In consequence, this maximum allowable operation temperature limits the amount of boron that can be deposited on CNF because a boron excess leads to a decay of conversion at temperatures below 698 K.

Figure 6. Stability tests in propane dehydrogenation of 1.5%B-CNF at 698 K (a) and of 2%B-CNF at 748 K (b). Left axis: (●) propane conversion, (▲) O_2 conversion, (□) propene selectivity. Right axis: (△) propene yield. Feed: 60 ml/min of a mixture of propane: oxygen: argon (15:5:80).

3.3. Comparison of CNF doped with other heteroatoms (P,N) for oxidative propane dehydrogenation

The performance of CNF doped with boron, nitrogen and phosphorous precursors is compared within this section. The same nominal Phosphorous loading of 1.5 wt% was impregnated from two precursors, namely triphenyl phosphine and ammonium phosphate, and the catalysts were denoted as 1.5%P_{TPP}-CNF and 1.5%P_{phosphate}-CNF, respectively. Figure 7 shows the XPS P 2p peaks of phosphorous containing CNF catalysts and the species assigned to each peak are depicted in Figure S6 (supplementary information). Phosphorous species are clearly different for catalysts prepared from the two precursors. The component with B.E=136.0 eV is attributed in the literature to P₂O₅.^[18] This is the only phosphorous species detected for 1.5%P_{phosphate}-CNF catalyst. A peak with binding energy between 133.6-134.7 eV is attributed in the literature to pentavalent tetra-coordinated Phosphorous (PO₄ tetrahedra).^[18, 19] This later peak is present in 1.5%P_{TPP}-CNF, along with a prevalent peak at lower binding energy of 132.5 eV, which can be attributed, according to the literature, to two possible species, namely: (i) gradual dehydration and condensation of phosphoric acid into polyphosphates or (ii) interaction of phosphorous with the aromatic carbon ring system for instance when P is bonded to one or several C atoms.^[18]

The P/C ratio and O/C ratios determined by XPS (table 3) are much lower for 1.5%P_{TPP}-CNF than for 1.5%P_{phosphate}-CNF. The lower P/C ratio in 1.5%P_{TPP}-CNF can be explained because not all triphenylphosphine precursor remains anchored to CNF surface upon calcination. Some white powder was found in the outlet cold part of the calcination reactor evidencing that the less strongly adsorbed triphenyl phosphine evaporates during calcination (boiling temperature of triphenyl phosphine 650 K). Several triphenyl phosphine percentages were loaded on CNFs from 1.5 to 5 wt%. The P/C ratios determined by XPS after calcination were 0.9±0.1 irrespective of the initial loading, indicating that the amount of phosphorous species that remain on CNFs upon calcination is limited. The interaction of phosphorous precursor with CNF deserves further research. The O/C ratio is about half for 1.5%P_{TPP}-CNF in agreement with the less oxidized phosphorous species.

Table 3. Atomic ratios determined by XPS for phosphorous doped CNF using the two precursors.

catalyst	P/C	O/C	Position of P 2p
	by XPS	by XPS	XPS peak
	at%	at%	eV
1.5% P _{phosphate} -CNF	3.0	10.4	136.0
1.5% P _{TPP} -CNF	0.9	4.3	132.5

Figure 7. XPS P 2p peak of catalysts phosphorous-doped CNF prepared using the two precursor: 1.5% P_{TPP}-CNF and 1.5% P_{phosphate}-CNF.

N-doped CNFs were prepared by catalytic decomposition of ethylenediamine on a 20%Fe/Al₂O₃ catalyst and subsequently were purified from growth catalyst first with NaOH

and later with HCl as described in the experimental section. TEM micrographs revealed that the structure of the N-CNFs is of the bamboo type in contrast to fishbone-type of pristine CNF (Figure S7 supplementary information). XPS analysis of C and N 1s peaks (Figure S8 supplementary information) showed that the N/C ratio of these samples is 3.6 %. According to N 1s peak deconvolution, the nitrogen atoms are of different types (35 % pyridinic, 26% pyrrolic, 24% quaternary and 15% pyridine oxide).

In order to compare the selectivities at iso-conversion, a different set of experiments was conducted. The maximum reaction temperature was 673 K, *i.e.* lower than for experiments shown in section 3.2. Also the O₂ concentration was increased to 15% to prevent that O₂ is totally converted. First, ODH reaction was carried out at 673 K, varying the flow rate from 100 to 20 ml/min, which gave rise to several contact times and thus conversions. Later the temperature was decreased 10 K stepwise and the reaction was performed again at different flow rates. The propane and oxygen conversions increase as reaction temperature rises and as feed flow rate decrease (Figure S9 supplementary information). Panel (a) of Figure 8 shows conversions as a function of the temperature for all the catalysts at selected flow rates for each one to obtain coincident conversions at the same temperature. Panel (b) of figure 8 shows the selectivities to propene corresponding to the conversions in panel (a). Using N-CNF catalyst the onset of propane and oxygen conversions occurred at much lower temperatures than using the other catalysts, even for the highest flow rate tested. Except for N-CNF, for the rest of the catalysts it is possible to obtain similar conversions at the same temperatures by using different contact times. Therefore, panel b of Figure 8 compares selectivities at iso-conversion for CNF modified with the different heteroatoms. The selectivity follows this order CNF < 1.5%B-CNF < 1.5%P_{phosphate}-CNF < 1.5%P_{TPP}-CNF. The highest selectivity to propene (>70%) corresponded to CNFs modified with triphenylphosphine.

The microstructure of N-CNF, and hence the number of exposed edges, is also different to that of CNF (Figure S7 c,d supplementary information). Therefore, the catalytic performance cannot be attributed just to the presence of nitrogen. N-CNFs prepared here are more active but less selective to propene than pristine CNFs. This contrasts with reported results,^[7] in

which N-CNT were more selective to propene than undoped CNT. However, both catalyst have significant differences: (i) N-CNF here prepared have about double nitrogen content, (ii) pyridinic groups are predominant in our N-CNF while quaternary groups are prevalent in N-CNT prepared in that work. That work shows that a close relationship exists between the amount of quaternary nitrogen and C_3H_6 formation rates. N-doped carbon has been reported to activate O_2 molecule^[20] and this is claimed to be the reason for its outstanding performance as electrocatalyst in oxygen reduction reaction (ORR).^[21, 22] Nitrogen groups transfer electrons to O_2 to form different oxygen species. These species can be of electrophilic character such as superoxide (O_2^-) or peroxide (O_2^{2-}) or nucleophilic (O^{2-}). In ODH, the electrophilic species favour the selectivity to complete oxidation to CO_x while nucleophilic ones favours the selectivity to C_3H_6 . In ORR, it is also reported that depending on the type of nitrogen it is favoured the formation of more electrophilic^[23] or more nucleophilic nitrogen species.^[24] Thus, the different type of nitrogen could explain the discrepancy of selectivities to C_3H_6 between different N-doped CNFs.

The catalysts were characterized before and after ODH reaction by temperature programmed desorption (Figure S10 supplementary information). The quantification of desorbed CO_2 and CO is compiled in table 4. Catalyst N-CNF previously to reaction has a low amount of oxygenated groups but a high amount of oxygenated groups are developed during ODH reaction. The amount of these groups is comparable to those of CNF catalyst after reaction. Especially, those groups desorbing as CO_2 in N-CNF catalyst multiply by a factor of 5 after reaction. Therefore, carbon atoms in N-CNF are attacked by O_2 forming oxygenated groups, which can contribute to catalytic activity. It is clear that under the oxidizing conditions of ODH reaction, oxygenated groups are formed on all the catalysts, so that the significant differences in the amount of oxygenated surface groups of the several catalysts before reaction are equilibrated after reaction. After reaction, all the catalysts have amounts of CO and CO_2 desorbing groups in the same range. If there is some subtle difference between catalysts after reaction, it is that B and P modified CNFs, have more oxygenated groups than pristine CNFs. This is presumably due to the higher amount of oxygen linked to the dopant atoms. In addition, the CO/CO_2 ratio is larger for B and P doped CNFs suggesting the pivotal

role of CO desorbing groups in catalysing selective dehydrogenation to propene in agreement with the literature.^[5, 8]

Table 4. Quantification of TPD

	Before reaction			After reaction		
	CO	CO ₂	CO/CO ₂	CO	CO ₂	CO/CO ₂
	mmol/g	mmol/g		mmol/g	mmol/g	
CNF	1.17	0.56	2.07	1.49	0.28	5.3
N-CNF	0.73	0.07	10.8	1.79	0.34	5.2
1.5%B-CNF	2.55	0.21	12.1	2.65	0.31	8.5
1.5%P _{phosphate} -CNF	1.70	0.10	17.3	2.26	0.25	9.1
1.5%P _{TPP} -CNF	0.29	0.04	7.8	2.41	0.35	6.8

Operation temperatures below 673K not only ensure long-term stability of the catalyst but also enabled the determination of apparent activation energies (Figure S11 supplementary information), which were masked when working at higher temperatures due to diffusional limitations (Figures S12 of supplementary information). The apparent activation energies (table 5) were calculated for conversions both of O₂ and C₃H₈ lower than 10%. The apparent activation energies of propane conversion increased around 17-30% for all the doped catalysts with respect to pristine CNFs suggesting that C₃H₈ activation is slightly hindered after doping. The apparent activation energies of O₂ conversion decreased after doping, which points that the activation of O₂ is enhanced. The decrease of activation energy of O₂ after doping is more pronounced (30-60%) than the increase of that of C₃H₈. Therefore, the doping heteroatom seems to affect in a larger extent to the sites for O₂ activation. The smaller differences in the C₃H₈ activation energy suggest that the sites for C₃H₈ activation have similar nature in all the catalysts, although the sites are not equally selective.

Table 5. Apparent activation energies and performance at 673 K and 100 ml/min feed flow rate for all catalysts, except for N-CNF, whose performance is reported at 623 K.

	Conversion	Propene	Propene	Ea C_3H_8	Ea O_2
	%	selectivity	productivity*		
		%	$\text{Kg h}^{-1} \text{Kg cat.}^{-1}$		
CNF	5	48	0.28	62	266
1.5%B-CNF	0.6	83	0.16	77	148
N-CNF	4.3	26	0.09	73	131
1.5%P _{phosphate} -CNF	5.8	58	0.40	73	179
1.5%P _{TPP} -CNF	3.4	76	0.32	80	103

Figure 8. (a) Propane conversions as a function of reaction temperature for the several catalysts using different flow rates to achieve similar conversion. (b) Propene selectivity as a function of reaction temperature corresponding to conversions depicted in panel a. (×) CNF, 100 ml/min feed flow rate; (△) 1.5%B-CNF, 30 ml/min feed flow rate; (○) N-CNF, 100 ml/min feed flow rate; (□) 1.5%P_{TPP}-CNF, 45 ml/min feed flow rate; (■) 1.5% P_{phosphate}-CNF, 100 ml/min feed flow rate. Feed: a mixture of propane: oxygen: argon (15:15:70).

The different conversions, selectivities and activations energies (especially for O₂) depending on the dopants points to different mechanisms in each case. The nature of N doping is radically different from other dopants since it is substituting carbon in the graphitic lattice while B and P doped CNFs are linked to carbon via oxygen atoms as pointed out by XPS characterisation. Despite the different nature of the N dopant, some insight can be withdrawn from the comparison with the other catalysts. It is observed (table 4) that oxygen surface groups are also developed on N-CNF during reaction in amounts comparable to the other catalysts. These active sites are expected to be of similar nature to the active sites in the other catalysts except for the presence of N in its proximity. Therefore, it is probable that the significantly higher conversions and lower selectivities using N-CNF are due to electronic effects that activate O₂. On the other hand, upon doping with P and B dopants, conversion diminishes and selectivity increases which can be

attributed to the inactivation of unselective oxygenated sites, although electronic effects cannot be totally ruled out.

Despite the high selectivity under these conditions, the maximum productivities are around 0.3-0.4 Kg h⁻¹ Kg cat.⁻¹ (table 5) due to the low conversions attained at temperatures around 673 K. Performing a literature survey, the best CNF-based catalyst here prepared has propene yields and mass productivities comparable to the best reported results for other carbonaceous catalysts (table 6). These values do not reach industrial target, which is a propene yield around 50% and productivity around 1 Kg h⁻¹ Kg cat.⁻¹.^[1] The maximum yield in the literature is 26% for a V, Mo on SiO₂ catalyst with most catalysts having yields below 20%.^[1] The maximum reported propene productivities were 1.8 Kg_{C₃H₆} Kg_{cat}⁻¹h⁻¹^[25] for vanadia based catalyst and very recently a strikingly high productivity of 9 Kg_{C₃H₆} Kg_{cat}⁻¹h⁻¹ has been reported for V on Ti/SBA-15.^[26] It would be meaningful for applicability to compare data of productivities per volume of catalyst, which are not usually reported. Carbon materials have the advantage of their simplicity and that they are the active phase and support at the same time which can lead to higher activities per volume of catalyst. Higher conversion cannot be reached simply by increasing reaction temperature because of the stability standpoint and to the occurrence of homogeneous side reactions. The only way to increase productivity is by increasing conversion and selectivity for the same catalyst mass at a maximum temperature around 673 K to guarantee stable performance. To this end, new carbon-based catalysts with high loading of selective sites need to be devised and prepared. This can be accomplished by a precise inactivation of unselective sites with dopant elements or by tailoring the oxygenated groups, which can be accomplished as *e.g.* exploiting the different thermal stability of the oxygen functionalities.^[8] In this regard, triphenyl-phosphine precursor has proved to be more effective in inactivating unselective sites while keeping selective sites active compared to ammonium phosphate or boric acid precursors. Further research should be carried out to get more insight into the interaction between the dopant precursors and unselective oxygen sites. Regarding N-CNF, it is very promising because of its high activity but more in-depth studies are necessary to clearly ascertain the effect of nitrogen type and content on propene selectivity. Also co-doping with several heteroatoms needs to be researched because of the possible synergistic effects.^[27]

Table 6. Performance of some catalyst (carbon and vanadium based ones) in the literature

Reference	Catalyst	T (°C)	Conversion C ₃ H ₈ (%)	Selectivity C ₃ H ₆ (%)	Yield C ₃ H ₆ (%)	Productivity Kg h ⁻¹ Kg cat. ⁻¹
[6]	CNF (with Phosphorous)	450	42,07	39,63	16.6	0.187
[5]	CNT (with boron)	400	5	60	3	0.033
[28]	CNT (with Mo and P)	450	9	68	6,12	0.100
[29]	Ordered mesoporous carbon	400	21,6	25,2	5,44	n.d
[16]	V on Al in microreactor	600	21,9	58,2	12,74	n.d
[26]	V/TiSBA15	500	6	60	3	9

Conclusions

Doping of CNFs with boron or phosphorous enhanced the selectivity to propene at isoconversion. At a reaction temperature of 698 K, the propene yield is maximized with 1.5 wt% boron loading. Further amount of boron doping decreased the propane conversion due to the blocking of reactant activation sites by an excess of boron. At higher reaction temperatures, around 730 K and above, a 2 wt% boron on CNFs exhibits the highest propene yield but the performance is not stable in long term experiments. Pre-treatment of B-CNF at temperatures above 773 K have a detrimental effect on conversion due to the blocking of active sites by B₂O₃ clusters. A CNF catalyst containing 1.5 wt% boron and calcined at 773 K met the optimum compromise in terms of

propene yield. For a stable performance in long-term experiments, the maximum allowable temperature was 698 K. Phosphorus doping brought about enhanced selectivity at isoconversion compared to boron doping. The doping using triphenylphosphine precursor led to higher propene selectivities than doping using ammonium phosphate. The two precursors gave rise to different phosphorous species on CNFs, which are more reduced for the catalyst prepared employing triphenylphosphine. Using this precursor, only that adsorbed more strongly on CNF surface is retained upon calcination while that weakly absorbed evaporates in the gas flow. CNFs doped with nitrogen groups during their growth were the most active in propane partial oxidation but also the least selective to propene. TPD characterisation indicated that, independently of initial surface oxygenated groups, new groups are generated during reaction. Catalysts doped with B and P exhibited larger CO/CO₂ ratios after reaction than pristine CNFs, pointing to the crucial role of CO desorbing groups in the selective formation of propene. Some researching lines are worth to be explored in the future such as increasing the density of pure selective sites, tuning the type of nitrogen or co-doping with several heteroatoms.

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Entry for the Table of Contents

Modification of carbon nanofibers with heteroatoms tunes the selectivity to the alkene in oxidative dehydrogenation of propane. The selectivity is affected by the type of heteroatom and also by the compound used as precursor because they lead to different inactivation of unselective oxygenated sites on carbon.

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CNFs modified with boron, phosphorous and nitrogen as metal-free catalyst for propane oxidative dehydrogenation