



Research article

Selective nitrogen functionalization of phosphorus-containing activated carbons



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ARTICLE INFO

Article history:

Received 12 May 2016

Received in revised form 29 August 2016

Accepted 3 October 2016

Available online 17 October 2016

Keywords:

Activated carbon

Nitrogen functionalization

NaBH₄

Phosphorus

Ninhydrin test

ABSTRACT

Nitrogen-containing activated carbons are materials of great interest. However, their main preparation methods are not able to control the formation of specific nitrogen groups on the carbon surface. The method here proposed is the selective nitrogen functionalization of activated carbons, by different oxidation and reduction treatments. Results indicated that the presence of stable phosphorus groups in the carbon obtained by chemical activation with phosphoric acid (ACP), favored the incorporation of higher amounts of nitrogen heteroatoms, mainly in form of nitro groups, during the treatment with only nitric acid. Subsequently, the activated carbons were reduced by thermal or chemical treatments, this last one by only using NaBH₄ as reducing reagent. Both methods were successfully used to reduce the nitro groups. Thermal reduction produced more condensed nitrogen (such as pyridinic and pyrrolic) structures in the activated carbons, containing (ACP) or not (AC) phosphorus groups on their surfaces. However, chemical reduction provided the selective formation of amine groups only with ACP carbons, suggesting the important role of phosphorus groups in the mechanism of amine formation. The presence of amine groups was confirmed by Ninhydrin test, for the first time, used in the detection of amino groups bonded to the carbon surface.

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1. Introduction

In recent decades, activated carbons are playing an important role in processes such as catalysis [1–3], adsorption [4,5], and electrochemistry [6,7]. This material has unique properties (e.g. cheap price, well developed porous structure and high chemical stability), that makes it suitable for these applications.

The capability of modifying the properties in terms of porosity and surface chemistry in activated carbons is also an important feature. In this sense, the surface of activated carbons can be modulated in terms of porosity and chemistry by different activation processes [8–12]. However, there is an increasing interest in modifying the surface chemistry, once the activated carbon has been prepared, by bonding different heteroatoms to its surface [13,14]. Specially, the incorporation of nitrogen is receiving a great interest [15–17].

In this sense, different nitrogen functionalities provide the material additional physicochemical properties for many applications. For instance, nitro groups grafted to the surface of the activated carbon, produce an improvement on NO oxidation rate [3]. Amide like groups have showed an increase on the adsorption capability and affinity in some molecules such as CO₂ [18]. Moreover, this kind of groups produces an enhancement in the catalytic properties of CoO_x/Nitrogen-containing-carbons composites when oxygen reduction reactions are analysed [19]. Amino groups bonded

to the surface of the activated carbons were successfully applied for biosensors applications, due to their ability of grafting organic molecules and biomolecules [20]. More condensed nitrogen structures (pyridinic, pyrrolic and quaternary functionalities) are also interesting, especially in electrochemistry [6,21] because they produce an increase in capacitance, improving that way the charge-exchange characteristics, for instance, these groups enhanced the electrochemical reduction of perchlorate [22].

The preparation of N-doped activated carbons has been already performed by different methods. Some authors obtained this kind of materials by carbonising nitrogen-containing precursors [4,23], while other authors prepared them by reactions of surface functionalization, such as, thermal treatment with ammonia or urea, treatments with melamine, ammoxidation with air and ammonia, and nitration [3,22,24]. However, these methods require high temperature and they are not able to control the formation of specific nitrogen groups on the carbon surface.

In this line, the use of a nitric acid treatment as a method for the incorporation of nitrogen heteroatoms has been recently reported [25]. This classic method has been used for years to incorporate carboxylic groups on the carbon surface [13,26]. However, this work pointed out the possibility of selectively obtaining nitro groups in activated carbons chemically activated with phosphoric acid [25].

Based on this previous work, the combination of oxidation and reduction treatments could open new possibilities to obtain, in a very controlled way, carbon materials with different nitrogen functionalities.

In the present work, the use of different treatments (nitric acid, and chemical and thermal reduction treatments) will be performed in order

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to obtain nitrogen-contained activated carbons with different nitrogen functional groups. The analyses of these type of groups will be carried out by different techniques (Temperature programmed desorption, X-ray photoelectron spectroscopy, and Ninhydrin test). The effect of the further presence of phosphorus on the amount and type of nitrogen groups incorporated will be also evaluated.

2. Experimental method

2.1. Reagents

Reagents of analytical grade were used in the experiments. HNO_3 65% and NaBH_4 98% were purchased from Sigma–Aldrich. H_3PO_4 was provided by Scharlab.

2.2. Preparation of activated carbon

Two different types of activated carbons were prepared by physical and chemical activation, by using olive stones supplied by Sociedad Cooperativa Andaluza Olivarera y Frutera San Isidro, Periana (Malaga), Spain, as precursor. Physical activation was performed by a carbonization and a partial gasification. Carbonization was carried out at 800 °C for 2 h under nitrogen (N_2 ; 99.999% purity purchased from Air Liquide) flow (150 cm^3/min STP). Then, the carbonized precursor was activated in a tubular furnace with a carbon dioxide (CO_2 ; 99.995% purity purchased from Air Liquide) flow (150 cm^3/min STP), at the same temperature for 7 h, reaching a 42.5% burn-off. Activated carbon obtained by physical activation presented a yield of 13.9% and was denoted as AC. On the other hand, a chemical activation process was used. In this case, the precursor was impregnated with H_3PO_4 85% (w/w) aqueous solution, at room temperature, and dried for 24 h at 60 °C, in a vacuum dryer. The impregnation ratio value ($\text{H}_3\text{PO}_4/\text{olive stone mass ratio}$) used was 3. Once impregnated and dried, the substrate was activated in a tubular furnace under continuous N_2 flow (150 cm^3/min STP) at 500 °C for 2 h [1,10]. The obtained sample was washed with distilled water at 60 °C until constant pH in the eluate, and then, it was vacuum-dried for 24 h at the same temperature. Activated carbon obtained by this method presented a yield of 45.7% and was denoted as ACP.

2.3. Surface modification of the activated carbons

Various treatments, which consisted of different oxidation/reduction processes, were performed to obtain activated carbons with different functionalizations. The oxidation process was carried out by nitric acid treatment. This treatment was performed by introducing 1 g activated carbon in a batch reactor, where 50 mL of 5 M HNO_3 solution was added. Reaction occurred in constant stirring at 80 °C for 5 h. After finishing the reaction, sample was washed with distilled water at 60 °C, until constant pH in the eluate was reached [25]. Samples obtained following this treatment were denoted by adding -N to the initial activated carbon name, e.g. ACP-N. The yields after nitric acid treatment were upper than 95%.

On the other hand, two kinds of reduction processes were also studied, a chemical reduction and a thermal one. The chemical reduction was achieved by using NaBH_4 as reducing agent. In this process, 0.9 mg of activated carbon was mixed into 50 mL of ethanol. Then, a solution of 0.74 g of NaBH_4 dissolved into 50 mL of ethanol was slowly dripped over the carbon containing solution, and maintained for 24 h in continuous stirring, at room temperature. Once the reaction was finished, the sample was washed with distilled water at 60 °C until constant pH in the eluate was reached. Samples obtained by this treatment were named adding -B to the initial activated carbon name. The yields after NaBH_4 treatment were upper than 98%.

The thermal reductions were carried out at two different experimental conditions. For the low temperature treatment, the activated carbon was heat treated at 300 °C, at a heating rate of 10 °C/min, in a

tubular furnace under constant N_2 flow for 1 h. Samples obtained in this process were named by adding - Δ to the name of the activated carbon. In the case of high temperature thermal reduction, samples were heated from room temperature up to 930 °C, at a heating rate of 10 °C/min, in a tubular furnace under constant N_2 flow (200 cm^3 STP/min). Samples thus obtained were named by adding -HT. The yields after the low temperature treatment were upper than 99%. In contrast, the yields obtained for the high temperature treatment were around 80%.

2.4. Characterization of samples

The porous structure of the samples was characterized by N_2 adsorption–desorption and CO_2 adsorption at –196 and 0 °C, respectively, using a micromeritics instrument (ASAP 2020 model). The samples were previously outgassed for at least 8 h at 150 °C. From the N_2 isotherm, the apparent surface area (A_{BET}) was determined by applying the BET equation; micropore volume (V_t) and external surface area (A_t) were calculated using the t-method; mesopore volume (V_{mes}) was determined as the difference between the maximum adsorbed volume of N_2 (V_p), at a relative pressure of 0.99 and the micropore volume (V_t). From the CO_2 adsorption data, the narrow micropore volume (V_{DR}) and surface area (A_{DR}) were calculated using the Dubinin–Radushkevich equation.

Surface chemistry of the samples was analysed by X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), elemental analysis, scanning electron microscopy (SEM), and Ninhydrin test. XPS analyses of the samples were obtained by a 5700C model Physical Electronics apparatus, with Mg K α radiation (1253.6 eV). For the analysis of the XPS peaks, the maximum of the C1s peak was set at 284.5 eV and used as reference for the other peaks [27]. The peaks were deconvoluted by least squares using Gaussian–Lorentzian peak shapes and a Shirley-type background line.

TPD profiles were obtained in a custom quartz fixed bed reactor placed inside an electrical furnace. The samples were heated from room temperature to 930 °C at a heating rate of 10 °C/min in N_2 flow (200 cm^3 STP/min). The amounts of CO and CO_2 desorbed from the samples were monitored by nondispersive infrared (NDIR) gas analysers (Siemens ULTRAMAT 22).

Elemental analysis of the samples was performed using a Perkin-Elmer 2400 CHN system, and the oxygen content was calculated by difference. The ash content of the samples was obtained from the weight of the solid residue after exposure to air-TG at 900 °C.

The surface texture and structure of the samples were characterized by scanning electron microscopy (SEM). Scanning electron micrographs were obtained, at a high voltage of 20–25 kV, using a JEOL JSM-840 instrument equipped with an energy dispersive X-ray analysis (EDAX) modulus.

Ninhydrin method was initially introduced by Moore and Stein in 1948 [28] for the determination of amino acids and it is based on the formation of a coloured compound which can be measured by UV/Vis spectrophotometry. In this work, this test will be adapted and used for the first time, for the determination of amino groups bonded to the surface of the activated carbons.

This method uses Ninhydrin (1,2,3-Indantrione monohydrate, or triketohydrindene hydrate) as reagent. This compound reacts with primary amines through a series of reactions producing ammonia and a partially reduced form of ninhydrin, hydrindantin (Fig. 1a). Then, another molecule of ninhydrin condenses with ammonia and hydrindantin (Fig. 1b) to produce an intensely blue coloured compound, sometimes called Ruhemann's purple.

This method is very influenced by the experimental conditions [29]. So, the conditions have been optimized in order to selectively detect the amino groups bonded to the carbon surface. In this case, the conditions used were as follows: a ninhydrin solution with a concentration of 10 mg/mL in ethanol (96%) was added to the activated carbon sample

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