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Temperature dependence of the electrical conductivity of activated carbons prepared from vine shoots by physical and chemical activation methods

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ABSTRACT

A broadly varied series of activated carbons (ACs) was prepared from vine shoots (VS) by the method of physical activation in air, CO_2 and steam, and by the method of chemical activation with H_3PO_4, $ZnCl_2$ and KOH aqueous solutions. Here, the temperature dependence of the dc electrical conductivity for the ACs is studied from room temperature up to 200 °C. The bulk electrical conductivity of the carbon samples is found to be the result of a complex interplay between several factors, texture and surface chemistry likely being the most relevant ones. The best conductivity values are obtained for sample carbonized at 900 °C. The physical activation stage has been proved to decrease the conductivity of the carbonized products, the reduction being more pronounced for air than for CO_2 and steam. Such a detrimental effect of physical activation on conductivity has been associated with the formation of oxygen groups and structures on carbon surface rather than with the porosity development. The conductivity of ACs prepared by chemical activation is even lower than for physically activated samples, likely due to the higher degree of porosity development. All carbon samples, irrespective of the activation method and activating agent, behave as semiconductor materials and therefore the electrical conduction is related to an energy gap (E_g). The E_g values widely vary from 0.084 eV for the sample carbonized at 900 °C up to 0.659 eV for the AC prepared by physical activation in air.

1. Introduction

Activated carbon (AC, hereafter) is an amorphous carbon material characterized by its excellent textural properties (i.e. surface area, porosity and pore size distribution) and surface chemistry. It is well-known that these properties of AC strongly depend on the raw material and the method employed in its preparation process [1–4], including the activating agent as well as the operational conditions. A great variety of precursors with high carbon content and low amount of inorganic compounds are widely used in the large-scale manufacture of AC, such as woods, coals, lignite, coconut shell, peat, fruit stones, polymers, and so on [1,3,5–8]. Nowadays, the production of ACs from industrial and agricultural waste products is an issue of active research, with a view not only to their controlled removal and valorization but also to prepare lower-cost ACs [9].

Vine shoots (VS, henceforth) are an agricultural waste generated in most of the European Mediterranean countries as a result of the pruning works carried out yearly in all vineyards after the grape harvest. The annual production of VS in Spain is in the order of several million tons [10], and such an amount has been estimated to be at around 87,725 tons only for the Autonomous Community of Extremadura (south-west Spain) [11,12]. Because of their low density and thereby high transportation cost, the valorization of VS is a very difficult task and as a result they are usually burnt in the open air with release of greenhouse effect gases. This solution is the fastest one but not the best one, both from economic and environmental standpoints. As a way of diversifying the applications of this agricultural residue and increasing its profitability, some previous works have shown that VS are an attractive precursor for the preparation of ACs [9,13–15], which have been successfully applied in the removal of dyes from water streams [16] and in the wine treatment [17].

AC has a wide range of applications, including water treatment, gas separation and storage, removal of pollutants by adsorption

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both from liquid and gaseous effluents, solvent recovery, in heterogeneous catalysis acting either as catalyst by itself or more commonly as catalyst support, in electrocatalysis, sensors and actuators, and so on [1–3,18]. Recently, special attention has been focused on the use of AC as electrode material in electrical energy storage devices, mainly supercapacitors [19–28] and lithium ion batteries [29–33]. Among other factors (specific surface area, pore size distribution, chemical and thermal stability, presence of electroactive surface functional groups and structures, electrolyte, and so forth [22,24,34,35]), electrical conductivity has been shown to play a major role on the potential application and performance of ACs in the aforesaid devices [36,37]. On the other hand, the properties of the carbon support, especially its electrical conductivity, largely determine the electrochemical performance of carbon-based electrocatalysts [38]. Therefore, it becomes apparent that the measurement of the electrical conductivity of ACs at different temperatures is essential in order to assess some of their potential applications. Moreover, based on a previous literature review, the influence of the preparation process of AC (i.e. activation method and activating agent) on its electrical behavior over a wide temperature range has not been reported yet. In fact, we only found a few papers concerning the analysis of the temperature-dependent electrical conductivity for ACs prepared from coconut shell [39] and rice husk [40] by chemical activation with KOH and H_3PO_4, respectively, and from Kapton® films [41] and rayon [42] by physical activation in CO_2 and steam.

In the present work, the temperature dependence of the dc electrical conductivity is studied for a broadly varied series of ACs, which were previously prepared from VS by physical and chemical activation methods and characterized elsewhere [9]. Thus, the influence of both the activation method and the activating agent on the conductivity and electrical behavior of the ACs is investigated. The systematic use of complementary techniques for the chemical, textural and electrical characterization of the materials reveals the general trends in the electrical properties of the VS derived-ACs.

2. Experimental

2.1. Raw material

The VS (*Vitis vinifera* variety) used in the present study were grown and collected in a vineyard located in the wine-producing region named Tierra de Barros (Badajoz province, south-west Spain). The as-received VS were air-dried, size-reduced and sieved, the fraction of particle sizes lower than 1 mm being selected for the subsequent preparation of the various ACs.

2.2. Preparation and characterization of the ACs

The preparation of the ACs was carried out following the methods described in detail by Ruíz-Fernández et al. [9,16], which are summarized in Table 1 together with the codes assigned to the resulting products. The textural characterization of the ACs was accomplished by N_2 adsorption at −196 °C, mercury porosimetry, and helium and mercury density measurements. The specific surface area (S_{BET}) was estimated by applying the Brunauer, Emmet and Teller equation [43] to the experimental N_2 isotherms. The theoretical background for microporosity characterization was based on Dubinin's theory. Thus, the analysis of the adsorption isotherms by the Dubinin–Radushkevich (D–R) equation led to the values of the micropore volume (W_0) [44]. The mesopore (V_{me}) and macropore (V_{ma}) volumes were derived from the mercury intrusion curves. Finally, the total pore volume (V_T') was calculated from W_0, V_{me} and V_{ma}. These textural data for the prepared ACs have been previously reported elsewhere [9], and are collected in Table 2.

The surface functional groups and structures of the ACs were qualitative and quantitative analyzed by FT-IR spectroscopy and Boehm's method [45], respectively. Using a Perkin Elmer® 1720 spectrometer, the spectra were recorded between 4000 and 400 cm^{-1}, with 50 scans being taken at 2 cm^{-1} resolution. Pellets were prepared by first size-reducing a certain amount of the ACs

Table 1
Methods of preparation and sample codes for ACs.[a]

Substratum	Mass (g)	Atmosphere; AA	Flow (mL min^{-1}); AA:VS ratio	MHTT (°C)	t (h)	Code
VS	10	N_2	80	600	2	C600
VS	10	N_2	80	900	2	C900
C600	1.5	Air	10	275	1	A
C900	1.5	CO_2	10	750	1	CD
C900	1.1	N_2-steam	80 (N_2)	750	1	S
VS	25	H_3PO_4	5:1	85	2	PA-IP
VS	25	$ZnCl_2$	5:1	85	7	ZC-IP
VS	25	KOH	2:1	85	2	PH-IP
PA-IP	10	N_2		500	2	PA
ZC-IP	10	N_2		500	2	ZC
PH-IP	10	N_2		800	2	PH

[a] Abbreviations: VS, vine shoots; AA, activating agent; MHTT, maximum heat treatment temperature; t, isothermal time at MHTT.

Table 2
Textural parameters of the ACs.

Sample	S_{BET} (m^2 g^{-1})	W_0 (cm^3 g^{-1})	V_{me} (cm^3 g^{-1})	V_{ma} (cm^3 g^{-1})	V_T'[a] (cm^3 g^{-1})
C600	34	0.010	0.07	0.54	0.62
C900	5	0.001	0.08	0.38	0.46
A	322	0.16	0.03	0.58	0.77
CD	293	0.14	0.07	0.41	0.62
S	572	0.26	0.17	0.69	1.12
PA	1363	0.48	0.69	0.47	1.64
ZC	1726	0.59	0.81	0.37	1.77
PH	791	0.37	0.07	1.13	1.57

[a] $V_T' = W_0 + V_{me} + V_{ma}$.

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