CARBON 68 (2014) 520–530

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

Tailoring the surface chemistry and porosity of activated carbons: Evidence of reorganization and mobility of oxygenated surface groups

Jose F. Vivo-Vilches, Esther Bailón-García, Agustín F. Pérez-Cadenas, Francisco Carrasco-Marín, Francisco J. Maldonado-Hódar *

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

ARTICLE INFO

Article history:
Received 24 May 2013
Accepted 13 November 2013
Available online 21 November 2013

ABSTRACT

An activated carbon with developed porosity and surface area (S_{BET} = 2387 m^2 g^{-1}) was prepared by chemical activation and then oxidized with ammonium peroxydisulfate. The oxidation treatment destroyed mesopore walls leading to a severe surface area reduction. Specific thermal treatments were carried out in different portions of the oxidized sample to selectively remove the oxygenated surface complexes. The combination of different techniques revealed that thermal treatment between 300 and 500 °C produces a strong reorganization of oxygenated groups on the chemical structure of carbons. CO_2-evolving groups (around 75 wt.%) are selectively transformed into CO-evolving groups. These processes only occur inside the pores, and involve CO_2 desorption and re-adsorption in this temperature range. At a higher treatment temperature (700 °C), re-oxidation is prevented and the surface chemistry becomes quite similar to the original activated carbon.

1. Introduction

The performance of carbon materials as adsorbents, catalysts or catalyst supports depends on the combination of porous and chemical surface properties, which in turn, control the nature and strength of the interactions between the carbon material and the corresponding target molecule. One of the main advantages of carbon materials is their versatility, in that their physicochemical properties can be easily adapted to one specific application.

Different types of new carbon materials can be prepared today with controlled porosity using techniques such as nanocasting [1], sol–gel and controlled drying to obtain aerogels, xerogels or cryogels [2,3], etc. However, most of activated carbons are prepared using cheap raw materials like coal [4] or different types of residues such as old tires [5], sludge from waste water treatment [6], agricultural by-products, available in abundance around the world and which vary depending on the geographic area (olive stones, almond shells, coconut, etc.) and even pruning off-cuts [7,8]. Pore size distribution and surface area depend on the nature of the raw material, the activation procedure (physical activation or chemical activation, activating agent, temperature and activation time) and the activation (burn-off) degree [9]. All these aspects should be optimized in each case to obtain the desired porosity, and a balance must be struck between the characteristics of the product (porosity, mechanical properties, etc.) and the cost (yield) of the process. Many previous researchers have tried to analyze and predict the influence of experimental conditions in an attempt to optimize the product while keeping the cost of the process as low as possible [9,10].

We observed that an extensive textural study was performed in most of the manuscripts using porous materials. Less attention, however, is paid in general to the influence

* *Corresponding author:* Fax: +34 95824852.
E-mail address: fjmaldon@ugr.es (F.J. Maldonado-Hódar).
0008-6223/$ - see front matter
http://dx.doi.org/10.1016/j.carbon.2013.11.030

of chemical properties, although surface groups based on different heteroatoms (O, N, S, halogens, etc.) are specifically generated by the treatment of carbon materials both in gas and liquid phase [11]. The control of surface chemistry is a powerful tool for developing specific adsorbents and catalysts. It is well known that surface chemistry strongly influences the behavior of carbon materials in the adsorption of organic molecules from solutions, controlling electrostatic/non-electrostatic interactions [12]. Specific chemical groups, like sulfur surface groups, were introduced to increase the mercury adsorption [13,14], and oxygenated surface groups (OSG) were used to favor the separation/capture of CO_2 from mixtures of gases [15].

OSG are the most extensively studied of the various types of surface chemical groups, [16–18]. In the activation process, OSG are the intermediate species before they are evolved as gaseous CO or CO_2 [9]. In catalytic applications, acid carbons were produced by oxidation processes for fine chemistry applications [16]. OSG influence the metal dispersion of supported catalysts [17] and have been used to anchor active metal-complexes [18]. Some OSG are acidic (carboxylic, lactones, anhydrides, phenol) while other such as chromene or pyrone groups are classified as basic centers [11,19]. Parameters such as hydrophobicity or the acid/base nature of the carbon surface can therefore be modified by the oxidation process and a controlled removal of the groups generated [20]. All these processes involving the generation and removal of OSG imply the mobility and transformation of these chemical species. Theoretical studies of this question have been made using different approaches (density functional theories or computational chemistry calculations) [21,22], but in general, there is a lack of information and experimental proof. In previous studies [20], we observed that oxygenated surface groups can be removed selectively by heating oxidized samples in an inert atmosphere: the oxygen content decreases linearly as the treatment temperature increases. After these thermal treatments, both CO-evolving groups and to a lesser extent CO_2-evolving groups show some degree of mobility on the carbon surface, and a significant amount of CO is evolved below the treatment temperature, when the sample is heated again from room temperature without air exposure. This shows that the thermal stability of some of these groups decreases because they move to previously generated free sites.

In this work, a highly porous activated carbon was obtained by chemical activation of carbonized olive stones and deeply oxidized by treatment with $(NH_4)_2S_2O_8$. Textural and chemical transformations induced by the formation/elimination of OSG after oxidation, thermal treatments and storage in air were analyzed using different techniques. We present experimental evidence of the mobility of oxygenated surface groups and the transformation of acidic CO_2-evolving groups into CO-evolving groups.

2. Materials and methods

2.1. Preparation of carbon materials

Olive stones were milled and sieved to 1.0–2.0 mm, treated with sulfuric acid (1 N) to remove the rest of pulp and washed until all sulfates had been removed. An initial carbonization was carried out by heating at 10 °C min^{-1} to 400 °C and a soak time of two hours under a nitrogen flow of 300 cm^3 min^{-1} using a tubular furnace (from Heraeus) equipped with a stainless steel tube (200 cm long × 8 cm diameter × 0.8 cm wall) with reduction made by steel welding and graphite joints between the taps.

The purity of the N_2 flow was 99.999% (H_2O, CO and O_2 contents below 3 ppm), and air leaks were prevented by placing a Gas Purifier MDL III from Supelco (Ref. 23,800-U) at the entry to the furnace, which removed the possible residues of H_2O, O_2, CO and CO_2. The composition of the N_2 flow was identical at the entry and the exit of the furnace tube (analyzed by MS), the leak absence was carefully checked before any sample preparation and the system was purged for 1 h before heating. After thermal treatments, samples were cooled in the same N_2 flow to room temperature and finally stored in a desiccator.

The carbon yield was 30%. Chemical activation was carried out using a mixture of this carbonized material and KOH in a 1:7 mass ratio. This mixture was treated under nitrogen flow (300 cm^3 min^{-1}) for 2 h at 350 °C followed by three hours at 850 °C (heating rate of 10 °C min^{-1}). Cooling to ambient temperature was performed by keeping the sample under nitrogen atmosphere. Finally, the sample was demineralized with HCl and HF, which also removed the excess base (KOH), washed with distilled water until chlorides had been removed and dried in an oven at 110 °C for 24 h before storage. This sample was labeled as CA.

2.2. Chemical surface modifications

Ammonium peroxydisulfate ($(NH_4)_2S_2O_8$) was chosen as an oxidizing agent. CA was mixed with a saturated solution of this salt on H_2SO_4 1 M. After 24 h under stirring at room temperature, oxidized carbon was filtered and washed with distilled water until sulfates had been removed [17,23,24]. This material was dried at 110 °C and labeled as CAOX. Thermal treatments under nitrogen atmosphere (150 cm^3 min^{-1}) at 300, 500 and 700 °C (10 min, 20 °C min^{-1}) were carried out on different portions of CAOX, following the same experimental procedure described previously, in order to remove some of the oxygenated surface groups (OSG) selectively, thus obtaining three samples CAOX300, CAOX500 and CAOX700.

2.3. Textural characterization

The morphology of carbons was analyzed using a scanning electron microscope (Leo, Carl Zeiss, Geminy-153). Images were obtained at excitation energy of 20 kV. Textural properties of ACs were determined by adsorption isotherms of N_2 (−196 °C) and CO_2 (0 °C) using an Autosorb 1 from Quantachrome after outgassing samples overnight at 110 °C under high vacuum (10^{-6} mbar). Parameters such as BET surface area, micropore volume (W_0) and micropore mean width (L_0) were calculated by applying BET, Dubinin-Radushkevich and Stoeckli equations respectively to the corresponding isotherms [25,26]. The pore size distributions (PSD) were determined by applying Quenched Solid Density Functional Theory (QSDFT), assuming slit-shaped pores and BJH derived methods [27,28] to the N_2 adsorption isotherms. Mesopore volume (V_{meso}) was estimated according to Gurvitch's rule,