Available online at www.sciencedirect.com
SCIENCE DIRECT®

Applied Surface Science 252 (2006) 5984–5987

applied surface science

www.elsevier.com/locate/apsusc

Preparation of activated carbons previously treated with hydrogen peroxide: Study of their porous texture

M. López de Letona Sánchez [a], A. Macías-García [a], M.A. Díaz-Díez [a], E.M. Cuerda-Correa [b,*], J. Gañán-Gómez [a], A. Nadal-Gisbert [c]

[a] *Área de Ciencia de Materiales e Ingeniería Metalúrgica, Escuela de Ingenierías Industriales, Universidad de Extremadura, 06071 Badajoz, Spain*
[b] *Departamento de Química Inorgánica, Facultad de Ciencias, Avda de Elvas S/N, 06071-Badajoz, Spain*
[c] *Escuela Politécnica Superior de Alcoy (U.P.V.), Pª Viaducto no. 1, 03801 Alcoy, Spain*

Abstract

Cedar wood was used as raw material for the preparation of activated carbons by treatment with hydrogen peroxide of different concentrations. The samples were next carbonised and activated under CO_2 atmosphere. The activated carbons were characterised by means of the adsorption isotherms of N_2 at 77 K, as well as by applying the Density Functional Theory (DFT) method and mercury porosimetry. The experimental results corresponding to the activated samples indicate a more remarkable porous development as a consequence of the treatment with hydrogen peroxide, probably due to the elimination of surface complexes produced during the activation step. The DFT diagrams point out that the activating treatment favours the development of medium and narrow-size micropores whereas the carbonisation process leads to the development of wide micropores of size close to that corresponding to mesopores.

PACS: 61.43.Gt; 61.43.Hv; 68.47.-b

Keywords: Activated carbon; Hydrogen peroxide; Average pore size distribution

1. Introduction

Activated carbons (ACs) are well known as porous solids with a highly developed surface area. These materials are becoming more and more interesting on account of their excellent properties as adsorbents, which make it possible to use them in purification and pollutant removal from both liquid and gaseous media [1–3]. ACs are also effective as catalysts and catalyst supports [4–9]. Therefore, a number of applications have been developed from the industrial standpoint in different fields. Accordingly, a remarkable growth in the demand of ACs for industrial uses has taken place in the last years.

The preparation of activated carbons from lignocellulosic materials by physical activation is a process of the utmost importance from the industrial standpoint. Many of such materials are suitable to be used as precursors of high quality activated carbons that find an application in gas and liquid phase adsorption [10–13].

Two methods are mainly used to prepare activated carbons: physical activation [14,15] and chemical activation [16,17]. Both of them begin with precursor materials having high carbon content. The purpose is to develop the pore volume or size in order to increase their adsorption capacity.

Many materials can be used as precursors to prepare activated carbons [18–27]. A particular material is usually chosen based on factors such as low content of inorganic matter and a high content of volatile matter, ease of handling, and degradation stability during storage [28–33].

In this work, small pieces of cedar wood as well as shavings from a local furniture manufacturer were used as raw material for the preparation of activated carbons. The physical activation process has been modified by the introduction of a previous step consisting in the treatment of the raw material with hydrogen peroxide of different concentrations.

---

* Corresponding author. Tel.: +34 924 289300x9038.
E-mail address: emcc@unex.es (E.M. Cuerda-Correa).

0169-4332/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2005.11.022

2. Experimental

Cedar wood was treated with 200 mL of aqueous solution of hydrogen peroxide 1, 3, 6 and 9N for 4 h and next washed thoroughly with distilled water. Afterwards, the samples were carbonised for 2 h under N_2 flow (100 mL min^{-1}). The carbonisation temperatures were 600, 700 and 800 °C, the heating rate being 5 °C min^{-1}. The samples obtained according to the treatment here exposed will be referred to as C-H_2O_2–T-Conc, where T represents the carbonisation temperature and Conc is the concentration of hydrogen peroxide solution used in the previous treatment. The sample showing optimal properties was selected for its subsequent activation under CO_2 flow (100 mL min^{-1}) at 700, 800 and 900 °C for 4 h, the heating rate being 5 °C min^{-1}. The samples prepared in this second stage will be referred to as A-H_2O_2–T, where T represents the activation temperature. All samples were characterised by physical adsorption of gases with the aid of an Autosorb A-1 equipment. The mercury porosimetries were performed in a Quantachrome porosimeter.

3. Results and discussion

3.1. Preparation and textural characterisation of the carbonised samples

Previous studies carried out using hydrogen peroxide as oxidising agent indicate that neither the contact time nor the oxidising agent concentration modify the yield of the oxidation process in a significant manner. In all cases the yield is very close to 100%, the weight losses remaining nearly constant as the hydrogen peroxide concentration increases (see Table 1). This fact may be due to the introduction of oxygen groups in the surface of the raw material during the oxidation process. The results obtained for the carbonised samples (see Table 2) indicate that temperatures above 600 °C lead to a total carbonisation of the sample, as the yield of the process does not vary significantly at higher temperatures. On the other hand, the yield of the process is remarkably lower (26.9–27.9%) than those obtained in the prior treatment of the raw material (close to 100%). This fact may indicate that, at least apparently, the previous treatment does not affect the raw material but exerts a noticeable influence on the carbonisation process, probably due to the release of oxygen retained in the raw material previously treated with hydrogen peroxide.

Table 1
Influence of the treatment with H_2O_2 on the raw material

Treatment	Yield (%)
H_2O_2, 1N	99.2
H_2O_2, 3N	99.1
H_2O_2, 6N	99.2
H_2O_2, 9N	99.2

The adsorption process of N_2 at 77 K by the carbonised samples takes place in a slow manner due to the fact that the average pore size of the materials is very close to that of the N_2 molecule [34]. Thus, the access of the molecules to the pores is handicapped and a long equilibrium time is required.

From the adsorption isotherms of N_2 at 77 K by the carbonised samples (Fig. 1), it may be concluded that all samples are very similar, since the volume of N_2 adsorbed at a given relative pressure value is very close for all samples. Hence, the surface and porosity of the samples will be relatively low and similar in all cases. This assertion is corroborated from the results summarized in Table 2, which indicate that the treatment with hydrogen peroxide favours the development of the porous texture in a moderate manner.

Accordingly, sample C-H_2O_2-600-9N was selected as precursor for the activation procedure, as the preparation of this sample requires lower temperature and, consequently, a noticeable reduction of the costs is achieved.

Fig. 2 depicts the DFT diagram of the carbonised samples. It may be observed that, as expected, the pore size distribution of the carbonised samples is very similar in all cases. The average pore size of the samples included in Fig. 2 moves from large micropores (average pore size equal to 15.41 Å for sample C-H_2O_2-600-9N) to medium size supermicropores (average pore size equal to 17.64 Å for sample C-H_2O_2-700-9N, or 18.46 Å for sample C-H_2O_2-800-9N). This fact indicates that the thermal treatment favours the formation of large micropores showing a diameter close to that corresponding to mesopores.

Table 2
Textural characterisation of the carbonised samples

Sample	Yield (%)	V_{mi} (cm^3 g^{-1})	V_{me} (cm^3 g^{-1})	V_{ma} (cm^3 g^{-1})	S_{BET} (m^3 g^{-1})
C-H_2O_2-600-1N	27.9	0.094	0.054	0.035	250
C-H_2O_2-600-3N	27.4	0.097	0.054	0.035	256
C-H_2O_2-600-6N	27.2	0.095	0.057	0.036	263
C-H_2O_2-600-9N	27.2	0.101	0.057	0.037	263
C-H_2O_2-700-1N	27.5	0.098	0.055	0.038	290
C-H_2O_2-700-3N	27.2	0.097	0.055	0.039	292
C-H_2O_2-700-6N	27.0	0.099	0.055	0.039	292
C-H_2O_2-700-9N	26.9	0.100	0.057	0.040	295
C-H_2O_2-800-1N	27.4	0.100	0.057	0.039	286
C-H_2O_2-800-3N	27.1	0.104	0.055	0.040	284
C-H_2O_2-800-6N	26.9	0.108	0.051	0.040	285
C-H_2O_2-800-9N	26.9	0.107	0.050	0.043	285