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Stability of an acid activated carbon based bifunctional catalyst for the raw bio-oil hydrodeoxygenation

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ABSTRACT

The performance (activity, selectivity and stability) of a Pt-Pd catalyst supported on a phosphorus-containing activated carbon (ACP) has been studied in the hydrodeoxygenation (HDO) of raw bio-oil, and compared with another bifunctional catalyst prepared with a FCC (Fluid Catalytic Cracking) catalyst as acid support. Experiments have been carried out in a fixed bed reactor under the following conditions: 400–450 °C; 65 bar; space time, 0.18 g_{cat} h $g^{-1}{}_{bio\text{-}oil}$; H_2:bio-oil ratio, 20 $cm^3{}_{H2}$ (STP) $cm^{-3}{}_{bio\text{-}oil}$; time on stream, 0–10 h. The catalyst reaches a pseudo-steady state at 450 °C after 6 h of time on stream, preserving a constant activity as a consequence of the simultaneous formation and hydrocracking of the deposited coke. In these conditions, the yield of C_{5+} hydrocarbons is 20 wt%. This organic liquid fraction mainly contains aromatics, and thus, it may require an additional mild hydrocracking treatment for its valorization as fuel. On the other hand, the gas fraction obtained can be used directly as fuel, and the aqueous liquid fraction (with a high concentration of methanol, 58 wt%) is interesting as co-feedstock with methanol in a methanol to olefins (MTO) unit.

1. Introduction

Fast pyrolysis of lignocellulosic biomass is an attractive process to obtain fuels and raw materials. An advantage of this route in relation to the other ones from biomass, is that it can be carried out in geographically delocalized units, and its liquid product (bio-oil) can be valorized at large scale in refinery units. Moreover, fast pyrolysis technology has been extensively developed and it allows for obtaining up to 75 wt% of bio-oil in relatively simple units and involving production costs lower than the required ones for competing technologies based on other thermochemical routes [1–3].

Bio-oil contains hundreds of organic compounds mostly in low concentrations (acids, alcohols, aldehydes, esters, ketones, and a large proportion (20–30 wt%) of lignin-derived phenols) [4], with a significant amount of water (up to 50 wt%). Its main properties (poor stability, low heating value, poor volatility, corrosiveness, high viscosity) exclude its direct usage as internal combustion engine fuel. This drawback has encouraged several transformation routes for enhancing its composition [5,6]. Main strategies are: (i) bio-oil cracking-deoxygenation; associated with pyrolysis, using an acid catalyst (usually a zeolite) in situ in the pyrolysis reactor [7,8], or in a fixed bed reactor coupled on-line in order to transform pyrolysis reactor effluents [9,10]; (ii) bio-oil hydrodeoxygenation (HDO); even though it requires a high H_2 consumption and working at relatively harsh conditions, it allows for obtaining a product with enhanced quality for fuel applications [11,12]. Reactions that take place in the HDO process are [13]: hydrogenolysis of the C–O bond (forming water as a byproduct), dehydration, decarboxylation, hydrogenation of unsaturated compounds and hydrocracking (C–C bond cleavage through a carbocation mechanism).

It is widely assumed that, the large scale bio-oil valorization route requires using the existing refinery infrastructure, co-feeding the bio-oil with the standard feedstock to fluid catalytic cracking (FCC) or to hydroprocessing units [3,14,15]. Considering the versatility of the FCC unit and its presence in most refineries, this route has been extensively studied, particularly using bio-oil model compounds, or its fractions or the pretreated bio-oil (hydrogenated) [16–19]. The results obtained from the cracking of vacuum gas oil (VGO) and raw bio-oil mixture (20 wt%) under FCC conditions, have shown the advantages of co-feeding bio-oil due to the existence of mechanistical synergies between oxygenates and hydrocarbons [20]. On the other hand, this route offers the following disadvan-

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tages: low gasoline selectivity and low carbon utilization due to the fact that part of it is converted into CO and CO_2 by decarbonylation and decarboxylation, respectively. Furthermore, feeding a high proportion of bio-oil into the FCC leads to gasoline with high concentration of oxygenates that require further treatments [20].

The hydroprocessing of bio-oil and its oxygen containing model compounds is interesting because it is less limited than their cracking, and can be tuned in order to obtain a fuel directly or to partially deoxygenate bio-oil [21,22], with the disadvantage of using hydrogen in the unit. Hydroprocessed bio-oil has been used in turbines [23,24] or for a subsequent valorization through cracking or hydrocracking (targeting the conversion of phenols and furans) [25]. The range of operating conditions studied for hydroprocessing bio-oil, in terms of pressure and temperature, is very wide [14], as well as the catalysts studied: noble metals (Pt, Pd, Ru, Rh) and transition metals (Ni, Mo, Co, W) based catalysts, bimetallic catalysts (Pt-Pd, Rh-Pd, Pt-Sn, NiMo, NiW, NiCo, CoMo), among many others. The catalyst supports studied include Al_2O_3, γ-Al_2O_3, ZrO_2, TiO_2, MgO, mesoporous zeolites and activated carbons [26]. The acidic sites in the bifunctional catalysts are of vital importance to deoxygenate the most refractory compounds of bio-oil, specially phenols, owing to the simultaneous methyl transfer and hydrodeoxygenation reactions [27,28].

The activated carbons (ACs) have shown promising performance in this HDO of bio-oil due to their chemical stability, high specific surface area, tailored pore size distribution for specific reactions and their capacity to be functionalized and prepared with different physical shapes (granules, extrudates, pellets, fibers, etc.) [29]. In addition, they are obtained from different low-cost sources, such as, biomass and wastes and, because of their characteristics, noble and transition metals supported on activated carbons have been used in bio-oil HDO [3,30]. Sanna et al. [31] have studied bio-oil aqueous fraction HDO in two sequenced stages at 125 and 250 °C, with Ru/AC and Pt/AC catalysts, respectively.

The aim of this work is to validate the potential catalytic performance of a Pt-Pd phosphorous-containing activated carbon for a first HDO stage of raw bio-oil process at high temperature (400–450 °C). Our motivation is driven by (i) the outstanding performance of this catalyst for tire-oil hydrocracking [32], and (ii) the requirement of delivering a stable catalyst for bio-oil HDO, which is a process strongly controlled by a severe coke deposition [31]. Two types of bifunctional catalysts (Pt-Pd on phosphorous-containing activated carbon and on FCC catalyst) have been synthesized, characterized and tested in the bio-oil HDO. Coke deposition have been also studied.

2. Experimental

2.1. Catalysts preparation and characterization

Two bifunctional catalysts were prepared, using Pt-Pd as the metallic function and different supports which provide the acidic function: (i) a phosphorous-containing activated carbon (ACP), and; (ii) a commercial equilibrated FCC catalyst (used in an industrial unit, that guarantees the stability of the catalyst). These catalysts were named as Pt-Pd/ACP and Pt-Pd/FCC, respectively.

ACP support was prepared by chemical activation with H_3PO_4 [33]. The lignocellulosic precursor (olive stone) was impregnated with an aqueous solution of H_3PO_4 (85 wt%, 3 g of H_3PO_4 per g of precursor), and then, it was activated in a tubular furnace under a continuous flow of N_2 (150 cm^3 min^{-1}), rising the temperature at 10 °C min^{-1}, up to 500 °C for 2 h. The activated carbon obtained was cooled in the tubular furnace, washed with distillated water at 60 °C (until phosphate was not detected in the eluent), and dried in a vacuum drier at 100 °C. ACP was sieved to a particle size of 100–300 μm. It should be noted that activated carbons prepared by this method show acidic sites which are active in alcohols dehydrations [33–35]. The Pt-Pd/ACP bifunctional catalyst was prepared incorporating Pt and Pd by simultaneous incipient wetting impregnation, with an aqueous solution of $HPtCl_6 \cdot 6HCl$ and $PdCl_2$ slightly acidified with HCl, with the adequate concentration to obtain a nominal value of Pt and Pd of 1 wt% and of 0.5 wt%, respectively. This relation is the adequate one to ensure a high activity and stability of Pt-Pd catalysts in the hydrogenation of phenols [36]. The impregnated support was heat-treated in a tubular furnace with a N_2 flow of 150 cm^3 min^{-1} at 400 °C for 4 h.

On the other hand, the FCC industrial support was tableted and sieved to the same particle size (100–300 μm) and the Pt-Pd/FCC catalyst was prepared by impregnation method at pH = 7 using $Pt(NH_3)_4(NO_3)_2$ and $Pd(NH_3)_4(NO_3)_2$ solutions as metal precursors, followed by water removal at 80 °C in vacuum [37]. The bifunctional catalyst was dried at 100 °C and calcined at 500 °C for 3 h in air. The metallic content of the FCC catalyst was determined by means of inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a Thermo spectrometer (XSeries 2 model), subsequent to subjecting the sample to acid digestion in HF at 90 °C.

Porous structure of the catalysts was characterized by N_2 adsorption-desorption at −196 °C in a Micromeritics ASAP 2020. Samples were previously outgassed for 8 h at 150 °C under vacuum. From N_2 adsorption-desorption isotherm, specific surface was calculated using the BET equation, and micropore volume was calculated using the *t*-method. Pore size distribution and average pore diameter were also estimated from N_2 adsorption isotherm by BJH method.

TEM analyses were performed on a Philips CM200 microscope equipped with a supertwin lens to study the catalyst morphology; in addition, particle size was calculated by counting particles in different TEM micrographs. The surface chemical state and elemental identity were measured by X-ray photoelectron spectroscopy (XPS) in a 5700C model Physical Electronics apparatus with MgKα radiation (1253.6 eV). The C 1s peak was located at 284.5 eV [38] and it was used as reference to locate the other peaks. Fitting of XPS peaks was done by least squares using Gaussian-Lorentzian peak shapes. Metallic surface and dispersion were determined by CO chemisorption, carried out in a Micromeritics ASAP 2010.

Acidic properties of the catalysts were determined by temperature programmed desorption (TPD) up to 550 °C, of NH_3 previously adsorbed at 150 °C, using a Setaram DSC thermogravimetric-calorimeter analyzer coupled on-line to a Balzers Quadstar 422 mass spectrometer. Samples were firstly submitted to stripping with He at 550 °C. Brønsted and Lewis acidic sites ratio was determined after pyridine adsorption at 150 °C, based on the 1545 and 1455 cm^{-1} FTIR signals ratio, using a Nicolet 6700 apparatus equipped with a Specac catalytic chamber. For these experiments, a tablet of ca. 30 mg of fresh catalyst was prepared by grinding and pressing the grains at 10 t cm^{-2} for 10 min. The tablet was submitted to a heat pretreatment at 380 °C and vacuum, and the signal was recorder with a frequency of 0.2 min^{-1}.

2.2. Bio-oil

Bio-oil was obtained by fast pyrolysis of black poplar sawdust at 440–450 °C, using a pilot plant provided with a conical spouted bed reactor with a capacity of 25 kg h^{-1} [39]. It was characterized (Table 1) by elemental analysis (Leco TruSpec CHN Macro and additional module TruSpec S) to determine the contents of C, H, N, S and O content by difference (it is worth mentioning the negligible N and S contents in the feed), and the concentrations of the component families were determined by GC–MS (Shimadzu GC–MS QP2010, column BPX5; length, 50 m; internal diameter, 0.22 mm). Water