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Research article

Role of surface phosphorus complexes on the oxidation of porous carbons

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ABSTRACT

Chemical activation of olive stone with phosphoric acid produces activated carbons with relatively high content of P surface groups that remain very stable on the carbon surface at relatively high temperatures. Changes in the surface chemistry of a phosphoric acid activated carbon after subjecting it to thermal treatments in oxidizing and inert conditions are studied by temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and adsorption/desorption of NH_3. TPD and XPS results point out that P surface groups preferentially reacts with molecular oxygen, prior to carbon gasification, through the oxidation of C-P bond to form C-O-P ones, which are thermally stable at temperatures lower than 700 °C. At higher temperatures, these C-O-P type surface groups decompose to less oxygenated P groups on the carbon surface (of C-P type) generating CO (and CO_2) in the gas phase. These C-P type surface groups seem to be very reactive and are (re)oxidized upon contact with air, even at room temperature, forming again C-O-P type groups. Thus, the presence of these oxygen-containing P surface groups with an interesting redox functionality of high chemical and thermal stability seems to be responsible of the high oxidation resistance and high oxygen content (once exposed to ambient air) of this type of porous carbons.

1. Introduction

Activation of lignocellulosic materials with phosphoric acid is a well-established method for the preparation of activated carbons with a well-developed porous texture with potential uses in catalysis and adsorption applications. Besides, this method allows, depending on the activation conditions, the preparation of activated carbons with a relatively large amount of P surface complexes of very high thermal stability that confer to these carbonaceous solids high surface acidity and oxidation resistance, increasing the possibilities of these materials for applications in catalysis [1–10]. Another advantage is that these carbon materials can be prepared from different carbonaceous precursors, as agricultural wastes, that are abundant, environmentally friendly disposal and its cost decreases associated with activated carbon production. In the present study, olive stone, an important bio-waste of the agro-food industry in Spain, with a production of >450.000 ton/year [11], is used as carbon precursor.

The studies of phosphoric acid activated carbons by FTIR, XPS and solid-state NMR techniques pointed out that the remaining P over the surface of the carbon, directly generated during the preparation process under specific conditions, is most likely in form of C-O-P and C-P groups [1,11–14]. However, some discrepancies are found in the literature associated to the chemical stability of the surface P in phosphorus-containing carbons. In a classic paper, Mckee et al. [15] suggested that the C-P-O bonds are not very stable at high temperatures. Oh and Rodriguez proposed an alternative configuration of these C-P-O bonds based on the formation of pπ–dπ bond by overlapping p orbitals between P and O. They suggested that this type of bonding in which P =O groups is replacing two edge carbon atoms would be thermally stable to high temperatures [16]. Lee and Radovic [17] showed that the structure with C-O-P bonding is more stable and able to survive longer than the structure with C-P-O bonding, using quantum mechanical modelling. This was later supported by Puziy et al. [12,13] based on IR, XPS and P-NMR methods, since high thermal treated carbons revealed a high contribution of condensed phosphates attached by C-O-P linkage to carbon matrix. Nevertheless, Wu and Radovic proposed later that the O-P bond in the C-O-P system is the weakest one based on ab initio molecular orbital calculations [14]. They concluded that when the treatment temperature is increased to high temperatures, the formation of C-PO_3 groups, probably, from decomposition of C-O-PO_3 ones seems to take place. Besides, the ab initio results showed that the C-P bond might be more stable than the C-O-P ones. On this question, Rosas et al. [7] observed the release of CO at high temperatures for phosphoric acid activated carbons during a TPD and this behavior was ascribed to the presence of C-O-PO_3 groups on the carbon surface at high temperatures that decompose to C-PO_3 ones.

The nature and concentration of these phosphorus functional groups on the surface of the carbon material has a significant influence on the catalyst performance, since this groups act as anchoring sites for the active phase in the preparation of supported catalysts or they can even be the active sites for specific catalytic reactions. In fact, activated carbons

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prepared by chemical activation using phosphoric acid have been successfully used as acid catalysts in alcohol dehydration reactions [3,18] and for the decomposition of H_2O_2 [6]. The results reported for alcohols dehydration reactions show that the presence of oxygen in the reaction atmosphere not only leads to a significant enhancement of alcohol conversions, but also inhibits catalyst deactivation and allows steady state conditions to be reached. In addition to its use as solid acid catalyst, redox functionality has been also incorporated by impregnation of these phosphorus containing activated carbons with vanadium species, obtaining a bifunctional catalyst that is active for hydrocarbon partial oxidation reactions [4,10]. The use of phosphoric acid activated carbons as catalysts supports for the selective oxidation of benzene, toluene, and xylene (BTX) [2] has also been reported. Oxygen plays a key role not only in all these catalytic processes, but also in the catalyst performance, since the carbon surface chemistry is modified during the reactions involving oxidizing conditions. Recent investigations have also showed that the presence of C-P type phosphorus groups enhances the functionalization of these materials with nitric acid [19]. Therefore, there is a growing interest on these materials in catalysis and the study of the chemical surface modification under oxidative conditions is investigated in the present work.

In addition to this, enrichment of surface oxygen groups on phosphoric acid activated carbons has been observed in most of the above mentioned works, despite the carbons were prepared at relatively high temperatures or were treated to high temperatures under inert conditions. In this sense, it would be of interest to study whether surface re-oxidation may take place on this type of activated carbon during different storage conditions. Therefore, the main purpose of the present work is to study the role of the P surface groups on carbon surface oxidation and reduction reactions. For that, an extensive study of the evolution of oxygen and P surface complexes of an activated carbon prepared by activation of olive stone with phosphoric acid before and after thermal treatments in air and inert atmosphere has been carried out using temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). As a baseline, an activated carbon with similar textural characteristics, but without surface P groups, was also prepared by physical activation of olive stone (CO_2 partial gasification) at the same temperature.

2. Experimental section

2.1. Activated carbons preparation

Two different activated carbons (with and without phosphorus) were prepared through different pathways: chemical activation with phosphoric acid and physical activation by partial gasification with CO_2. Olive stone waste was used as carbonaceous precursor, in both cases. The olive stone waste was cleaned with deionized water, dried at 100 °C and ground with a roller mill to obtain samples of 400–800 μm particle size. For the chemical activation process, the raw material was impregnated with concentrated H_3PO_4 (85 wt%, Sigma Aldrich) at room temperature, with a weight ratio of 2/1 (H_3PO_4/olive stone) and dried for 24 h at 60 °C. The impregnated samples were activated at 800 °C under continuous N_2 (purity 99.999%, Air Liquide) flow (150 cm^3 STP/min) in a conventional tubular furnace. The activation temperature was reached at a heating rate of 10 °C/min and maintained for 2 h. The activated sample was cooled inside the furnace under the same N_2 flow and then washed with distilled water until negative phosphate analysis in the eluate [20]. The resulting activated carbon, denoted by ACP2800, was dried at 60 °C and, then, grinded and sieved (100–300 μm).

For the physical activation process, a procedure described previously by our research group was followed [21], in which the gasification conditions, i.e. gasification temperature and reaction time, as well as the particle size, were set in order to warrant chemical reaction control to achieve a carbon burn-off value of around 55%. An olive stone char was obtained by carbonizing the raw material under N_2 flow at 800 °C. This char was heated under N_2 atmosphere to the gasification temperature (800 °C). Then, the gas feed was switched to CO_2 (99.998%, Air Liquide) with a flow rate of 150 cm^3 STP/min for 7 h. The resulting activated carbon, denoted by ACG800, was washed under stirring at room temperature for 1 h with 1% HCl in order to remove mineral components. ACG800 sample was chemical activated with H_3PO_4 following the same procedure than that performed to prepare ACP2800, resulting in ACG800-P2 carbon.

2.2. Thermogravimetric analysis

Thermogravimetric analysis (TG) were performed in a CI Electronics MK2 balance under air flow (150 cm^3 STP/min) from room temperature to 900 °C at a heating rate of 10 °C/min, with a sample weight of about 20 mg. Simultaneous thermal-gravimetric analysis and differential thermal analysis (TGA/DTA Mettler-Toledo) was used for investigating the re-oxidation process at room temperature after a thermal treatment at 900 °C. In this way, sample weight variation and heat involved in the process were simultaneously analyzed.

2.3. Porous texture characterization

The porous texture of the samples was characterized by N_2 adsorption–desorption at −196 °C and by CO_2 adsorption at 0 °C, using an ASAP 2020 apparatus (Micromeritics). Samples were previously outgassed at 50 Torr and 150 °C for 8 h. From the N_2 adsorption/desorption isotherm, the apparent surface area (A_{BET}) was determined from the BET equation [22]. The micropore volume (V_{DR}) was obtained by the Dubinin-Radushkevich (DR) method applied to the CO_2 and N_2 adsorption isotherms [23]. The mesopore volume (V_{mes}) was determined as the difference between the adsorbed volume of N_2 at a relative pressure of 0.95 and the micropore volume (V_{DR}), covering only the pore sizes between 2 and 40 nm, according to the Kelvin equation [24].

2.4. Surface chemistry characterization and elemental composition

Ultimate analysis of the carbons was carried out in a Leco CHNS-932 system, being the oxygen content calculated by difference. The total amount of P was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES).

The surface chemistry of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) using a *5700C model Physical Electronics* apparatus with *MgKα* radiation (1253.6 eV). For the analysis of the XPS peaks, the C_{1s} peak position was set at 284.5 eV and used as reference to locate the other peaks position. The deconvolution of the peaks was done using Gaussian-Lorentzian curves and a Shirley type background line.

Temperature-programmed desorption (TPD) profiles were obtained in a customized quartz fixed-bed reactor placed inside an electrical furnace and coupled to a mass spectrometer (Pfeiffer Omnistar GSD-301) and to non-dispersive infrared (NDIR) gas analyzers (Siemens ULTRAMAT 22) in order to quantify CO, CO_2, H_2 and H_2O (calibration error < 1%). In these experiments, ca. 100 mg of the sample was heated from room temperature to 1000 °C at a heating rate of 10 °C/min in nitrogen (purity 99.999%, Air Liquide) flow (200 cm^3 STP/min). The absence of any leak was carefully checked before each experiment and the samples submitted to this thermal treatment were denoted by -TT.

XPS and TPD analysis were also carried out in order to characterize the oxygen surface groups (OSG) of the activated carbon generated after oxidations in air (purity 99.999%, Air Liquide) at different temperatures. The samples were heated from room temperature up to 120, 180, 240, 325 and 350 °C at a heating rate of 10 °C/min in nitrogen flow (200 cm^3 STP/min) that was changed to air at the same flow rate when the chosen temperature was reached and maintained for 2 h. After these 2 h of experiment, the inlet gas was again changed to