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Lignocellulosic-derived mesoporous materials: An answer to manufacturing non-expensive catalysts useful for the biorefinery processes

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ABSTRACT

The synthesis procedure and characterization of a mesoporous carbon obtained from biomass waste by a simple method, generating a low-cost material, with the corresponding waste revaluation are described. The use of phosphoric acid during the activation of the waste material induces the presence of stable phosphate groups, with acid characteristics, on the surface of the mesoporous carbon, which could find many applications as an acid solid catalyst. In addition, such phosphate groups increase the stability of the carbon material under oxidizing conditions at relatively high temperatures, increasing the range of catalytic applications in which this material could be used. This paper also shows how the redox functionality can be incorporated on the surface of this carbon material by impregnation with vanadium oxide species. The corresponding carbon supported vanadium oxide catalyst is active and relatively selective in the propylene partial oxidation to oxygenates. It is also discussed how the catalytic behavior of such vanadium-containing catalysts can be improved by the use of Zr as dopant.

1. Introduction

Biorefineries use biomass as an abundant and renewable resource for the production of energy, biofuels and valuable chemicals though different processes that requires the use of a catalyst [1,2]. Thus, the use of biomass waste for the preparation of the catalytic materials required by the biorefineries could be interesting. Nowadays, a general tendency in the design of catalytic materials is based on nanostructured catalysts, since they present valuable advantages from both industrial and academic points of view [3]. By this way, the active phases should be supported on a non-expensive material that acts as support, in order to avoid syntherization of the active phase, reducing the amount of active phase required for a satisfactory catalytic performance and improving the mechanical properties of the catalyst.

Moreover, the nature of the specific support has a significant influence on the performance of the catalysts. In this sense, carbon materials are attractive as catalyst support since they can satisfy most of the desirable properties required for a suitable support [4]: high surface area, chemical stability, and, in addition, once the catalysts are deactivated, the supported oxide active phases can be easily recovered by gasification/oxidation of this carbon material, without net contribution to CO_2 emission. In the context of biorefinery, the carbon materials present an additional advantage since they can be obtained from biomass waste, which is an abundant and economical starting material.

However, carbon supports only could be used under certain conditions, for example, under an oxidant atmosphere they would gasify to CO_2 (or CO) at relatively low temperatures. Nevertheless, it has been shown [5–7] that it is possible to prepare carbon materials with a relatively large amount of phosphorus on the carbon surface by chemical activation of lignocellulosic materials with phosphoric acid. This activation procedure lead to phosphorus surface complexes in form of $COPO_3$, CPO_3, C_3PO and C_3P groups, which remain very stable on the carbon surface at relatively high temperatures and confer to the carbons a high oxidation resistance, acting as a physical barrier and blocking the active carbon sites for the oxidation reaction [8]. Thus, these phosphoric-activated carbon materials, with high oxidation resistance, open new possibilities for the use of carbon materials as catalytic supports for reactions that take place at relatively high temperatures under oxidizing conditions.

The synthesis and characterization of such carbon material are described in the present study, and also its catalytic applications. Since vanadium can be considered one of the key elements in the formulation of oxidation catalysts [9,10], vanadium species have been incorporated on the surface of a carbon material in order to evaluate their catalytic behavior for the partial oxidation

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of propylene. In addition, the effect of zirconium as promoter of these carbon-supported vanadium oxide catalysts has been also evaluated.

2. Experimental

2.1. Preparation of catalysts

In order to evaluate the effect of phosphorous in the catalytic behavior of the carbon support, two different activated carbons (with and without phosphorous) were prepared thought different pathways: chemical activation with phosphoric acid and physical activation by CO_2 gasification (Scheme 1). Olive stone waste (provided by Sociedad Cooperativa Andaluza Olivarera y Frutera, Periana) was used, in both cases, as starting material. 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 commercial H_3PO_4 (85 wt%, Sigma Aldrich) at room temperature, with a weight ratio of 3/1 (H_3PO_4/olive stone), and dried for 24 h at 60 °C. The impregnated samples were activated, at 500 °C, under continuous N_2 (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 at 60 °C until neutral pH and negative phosphate analysis in the eluate [11]. The resulting activated carbon, denoted by ACP, was dried at 100 °C and grinded and sieved (100–300 μm). For the physical activation process, it was followed a procedure described previously by our group [12,13], by this manner the gasification conditions, i.e. gasification temperature and reaction time, as well as the particle sizes are set in order to warrant chemical reaction control achieving a value of burn-off of around 55%. An olive stone char was obtained by carbonization of the precursor 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 was denoted by AC.

V-, Zr- and V + Zr-containing catalysts were prepared dissolving the required amount of precursor, NH_4VO_3 (99.99%, Sigma Aldrich) and/or $Zr(OCH_2CH_2CH_3)_4$ (70 wt% in 1-propanol, Sigma Aldrich), in a 0.5 M oxalic acid (99%, Sigma Aldrich) solution. This solution was kept under stirring until all vanadium and zirconium dissolves, then, the corresponding support (ACP or AC) was added. This mixture was dried in a rotator evaporator at 80 °C at a reduced pressure of 10–40 mmHg. The resulting solids were dried at 120 °C for 24 h and then calcined at 250 °C for 2 h in air. These catalysts were prepared with a total V + Zr coverage of 1 atom per nm^2 of activated carbon, and with different V/Zr molar ratio, which corresponds in weight percentage to 9.9 wt% of V atoms for 1V/ACP; 8.8 wt% of V atoms and 1.8 wt% of Zr atoms for 0.9V–0.1Zr/ACP; 7.8 wt% of V atoms and 3.5 wt% of Zr atoms for 0.8 V–0.2Zr/ACP.

2.2. Characterization of catalysts

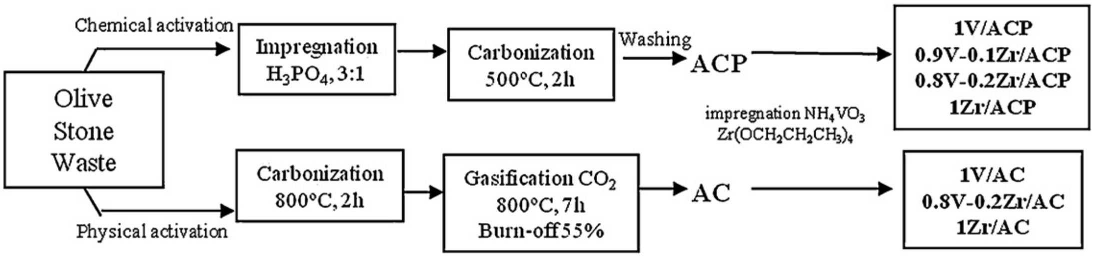
Oxidation resistance of the different catalysts and the carbon support were obtained by non-isothermal thermogravimetric analyses, carried out in a CI electronics thermogravimetric system. The thermobalance automatically measures the weight of the sample and the temperature as a function of time. Experiments were carried out in air atmosphere, for a total flow rate of 150 cm^3 (STP)/min, employing sample mass of approximately 10 mg. The sample temperature was increased from room temperature up to 900 °C at a heating rate of 10 °C/min. The porous structure of the activated carbons was characterized by N_2 adsorption–desorption at −196 °C and by CO_2 adsorption at 0 °C, carried out in an ASAP 2020 model of Michromeritics Instruments Corporation. Samples were previously outgassed during 8 h at 150 °C. From the N_2 adsorption/desorption isotherm, the apparent surface area (A_{BET}) was determined applying the BET equation, the micropore volume (V_t) and the external surface area (A_t) were calculated using the *t*-method [14] and the mesopore volume (V_{mes}) was determined as the difference between the adsorbed volume at a relative pressure of 0.95 and the micropore volume (V_t) [15]. The narrow micropore surface area (A_{DR}) and volume (V_{DR}) were obtained by the Dubinin–Radushkevich method [16] applied to the CO_2 adsorption isotherm.

X-ray photoelectron spectroscopy (XPS) analyses of the samples were obtained using a 5700C model Physical Electronics apparatus, with Mg Kα radiation (1253.6 eV). For the analysis of the XPS peaks, the C1s peak position was set at 284.5 eV and used as reference to position the other peaks while the fitting of the XPS peaks was done by least squares using Gaussian–Lorentzian peak shapes. Fourier transform infrared (FTIR) spectra of the samples were acquired at room temperature in the 300–3900 cm^{-1} region using a Nicolet 205xB spectrophotometer, equipped with a Data Station, at a spectral resolution of 1 cm^{-1} and accumulation of 128 scans. The pellets were prepared with 20 mg of sample mixed with 100 mg of dry KBr and pressed into disks.

The surface acidity was studied by adsorption and desorption of pyridine (Py) and 2,6-dimetilpyridine (DMPy) carried out in a thermogravimetric system (CI Electronics) at 100 °C. The inlet partial pressure of the organic bases was 0.02, and it was established saturating N_2 with the corresponding organic base in a saturator at controlled temperature. After saturation of the carbon, desorption is carried out at the adsorption temperature in nitrogen flow.

2.3. Catalytic activity measurements

The catalytic experiments were carried out in a fixed bed quartz tubular reactor (i.d. 12 mm, length 400 mm), working at atmospheric pressure. Catalyst samples (0.1–0.4 mm particle size) were introduced in the reactor and diluted with 1–2 g of silicon carbide (0.5–0.75 mm particle size) in order to keep a constant volume in the catalyst bed. The flow rate and the amount of catalyst were varied (from 25 to 100 cm^3 min^{-1} and from 0.25 to 1.0 g, respectively) in order to achieve different propylene conversion levels.



Scheme 1. Synthesis, procedure and nomenclature of the samples.