

Electrochemical Reduction of CO₂: Influence of Pre-treating the Carbon Support

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Abstract: The production of useful chemicals by electroreducing CO₂ it is a promising approach to reduce the levels of this greenhouse gas in the atmosphere. This is not a straightforward process due to the high stability of the CO₂ molecule and low selectivity however, these barriers can be overcome by using an appropriate catalyst. This research focus on the effect of pre-treating the carbon supports before incorporating the catalyst on the electroreduction of CO₂. We found that the electrochemical behaviour of the carbon supports is modified by the nature of the pre-treatment used. From the structure perspective, the results showed partial destruction of the carbon structure mainly after the oxidative treatments nevertheless, the introduction of defect sites in the carbon structure contributed to catalyst performance. This improvement was proved by the LSV data that showed the reduction of the current associated with the hydrogen reduction reaction.

Keywords: Carbon dioxide; Electroreduction; Energy; Catalysis.

1. Introduction

Climate change is a topic of great importance and a lot of effort is being made to mitigate our environmental problems. Currently, burning fossil fuels is the most widely used method for production of energy however, it releases pollutant gases, such as CO₂, into the atmosphere. One attractive solution to deal with the increasing levels of CO₂ in the atmosphere is to convert it into useful chemicals and fuels. The main obstacle to this approach is the high stability of the CO₂ molecule. However, under the appropriate conditions and using an electrocatalyst to overcome the high energy barrier, it can be electrochemically reduced. Nevertheless, the multiple electron transfers steps make the CO₂ reduction reaction very difficult to control. Also, the reduction products are catalyst specific and due to the high overpotential required the hydrogen evolution reaction (HER) hinders the CO₂ reduction reaction. In recent years the scientific community have been researching for new and more efficient electrocatalysts as reported in the recent reviews found in the literature [1, 2].

Together with the development of new catalysts the selection of suitable support for the catalyst is a crucial factor. In the field of electrocatalysis, carbon black has been the preferred catalyst support material [3] due to its unique properties such as the high stability regardless the pH media and the possibility to modify its textural and surface chemical properties [3]. The influence of three different carbon supports (carbon black, carbon nanotubes and reduced graphene oxide) was reported by Jiménez et al. [4] using copper based nanostructured catalysts deposited on carbon supports. This work reported that the catalyst based on carbon nanotubes showed the highest conversion rate. In addition, their results also showed that the interaction of the copper particles and the carbon support is an important factor in the carbon dioxide catalytic reduction process. Taking into consideration that the majority of the catalysts used nowadays are metallic [1] it is necessary to functionalize the carbon surface to favour the interaction with the metallic particles of the catalyst. Surface oxygen groups are known to be good anchoring sites for metallic particles [5] and they can be added to the carbon surface by oxidizing it with nitric acid or hydrogen peroxide [6]. Kumar et al. [5] showed that the oxidation of the Vulcan XC-72R carbon support with nitric acid leads to poor incorporation of the Pd particles when compared with the samples treated with KOH.

An alternative approach to modify the carbon surface properties is to introduce heteroatoms such as nitrogen or boron into the graphitized structure. Zhou et al. [7] prepared a dispersion of Pt nanoparticles on carbon nanotubes doped with nitrogen and reported an increase in the catalytic activity when compared with the non-doped samples. In the work of Ai et al. Cu catalysts were supported on boron-containing carbon nanotubes and the results showed an improvement in the catalytic activity [8]. Recently Ning et al. [9] reported high Faradaic efficiency using towards the formation of carbon monoxide using N-doped porous carbon as catalyst reported for carbon dioxide

electroreduction. The synergistic effect between the carbon support and the catalyst is an important factor in catalysis [10] and to our knowledge, there is still little information about the effect of carbon pre-treatment on its electrochemical activity towards the electrochemical reduction of CO₂.

The purpose of this study is to present a comprehensive study about the effect of pre-treating of the commercial Vulcan XC-72R and Ketjenblack EC-600JD carbon materials. Chemical and heat treatments were carried out on the as-received carbon materials and their physicochemical properties will be investigated and correlated with their catalytic behaviour. The carbon samples were analyzed by several techniques such as nitrogen adsorption-desorption isotherms, Raman and infrared spectroscopy and XPS. The catalytic performance of samples prepared was electrochemically evaluated using linear sweep voltammetry concerning the CO₂ reduction.

2. Experimental

2.1 Thermal treatment and functionalization of the carbon materials

The carbon materials used in this work were Vulcan XC-72R supplied by Cabot and Ketjenblack EC-600JD supplied by Akzo Nobel Polymer Chemicals. To perform their thermal treatments a small amount of the as-receive material was put in an alumina crucible and introduced in a close furnace under a nitrogen atmosphere. The temperature of the furnace was increased 5 °C min⁻¹ until it reaches 400 °C. After 4 h at the designated temperature, the furnace was cooled down.

For the oxidizing treatment, the as-received carbon material was suspended in a 1:1 (v/v) solution of HNO₃ (69%, Merck) or in a 7.6 M KOH (85+%, Sigma-Aldrich) solution. The suspension was heated up to 120 °C and left overnight under reflux. After the oxidation treatment, carbons were filtered, thoroughly washed with deionized water and dried at 60 °C.

Nitrogen atoms were introduced on the carbon structure by grinding the carbon material with melamine (99%, Supelco) in a proportion of 1:2 wt%. After the grinding process, the mixture was put in an alumina crucible and placed in a closed furnace under a nitrogen atmosphere. The furnace was heated up to 800 °C at 5 °C min⁻¹. After 4h at the designated temperature, the furnace was cooled down [11]. To introduce the boron atoms on the carbon structure, the carbon materials was grinded with B₂O₃ (98%, Sigma-Aldrich) in a proportion of 1:2 wt% and then the mixture was put in an alumina crucible and heated at 5 °C min⁻¹ up to 1200 °C in a hoven under nitrogen atmosphere for 4h (adapted from [12]).

2.2 Physicochemical characterization of the carbon samples

Textural properties were evaluated by the N₂ adsorption-desorption isotherms recorded at liquid N₂ temperature using a Quantachrome Autosorb-1. The specific surface area was calculated using the BET theory. The pore size distribution was calculated using the BJH method considering the desorption branch of the N₂ isotherm. The micropore fraction was determined using the t-plot method considering the lower relative pressure during the adsorption process. Before the measurements, the sample was degassed and heat-treated at 80 °C for 30 min., 120 °C for 30 min. and 300 °C for 150 min. under high vacuum conditions.

The X-ray photoelectron spectroscopy (XPS) analysis was made using a Kratos Axis Ultra HSA instrument. The spectra were obtained using a monochromatized Al K α source (15 kV, 90 W) and the survey spectrum was measured using a pass energy of 80 eV. For the individual peak region, a pass energy of 40 eV was used. Analyses of the spectra obtained were made using CasaXPS software.

Thermogravimetric analyses of the carbon supports were carried out using a Netzsch STA 449F3 instrument. The carbon materials were heated from room temperature to 900 °C at a heating rate of 5 °C min⁻¹ under airflow of 30 ml min⁻¹.

To identify the chemical groups present on the carbon surface, the samples were analyzed by Fourier transformed infrared spectroscopy, using a Bruker Vertex 70 instrument. For the analyses, the samples were diluted in KBr.

Raman spectra were obtained by a Labram Dilor–Jobin–Yvon–Spex spectrometer equipped with a CCD camera. The excitation wavelength was 532 nm and was produced by an Nd:YAG laser at a power of 25 mW. A density filter was used to prevent the thermal decomposition of the sample. Furthermore, the Raman spectrometer was equipped with an Olympus microscope with a 50x objective. Each Raman spectrum presented corresponds to the sum of 10 spectra recorded from 800 – 3800 cm⁻¹ during 10 s. Data acquisition and analysis were performed using the LabSpec 5 software.

2.3 Preparation of the carbon-supported copper electrocatalyst

100 mg of every carbon sample prepared was dispersed in 50 ml of n-pentane (Supelco) and was sonicated for 30 min. After that, an n-pentane solution containing 62.85 mg of copper (II) acetate (98%, Sigma-Aldrich) was added to the carbons suspension in order to obtain a 20% loading of copper on carbon.

2.4 Electrochemical measurements

The electrochemical experiments were conducted in a three-electrode cell using a Zahner IM6ex potentiostat controlled by the Thales software. A carbon rod was used as the counter electrode and an Ag/AgCl as the reference electrode. The working electrode consisted of carbon ink (5ml) that was prepared by dispersing 17 mg of the carbon sample in a 1:1 (v/v) aqueous solution of isopropanol (Fisher Scientific) and 17 μ l of Nafion solution (Sigma-Aldrich). The mixture was sonicated for 30 min in an ultrasonic bath and then it was airbrushed onto a carbon paper with a delimited area of 4 cm². All the electrochemical experiments were performed at room temperature using a 0.1 M KHCO₃ (99.7%, Sigma-Aldrich) as the electrolyte solution.

3. Results and discussion

Considering that carbon is a very strong absorber in the infrared region, the carbon samples were diluted in KBr.

Fig. 1 shows the FTIR spectra of the pristine and treated carbon samples. From these results, it can be concluded that the untreated carbon samples have a trace of oxygen groups. This oxygen may be due to the chemisorbed oxygen on the carbon surface after the synthesis [13]. In addition, there is a small amount of CH bonds (2800-2980 cm⁻¹) [14]. After the chemical treatment such as oxidation with HNO₃ it is expected the presence of bands at about 3400, 1630 and 1060 cm⁻¹ attributed to the presence of hydroxyl groups (-OH), carboxyl (-COOH), and carbonyl (-C=O) groups. The carbon samples treated either with HNO₃ or with KOH showed an increment in these functional groups. The samples treated with HNO₃ showed a C=O stretching at about 1700 cm⁻¹, a -OH bending at 1390 cm⁻¹ and a C-O stretching at about 1230 cm⁻¹ all assigned to the carboxylic group.

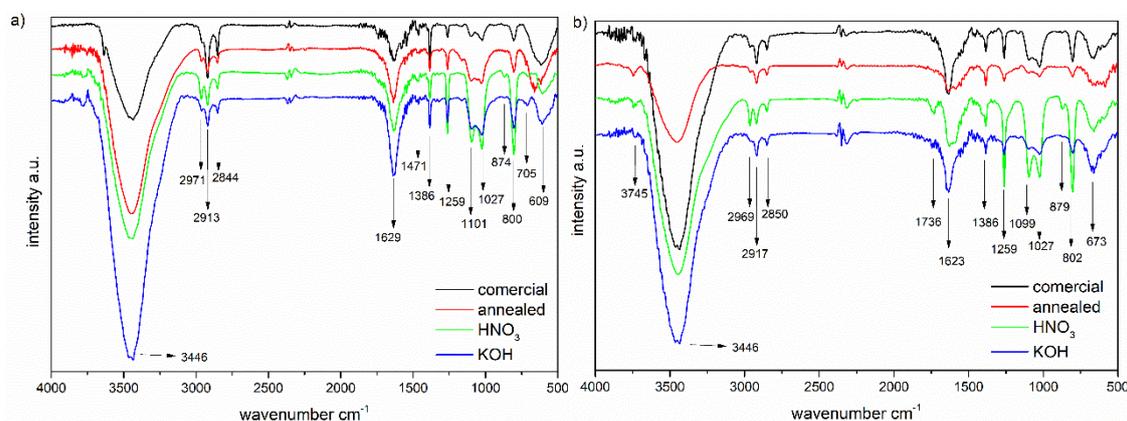


Fig. 1. FTIR spectra of the carbon substrates, a: Vulcan and b: Ketjenblack.

The textural modifications of the treated carbon samples were evaluated by N₂ physisorption and the N₂ adsorption-desorption isotherms of the carbon samples are depicted in Fig. 2. As it can be seen treating the carbon samples reduced its adsorption capacity however, without changing the isotherm profile and their hysteresis. The samples analyzed can be described by a type IV isotherm with an H3 hysteresis, which is typical of mesoporous solids with slit-shaped pores [15].

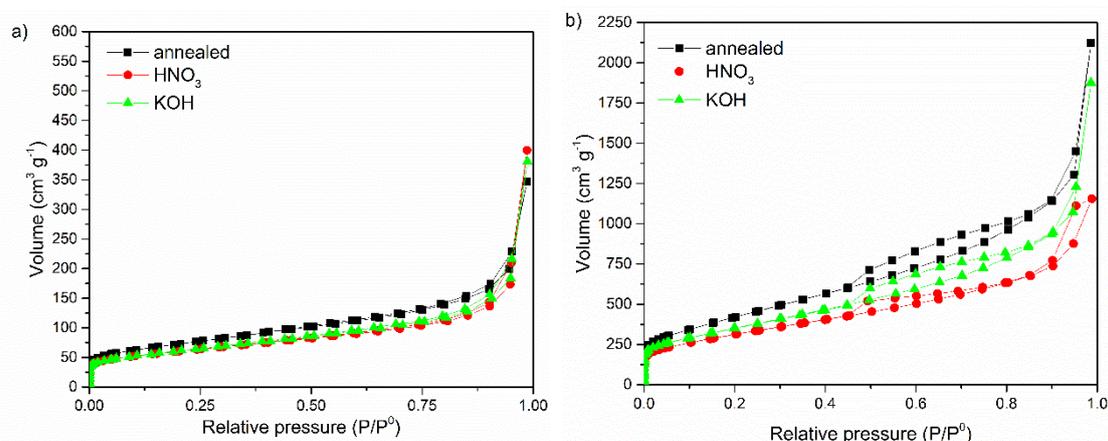


Fig. 2. N₂ adsorption-desorption isotherms of untreated and functionalized carbon substrates a) Vulcan and b) Ketjenblack.

Table 1 summarizes the results obtained from the N₂ physisorption analysis of the carbon samples. Pristine Vulcan sample presents an S_{BET} of about 279 m² g⁻¹ and a mesopore volume of about 0.48 cm³ g⁻¹. Treating the carbon samples lead to a decrease in the surface area may be due to partial destruction of the initial textural structure. This decrease is more pronounced as the severity of the treatment increased. In addition, a slight increase of the mesopore volume was observed after oxidation with HNO₃ which may be associated with the collapse of the pore walls due to the introduction of the oxygen groups.

Table 1. Textural parameters for the carbon supports.

sample		S _{BET} (m ² g ⁻¹)	V _{meso} (cm ³ g ⁻¹)	D _p (nm)
Vulcan	Untreated*	279.1	0.48	2.2
	Annealed	257.5	0.46	3.1
	HNO ₃	211.6	0.55	3.1
	KOH	214.8	0.52	3.9
Ketjen	Untreated*	1400.0	2.8	3.0
	Annealed	1465.5	2.9	3.1
	HNO ₃	1094.0	1.4	3.1
	KOH	1226.4	2.5	3.4

* based on the manufacturer data

Using X-ray photoelectron spectroscopy (XPS) it is possible to estimate the elemental atomic composition and it is possible to evaluate the chemical environment of carbon in the surface of functional groups. The XPS survey spectrum for the various carbon supports studied in this work are shown in Fig. 3. Atomic concentrations of elements present in significant quantities are resumed in Table 2. The HNO₃ and KOH treatments increased the oxygen content at the carbon surface when compared with the untreated samples. Among all the treatments used in this work and taking into account the improvement in the oxygen content on the carbon surface, KOH was considered the best treatment for Vulcan supports whereas HNO₃ was the best one for Ketjenblack supports, as shown in Table 2. This difference can be rationalized by taking into consideration the different levels of hydrophobicity of the carbon supports used.

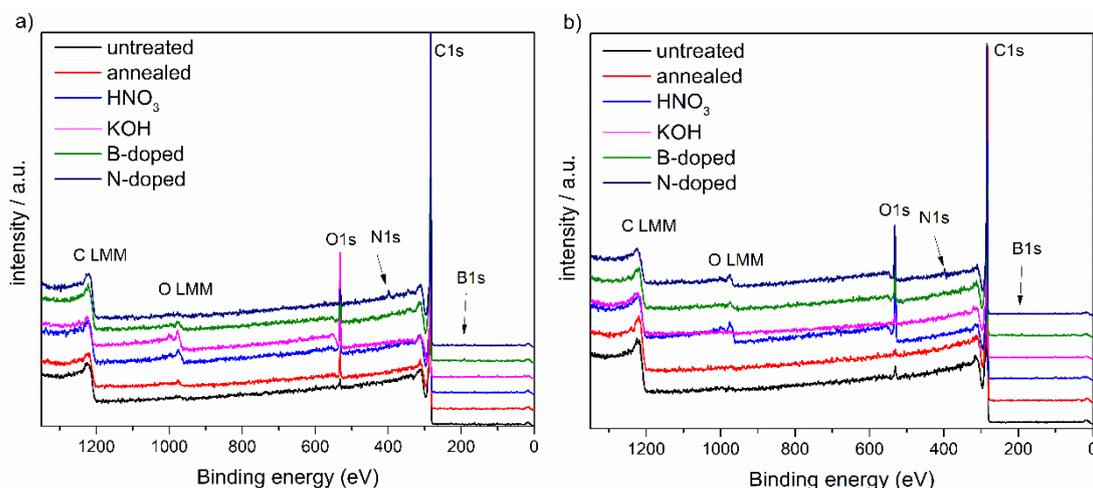


Fig. 3. XPS survey of untreated and functionalized a) Vulcan-based and b) Ketjenblack-based carbon samples.

In order to have a more detailed nature of the functionalities of the carbon supports, the individual regions of carbon, oxygen, boron and nitrogen were scanned and the curves were deconvoluted into their various components. The fittings of C1s and O1s components are displayed in Fig. 4 and Fig. 5 for the Vulcan and Ketjenblack supports, respectively. For both carbon blacks used in this work, the C1s region can be deconvoluted into seven components with bind energies of 285.0, 285.5, 286.5, 287.9, 289.0, 292.6 and 290.6 eV indicating the formation of various surface groups on the carbon supports. The main component is the symmetric peak centred at 285.0 eV that corresponds to the pure graphitic sites of the carbon supports. The asymmetric tailing observed for higher binding energies can be attributed to the existence of surface functionalization of the carbon [5]. The sets of peaks with binding energies between 285.5 and 289.0 eV can be attributed to the carbon neighbouring ester groups C-COO at 285.5 eV, C-O species such as ether or hydroxyl groups at 286.5 eV, C=O groups such as carbonyl groups at

287.8 eV and a carboxylic group at 288.9 eV [5, 7, 16]. The peaks visible at higher binding energies can be attributed to shake-up processes.

Table 2. Chemical composition of the samples analyzed based on the XPS results.

Carbon type	Treatment	C at%	O at%	N at%	B at%
Vulcan	Untreated	98.7	1.3		
	Annealed	96.5	3.5		
	HNO ₃	93.9	6.1		
	KOH	85.5	14.5		
	B-doped	70.1	20.4		9.5
	N-doped	97.6	1.8	0.6	
Ketjenblack	Untreated	98.9	1.2		
	Annealed	99.3	0.7		
	HNO ₃	90.6	9.4		
	KOH	98.7	1.3		
	B-doped	84.3	11.5		4.2
	N-doped	92.7	2.9	4.4	

The introduction of heteroatoms into the carbon structure is an effective route to modify the properties of given carbon material. To improve the interaction of the heteroatom and carbon it was used the carbon samples whose oxygen concentration was higher, considering the results showed in Table 3. After doping the samples with nitrogen, they were analyzed by XPS and the fitting of the N1s spectrum (Fig. 6 a') showed the presence of two components. One at about 398.9 eV ascribed to pyridinic-N (nitrogen atoms bonded to two carbon atoms) and the other at about 400.6 eV ascribed to pyrrolic-N (nitrogen atoms bonded to two carbon atoms and one hydrogen atom) [7]. Regarding the oxygen functionalities, the XPS data showed the presence of two components at 532.5 eV and 533.9 eV, corresponding to C-O-C and O-C=O groups [7, 16], respectively. The XPS data for the Ketjenblack based sample the N1s fittings showed the presence of three components. In addition to the pyridinic-N and pyrrolic-N groups, it was identified the presence of chemisorbed nitrogen oxide species (403.9 eV) [7]. In contrast, only the C-O-C oxygen functionality was detected. These results show the successful incorporation of nitrogen into the carbon structure and the formation of different functional groups which can modify its electrocatalytic behaviour. Furthermore, the oxygen functionalities detected pointed to the hydrophilic nature of the substrates however, the results indicate a smaller degree of hydrophilicity in the case of the Ketjenblack based sample [7, 17].

The carbon samples were also doped with boron and the XPS results are shown in Fig. 7. In the case of the Vulcan based support, the results showed the presence of three boron groups. B-C bond in BC₃ structure at 191.3 eV, B-O bond in BCO₂ structure at 193.9 eV [18]. It was also detected the presence of borate at 196.5 eV [19]. Regarding the Ketjenblack based samples, the B1s spectrum showed only the presence of the BC₃ and BCO₂ structures. The presence of boron oxide is confirmed by the O1s spectrum nevertheless these results showed the successful incorporation of boron into the carbon structure.

Fig. 8 shows the TGA profiles under airflow of the untreated and functionalized carbon samples. The pristine samples show a higher oxidation resistance than the functionalized samples. The diminishing of the oxidation resistance of the functionalized samples can be related to the partial destruction of the textural structure of the carbon material [20].

In addition, it is visible a small weight loss for lower temperatures that can be related to the desorption of the oxygen species. This was more evident in the case of the samples treated with HNO₃.

Raman spectroscopy was used to further study the microstructure of the carbon samples. Fig. 9 display the recorded Raman spectra for both Vulcan and Ketjenblack samples as well as an example of the de-convolution made. The peaks at about 1340 cm⁻¹ and 1590 cm⁻¹ corresponds to the D and G bands, respectively. The so-called D band is originated from the symmetry breakdown for carbons situated at the edge of the graphite sheets, whereas the G band refers to the in-plane vibration of the sp²-bonded carbon atoms [21]. Within all the samples analyzed the Raman shift ascribed to the G band remains almost constant. In contrast, there is a slight variation on the Raman shift for the D band, indicating small differences on the carbons located at the edge graphite sheets. In order to do a more comprehensive analysis, the Raman spectra were de-convoluted and fitted. Apart from these main peaks, the de-convolution showed the existence of three defect-related peaks. A small shoulder at about 1200 cm⁻¹ related with some ionic impurities [22] and/or nanocrystalline diamond [21], which is always accompanied by another peak at around 1450 cm⁻¹ [23]. Finally, it was also observed a peak at about 1518 cm⁻¹ associated with the portion of amorphous carbon [21]. An example of the de-convolution made is depicted in Fig. 9c.

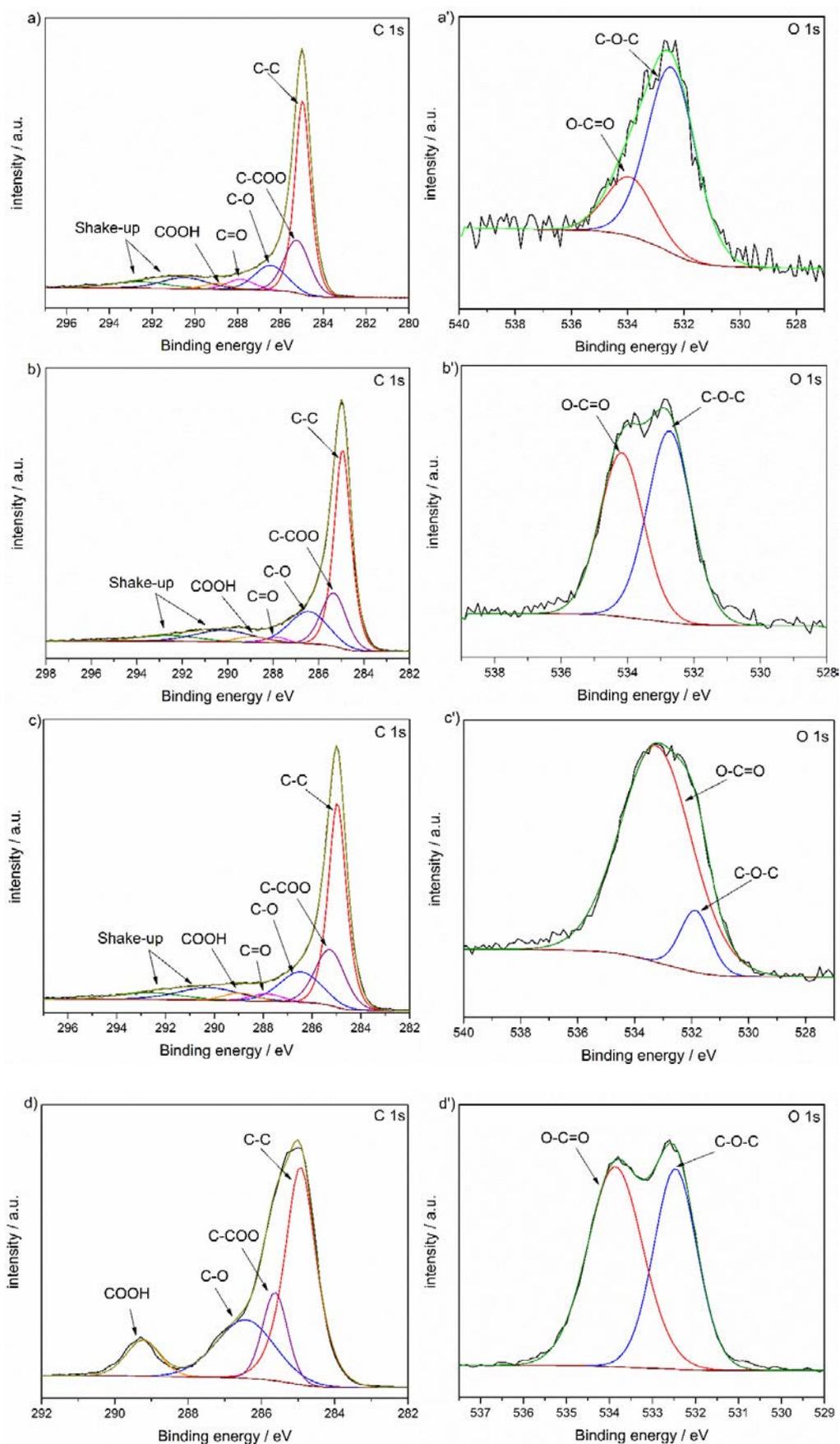


Fig. 4. XPs spectrum and its fitting for C1s and O1s regions of the Vulcan substrates a) and a') and after b) and b') annealing, c) and c') HNO₃ treatment and d) and d') KOH treatment.

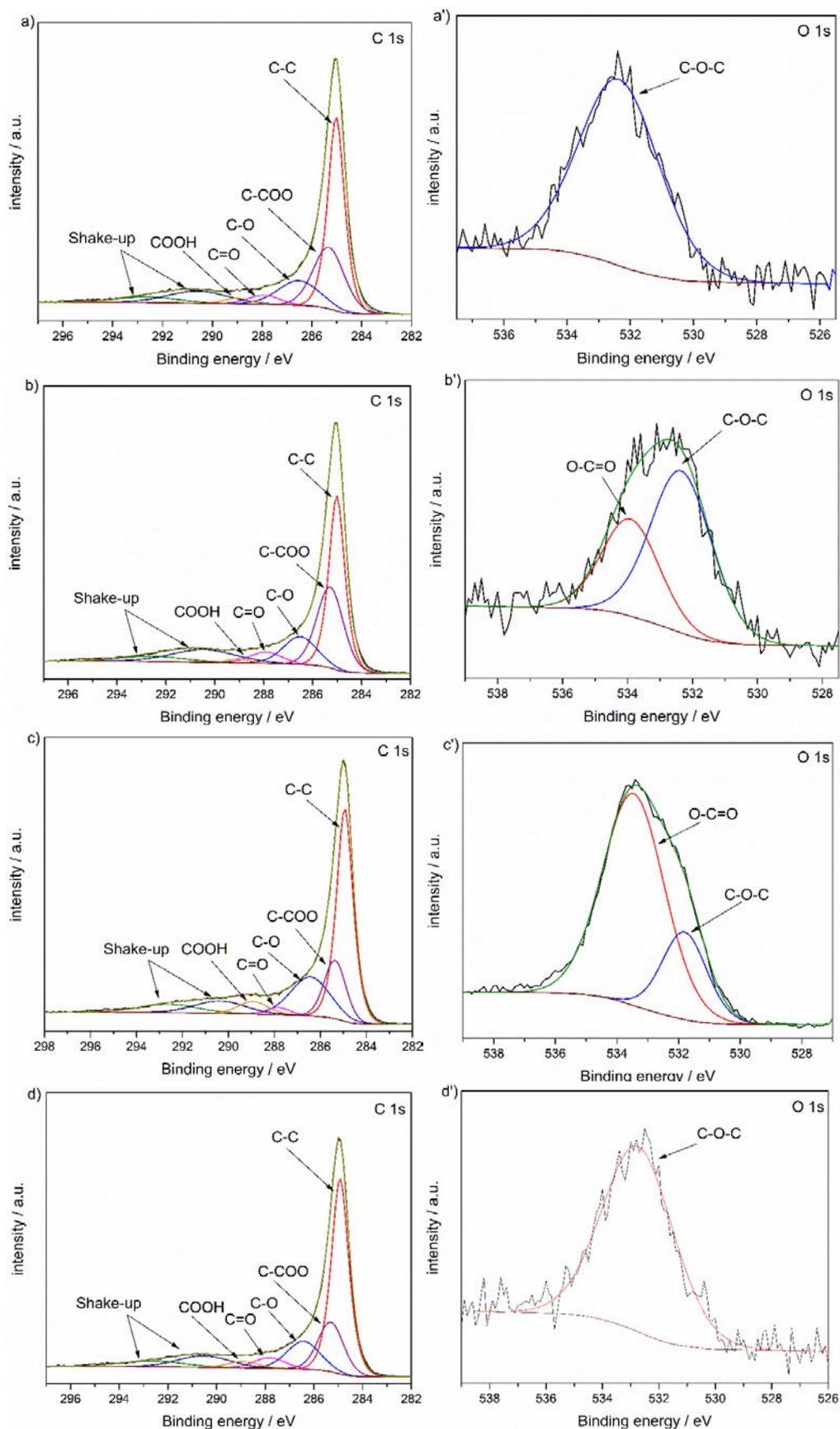


Fig. 5. XPS spectrum and its fitting for C1s and O1s regions of the Ketjenblack substrates a) and a') and after b) and b') annealing, c) and c') HNO₃ treatment and d) and d') KOH treatment.

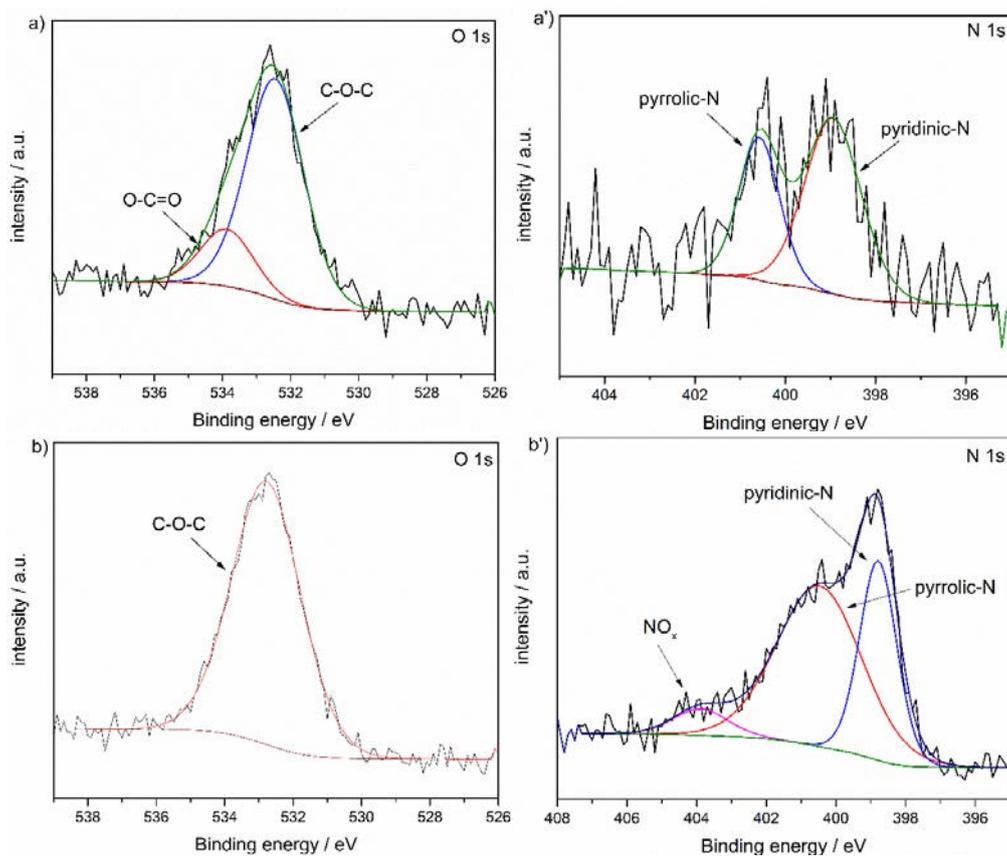


Fig. 6. XPS spectrum and its fitting for O1s and N1s regions for a) Vulcan and for b) Ketjenblack supports after doping with nitrogen.

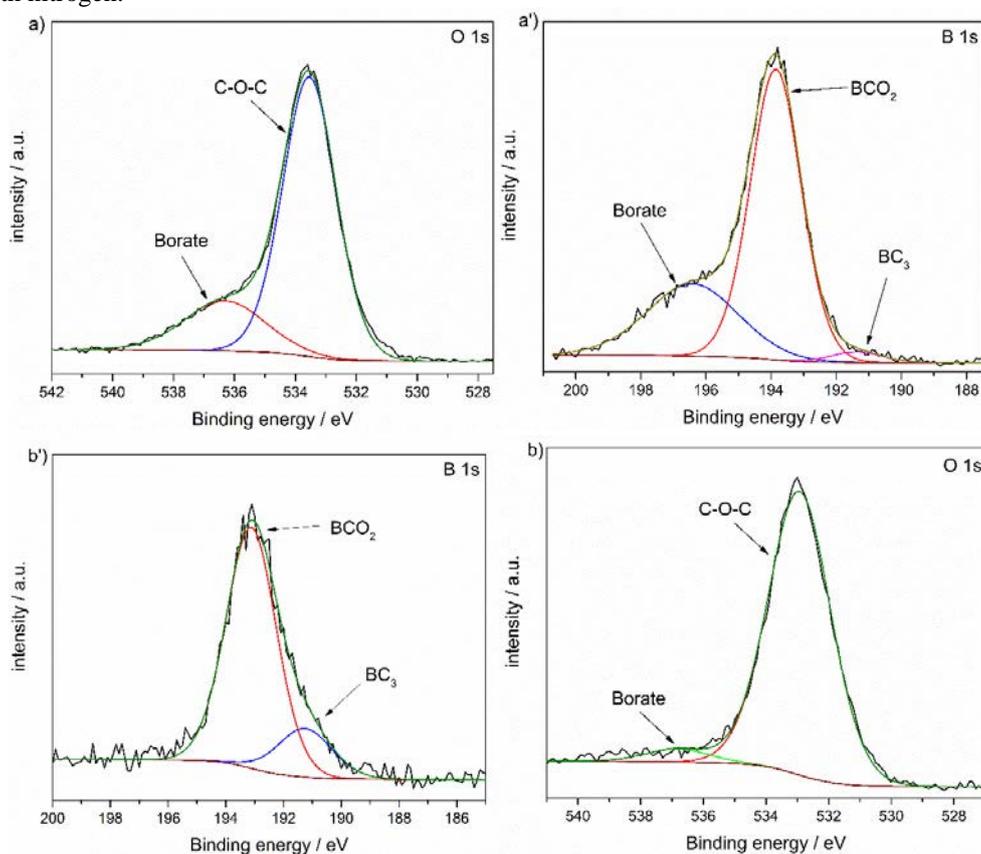


Fig. 7. XPS spectrum and its fitting for O1s and B1s regions for a) Vulcan and for b) Ketjenblack supports after doping with boron.

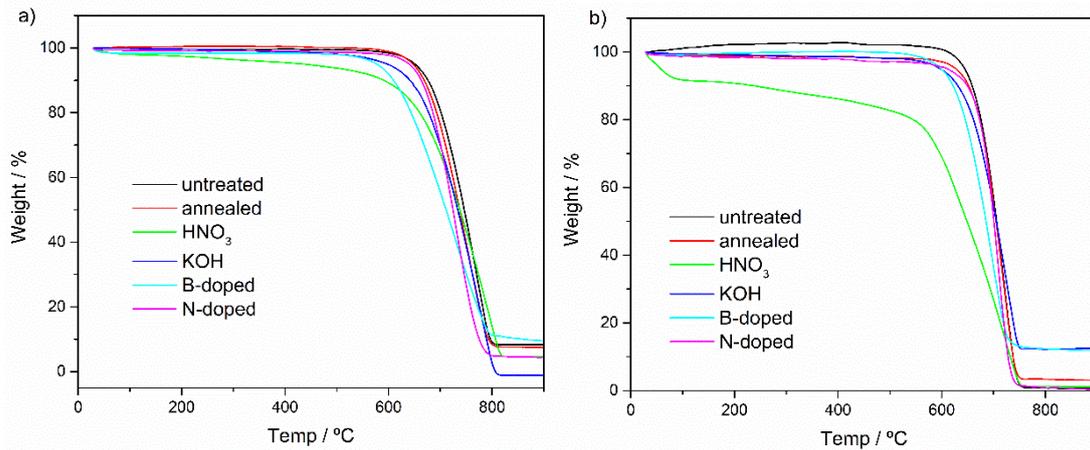


Fig. 8. TGA profiles in air of untreated and functionalized a) Vulcan and b) Ketjenblack carbon samples.

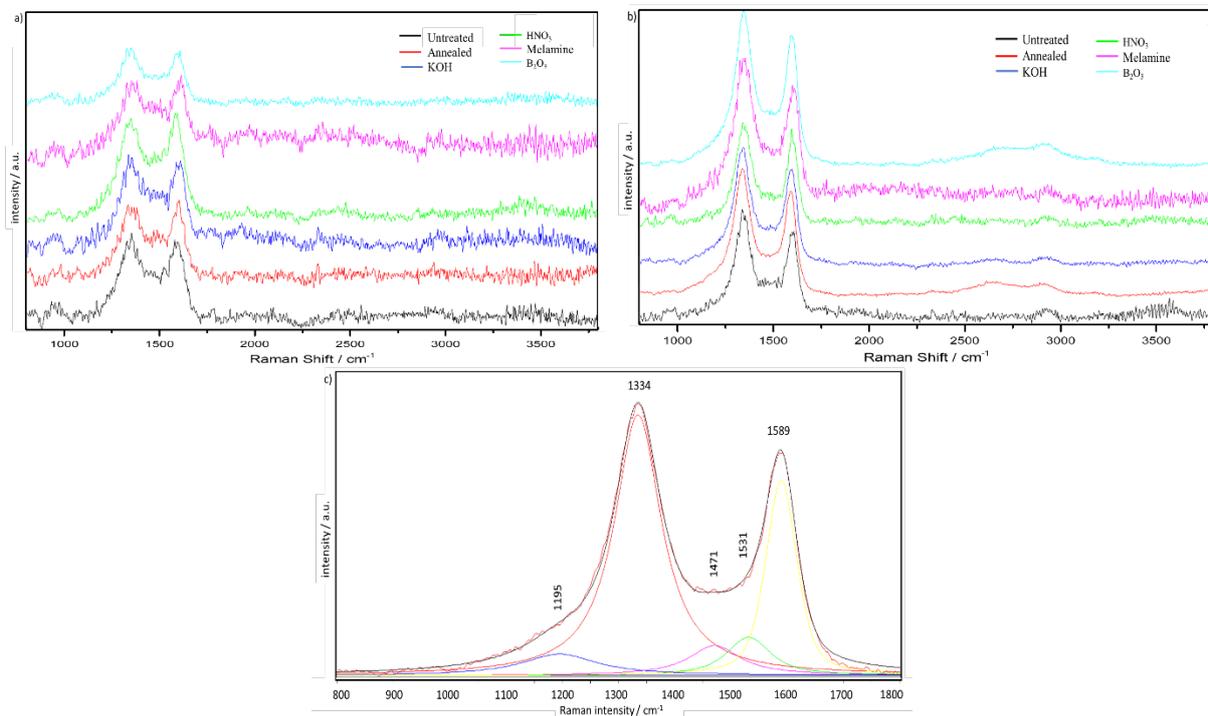


Fig. 9. Raman spectra of a) Vulcan-based and b) Ketjenblack-based carbon samples after functionalization; c) example of the de-convolution of the Raman spectra.

The extension of defects of the carbon samples can be estimated by calculating the I_D/I_G ratio (Table 3) as well as the in-plane crystallite size (L_a) calculated using Eq. 1 [24].

$$L_a = (2.4 \times 10^{-10}) \lambda^4 \left(\frac{I_D}{I_G} \right)^{-1} \quad (1)$$

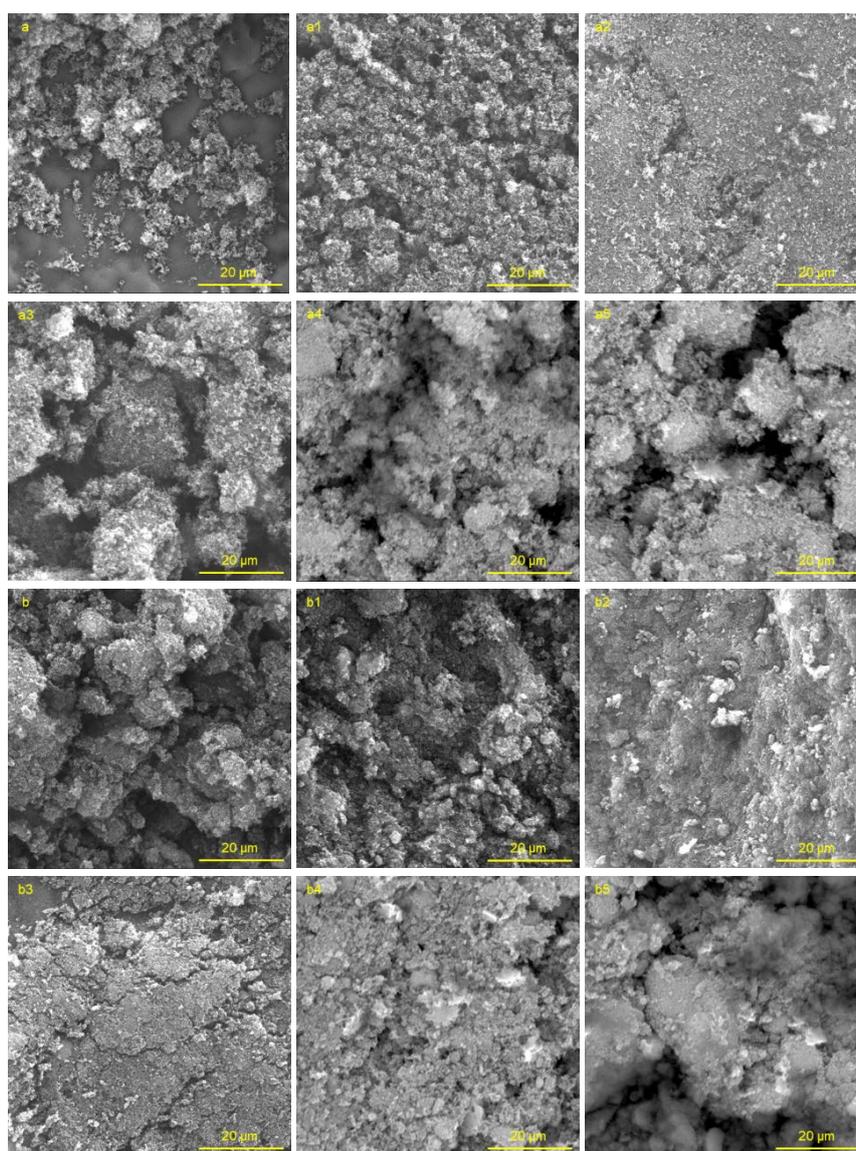
where λ is the laser wavelength in nm.

A higher I_D/I_G ratio indicates that more defects sites are present in the sample. Overall, our results show that Vulcan samples have a lower I_D/I_G ratio when compared with the Ketjenblack samples, as well as higher crystalline size. Analyzing the effect of the treatments made the results show that the degree of defects increased in the majority of the samples, due to the presence of oxygen-rich groups and to the presence of N- and B-doped layers. The increase of defects can facilitate the reaction of reduction of CO_2 .

The impact of the pretreatments on the morphology of the carbon samples was evaluated by SEM. Fig. 10 shows the SEM images of the pristine and treated carbon samples. From where it can be seen there are no significant morphological changes in the carbon samples with respect to the various treatments except for the aggregated particles visible in the chemical treated samples.

Table 3. Relative ratios of the D band to the G band and crystalline size, calculated from the Raman spectra.

Carbon type	Treatment	I_D/I_G	L_a (nm)
Ketjenblack	Untreated	1.28	15.0
	Annealed	1.34	14.3
	HNO ₃	1.18	16.3
	KOH	1.36	14.1
	B ₂ O ₃	1.23	15.6
	Melamine	1.30	14.8
Vulcan	Untreated	1.08	17.8
	Annealed	0.94	20.5
	HNO ₃	0.97	19.8
	KOH	1.24	15.5
	B ₂ O ₃	1.10	17.5
	Melamine	1.14	16.9

**Fig. 10.** SEM images of pristine a) Vulcan and b) Ketjenblack, and 1) annealed, 2) treated with HNO₃, 3) treated with KOH, 4) doped with nitrogen and 5) doped with boron.

The electrochemical performance of the carbon materials towards de CO₂ electroreduction was evaluated by linear sweep voltammetry (LSV). In this context, copper electrocatalyst supported on the different carbon materials were prepared. The LSV curves were obtained for each sample in 0.1 M KHCO₃ in the presence and absence of dissolved CO₂ are depicted in Figs. 11 and 12 for Vulcan and Ketjenblack-based support, respectively. The current

measured in the electrolyte saturated with nitrogen is associated with HER whereas for the CO₂ saturated solution the current measured is due to both HER and the electroreduction of CO₂. Having this in mind the catalysts prepared can either hinder the HER and/or favour the CO₂ reduction reaction. On this basis and from the data displayed on these figures it can be concluded that the electrocatalysts prepared using the treated carbon samples lead to an improvement in the catalytic activity in comparison with the untreated samples.

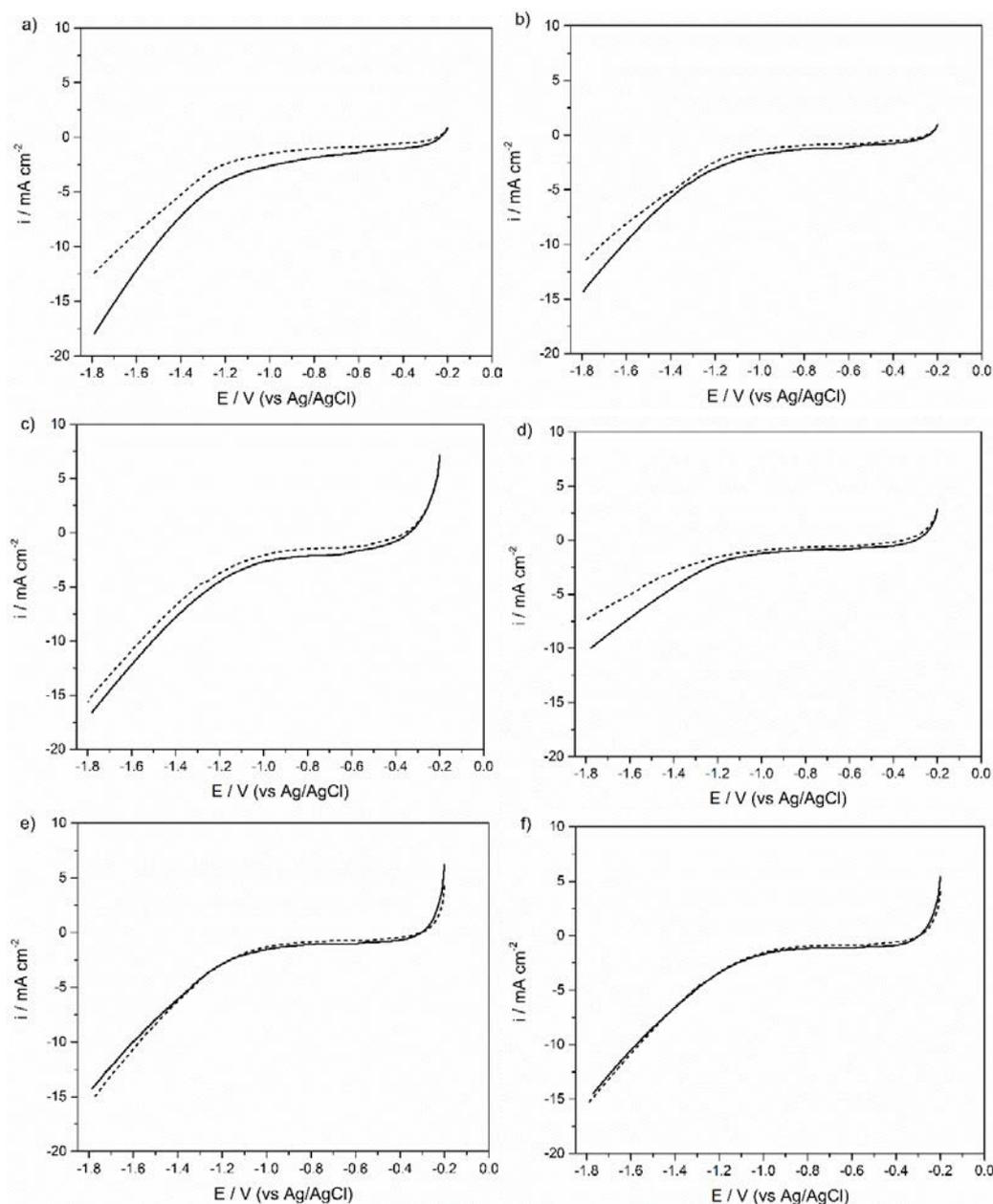


Fig. 11. Linear sweep voltammograms of the Vulcan-based carbon samples a) untreated, b) heat treated, c) oxidized in HNO₃, d) oxidized in KOH, e) doped with nitrogen and f) doped with boron in 0.1 M of KHCO₃ at room temperature and scan rate of 50 mV s⁻¹ (solid line refers to N₂ saturated solution and dash line refers to CO₂ saturated solution).

More detailed analysis and within the Vulcan-based electrocatalysts we can conclude that HER was hindered on the treated samples when compared to the untreated samples. The best performing carbon support suppressing HER was the electrocatalyst treated with KOH with a measured current of around -10 mA cm⁻² at -1.8 V in the nitrogen saturated electrolyte. Within the doped supports, no significant differences can be observed between the boron and nitrogen-doped carbon supports.

Interestingly, after dissolving CO₂ on the electrolyte the current measured at -1.8 V diminished when compared with the CO₂ free-electrolyte. Similar behaviour has been previously reported [25]. The authors believed that the decrease in the current was associated with the adsorption on the carbon surface of the species formed during the

reaction of reduction of CO_2 . In contrast, the current measured at -1.8 V, after dissolving CO_2 in the electrolyte increased when using the doped carbon supports nevertheless without showing significant differences between them.

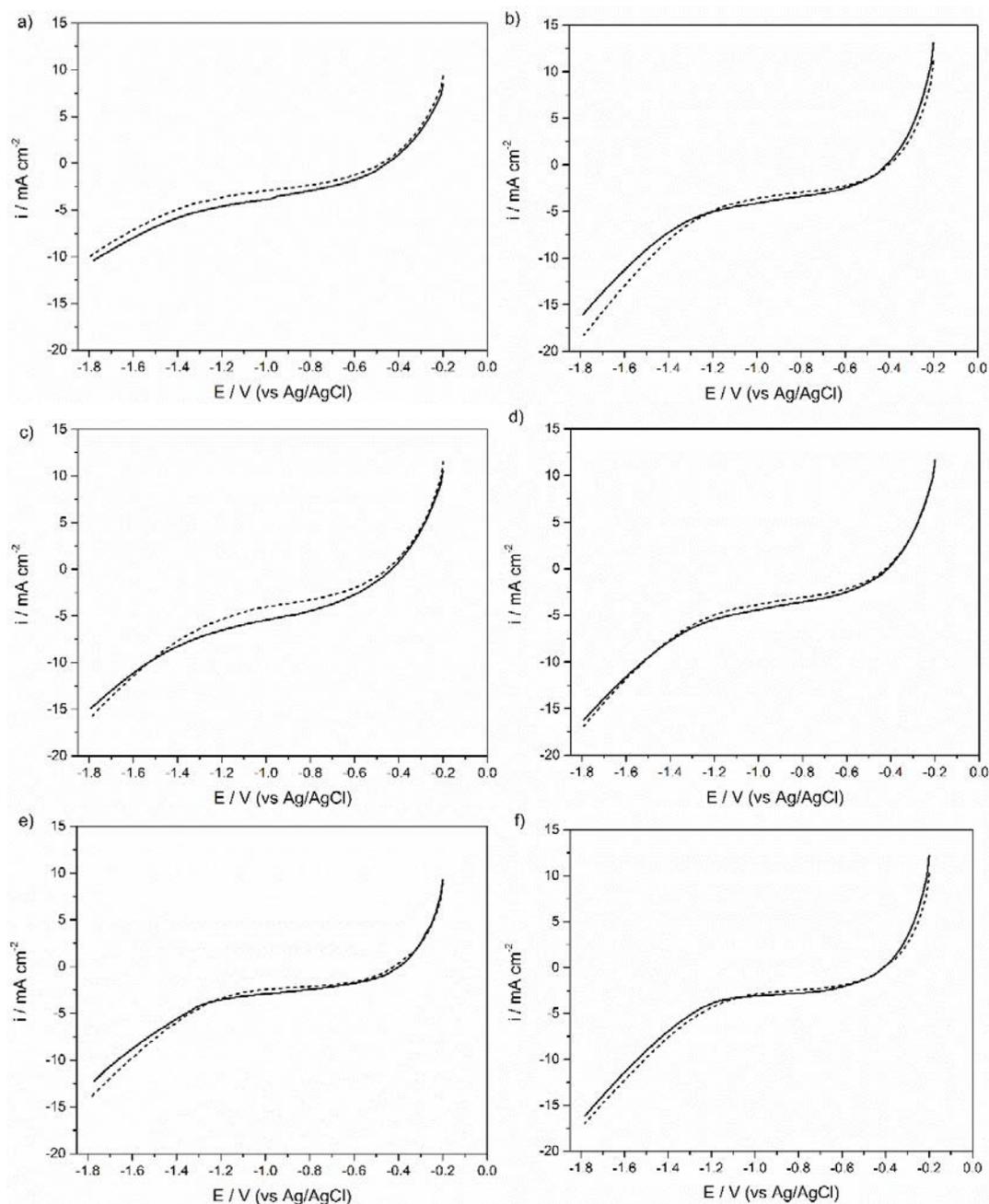


Fig. 12. Linear sweep voltammograms of the Ketjenblack-based carbon samples a) untreated, b) heat treated, c) oxidized in HNO_3 , d) oxidized in KOH , e) doped with nitrogen and f) doped with boron in 0.1 M of KHCO_3 at room temperature and scan rate of 50 mV s^{-1} (solid line refers to N_2 saturated solution and dash line refers to CO_2 saturated solution).

The samples prepared with Ketjenblack showed different behaviour. After the several treatments made, the current associated with HER increase when compared to the untreated carbon support. However, after dissolving CO_2 on the electrolyte we can see from Fig. 12 that the current measured at -1.8 V increased due to the reduction of the carbon dioxide, in contrast with the untreated sample where the current decreased in a similar way as previously discussed. From the treated samples the highest increase in the current measured (14.58%) was registered using the annealed carbon support, followed by nitric acid treatment (6.71%) and potassium hydroxide (3.38%). This difference can be related to the severity of the chemical treatment that leads to a smaller area when compared with the annealed sample, accordingly to the BET area mentioned before.

Regarding the doped carbon supports it is concluded from Fig. 12e and f) that the nitrogen-containing carbon support caused a 14.51% increase in the current measured against the 4.7% increase obtained with the boron-containing sample. These results are similar to those obtained for the Vulcan based electrocatalysts, where the nitrogen-containing catalysts showed a slightly better performance.

4. Conclusions

In this work, the effect of pre-treating and doping the commercial Vulcan XC 72R and Ketejenblack EC-600JD carbon substrates were investigated. After treatments, we registered a slight decrease in the surface area ascribed to the partial destruction of the carbon structure. Accordingly, to FTIR and XPS data the pre-treatments successfully introduced functional groups on the surface of the carbon structure, reaching a maximum oxygen content of 20 at% for the Vulcan-based support doped with boron. The doping process with either boron or nitrogen was accomplished and we obtained a maximum content of about 4 at% for the case of the Ketejenblack-based supports for both heteroatoms. In contrast, for Vulcan-based supports, we obtained a boron content of more than 9 at% and 0.6 at % for nitrogen. The electrocatalytic performance of the carbon supports prepared towards the electroreduction of the CO₂ were evaluated. It was found out that the pre-treatments affect not only the physicochemical properties of the carbon supports but also the electrocatalytic performance. HER diminished on the treated carbon copper supported electrocatalyst. After dissolving the CO₂ in the electrolyte, the adsorption of the reaction products leads to a decrease in the reducing current in case of the Vulcan based samples. Regarding the Ketjenblack samples, we register a 14% increase in the cathodic current after dissolving the CO₂ in the electrolyte, when compared to the untreated sample.

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