



Short communication

Phosphorus-containing activated carbon as acid support in a bifunctional Pt–Pd catalyst for tire oil hydrocracking



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ABSTRACT

A bifunctional Pt–Pd catalyst supported on phosphorus-containing activated carbon has been prepared, characterized and tested in the hydrocracking of a hydrotreated tire pyrolysis oil. The product has a very interesting composition: 48–78 wt% naphtha and 19–42 wt% diesel fractions, with moderate amounts of aromatics (<40 wt%) and sulfur (<250 ppm). The challenge was to prepare a stable, porous, selective and acid carbonaceous catalyst from a waste (olive stone), which has been confirmed from the catalytic properties and product distribution point of view. In fact, phosphate groups in the activated carbon are stable hydrocracking sites, with comparable performance to that of the acid sites present in amorphous SiO₂–Al₂O₃.

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1. Introduction

The sequenced pyrolysis and hydroprocessing of scrap tires offers the possibility of obtaining high quality fuels, which represents a great challenge for valorizing this waste at a great scale [1]. Flash pyrolysis allows for maximizing the liquid (scrap tire pyrolysis oil or tire oil) yield [2,3] which, together with adulterated carbon black, is an abundant and economically interesting tire pyrolysis product [4,5]. Tire oil has a relatively high calorific value but, on the other hand, it also has a high content of sulfur, heavy molecules – boiling point (BP) higher than 350 °C – and aromatics [3,6,7]. Typical hydrotreaters using Ni–Mo or Co–Mo catalysts are unable to upgrade the composition of tire oil up to a point that is required by environmental legislations [8]. To this aim, subsequent hydrocracking contributes to further lowering of sulfur and aromatics, but particularly converting heavy molecules into naphtha and diesel fractions. This hydrocracking of the pretreated tire oil has been studied using active phases like Pt, Pd or Ir supported over different supports (zeolites, innovative mesoporous materials) [8] with similar results to those obtained on the hydrocracking of aromatic refinery streams like light cycle oil (LCO) [9].

Activated carbons are prepared from different precursors like low-cost wastes [10], and present good features as catalyst supports, in terms of large specific areas, tunable surface groups, chemical stability, or easy metal recovery by combustion or gasification of the support [11–13]. Carbon materials are frequently subjected to additional treatments to increase their surface acidity by generating carboxylic groups on the surface. However, these functional groups are not thermally stable (they decompose at ~250 °C) [14]. Chemical activation with H₃PO₄ leads to a well-developed porous structure with thermally stable oxygen–phosphorus surface groups (mainly C–O–PO₃ and C–PO₃) that provide activated carbons with higher surface acidity and turn carbon into a more oxidation-resistant material [15], namely phosphorous-containing activated carbon (ACP), which has proven to have a promising catalytic performance in alcohol decomposition [14].

In this work, we have synthesized, characterized and tested a cheaper and more environmentally friendly bifunctional catalyst (Pt–Pd supported on an ACP) for the hydrocracking of a pretreated pyrolysis tire oil for readjusting its composition. Fresh and spent catalysts have been characterized using various techniques for studying its physico-chemical properties, as well as a qualitative analysis of deposited coke. Liquid reaction products have been analyzed by chromatographic (GC × GC) technique. Our ultimate goal is to prepare a bifunctional catalyst from agricultural waste (olive stone), with equivalent features to those of SiO₂–Al₂O₃ based catalysts, for mitigating a pressing environmental problem (waste tires).

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2. Experimental

The activated carbon was obtained using olive stone as precursor, impregnating it with an aqueous solution of H_3PO_4 (85 wt%, 3 g of H_3PO_4 per g of precursor) at room temperature and drying at 60 °C for 24 h. The impregnated precursor was activated in a tubular furnace under a continuous N_2 flow ($150 \text{ cm}^3 \text{ STP min}^{-1}$), rising the temperature at $10 \text{ }^\circ\text{C min}^{-1}$, up to 500 °C for 2 h. Then the catalyst was cooled inside the furnace under a N_2 flow and washed with distilled water at 60 °C until constant pH was reached and negative phosphate presence in the eluent was achieved [16]. The obtained activated carbon was dried in a vacuum drier at 100 °C and sieved to a particle size of 100–300 μm . Pt and Pd were incorporated on the support by simultaneous incipient wetting impregnation method, using an aqueous solution of $H_2PtCl_6 \cdot 6HCl$ and $PdCl_2$ slightly acidified with HCl. The impregnated support was calcined at 400 °C for 4 h with a N_2 flow of $150 \text{ cm}^3 \text{ STP min}^{-1}$ in a tubular furnace to yield a supported catalyst with 0.5 wt% Pd and 1 wt% Pt. This ratio of Pt:Pd has proved to be valuable for having a stable catalyst against sulfur poisoning [17].

Scanning electron microscopy (SEM) was performed in a JSM 6490LV JEOL microscope at 25 kV. Transmission electron microscopy (TEM) was performed in a Phillips CM200 at 200 kV. N_2 adsorption-desorption isotherms were performed in a Micromeritics ASAP2020 apparatus at $-196 \text{ }^\circ\text{C}$. X-ray photoelectron spectroscopy (XPS) was carried out in a 5700 C model Physical Electronics apparatus. The acidity of the catalyst was studied by adsorption of *tert*-butylamine (*t*-BA) at 100 °C, using a Setaram DSC-111 calorimeter. Then, temperature programmed desorption (TPD) was performed, recording the butene signal (main cracking product) in a mass spectrometer ($m/z = 56$) and rising temperature at $5 \text{ }^\circ\text{C min}^{-1}$ up to 500 °C.

The tire oil was obtained in a sequenced process: (i) pyrolysis of scrap tires in a continuous conical spouted bed reactor at 500 °C [18], and (ii) hydrotreating in a previously described trickle bed reactor [6], aiming for reducing sulfur content and thus minimizing deactivation due to catalyst poisoning over the metallic Pt–Pd function. Hydrocracking of hydrotreated tire oil has been performed in a trickle bed reactor under the following conditions: space time, $0\text{--}0.28 \text{ g}_{\text{cat}} \text{ h g}_{\text{feed}}^{-1}$; 400–500 °C; 65 bar; H_2 /oil ratio of 1000 vol%; and time on stream (TOS) of 0–6 h. Prior to the reaction, the catalyst is reduced under atmospheric pressure at 400 °C. The feed has been diluted 50 vol% in *n*-decane.

The feed and reaction products have been analyzed offline by means of comprehensive gas chromatography (GC \times GC) using an Agilent 7890A apparatus provided with a flame ionization detector (FID), and coupled in line with mass spectrometry (Agilent 5975C inert XL MSD). Sulfur content has been measured using an Agilent 7890A apparatus equipped with a pulsed flame photometric detector (PFPD). The composition of the feed is: naphtha (BP = 35–216 °C), 27.9 wt%; diesel (BP = 216–350 °C), 50.3 wt%; and gasoil (BP > 350 °C), 21.8 wt%. As from a lump classification: paraffins and isoparaffins, 35.4 wt%; naphthenes, 22.0 wt%; 1-ring aromatics, 31.9 wt%; and 2-ring aromatics, 10.7 wt%. As from sulfur speciation: methylthiophene (M_1 DBT), 38 ppm; dimethylthiophene (M_2 DBT), 144 ppm; trimethylthiophene (M_3 DBT), 1019 ppm; tetramethylthiophene (M_4 DBT), 784 ppm.

Coke deposited on the catalyst was analyzed by temperature-programmed oxidation (TPO), using a TA Instruments TGA Q5000 IR apparatus.

3. Results and discussion

During the preparation of the activated carbon, 46 wt% carbonization yield is obtained. H_3PO_4 treatment catalyzed dehydration and recombination reactions favoring the aromatization in the activated carbon structure [10]. Table 1 summarizes the main properties of the bifunctional Pt–Pd phosphorous-containing activated carbon catalyst (Pt–Pd/ACP). The catalyst has a relatively high porosity, with an average

Table 1

Properties of the fresh and spent catalysts (440 °C, space time of $0.28 \text{ g}_{\text{cat}} \text{ h g}_{\text{feed}}^{-1}$).

	Fresh	Spent
<i>Porous structure</i>		
S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	1305	145
V_{microp} ($\text{cm}^3 \text{ g}^{-1}$)	0.512	–
V_{mesop} ($\text{cm}^3 \text{ g}^{-1}$)	0.829	0.449
Average pore diameter (Å)	52.3	106.0
<i>Surface and chemical analysis (XPS)</i>		
C1s (wt%)	88.40	91.71
O1s (wt%)	8.17	6.52
P2p (wt%)	2.18	1.02
Pd3d (wt%)	0.45	0.32
Pt4f (wt%)	0.80	0.43
Total acidity ($\text{mmol}_{\text{t-BA}} \text{ g}^{-1}$)	0.29	0.06

pore size of 52.3 Å, and high specific surface ($1305 \text{ m}^2 \text{ g}^{-1}$). The P:O ratio (Table 1) demonstrates the existence of phosphate groups on the catalytic surface [19] due to the H_3PO_4 treatment, generating acid sites [20]. Table 1 demonstrates that the acidity of the bifunctional catalyst and its surface area are comparable to those of a silica–alumina as support [8]. SEM image of the fresh catalyst (Fig. 1a) indicates that the surface of the catalyst has a very high porosity with irregular channel shapes and sizes of about 10–30 μm whereas TEM image (Fig. 1b) shows that the bimetallic Pt–Pd particles are well dispersed on the support with a homogeneous sizes of 7–15 nm.

The evolution with time on stream and space time of hydrocracking conversion is shown in Fig. 2a. Hydrocracking conversion (X_{HC}) has been defined as a function of the gasoil mass fraction (X_{Gasoil}) removed:

$$X_{\text{HC}} = \frac{X_{\text{Gasoil}}|_{\text{Tire oil}} - X_{\text{Gasoil}}|_{\text{prod}}}{X_{\text{Gasoil}}|_{\text{Tire oil}}} \quad (1)$$

During the 6 h on stream the catalyst deactivates until it reaches a pseudo-stationary state with very limited further decay. This situation is due to almost equal coke formation and coke precursor hydrocracking rates [21]. Temperature has a remarkable effect on product distribution as shown in Fig. 2b. Upon increasing process temperature, naphtha concentration increases at the expense of diesel and gasoil. A good compromise of product distribution is obtained at 480 °C with contents of naphtha and diesel of 53 and 45 wt%, respectively (Fig. 2a,b). Furthermore, the phosphate sites of the activated carbon are stable and have enough acid strength in order to promote the scission of the gasoil molecules contained in the tire oil.

Fig. 3 shows the composition of the feed and products (Fig. 3a) and the sulfur speciation (Fig. 3b) at different hydrocracking temperatures, where hydrodesulfurization conversion (X_{HDS}) has been defined based on total sulfur content (S) as:

$$X_{\text{HDS}} = \frac{S|_{\text{Tire oil}} - S|_{\text{prod}}}{S|_{\text{Tire oil}}} \quad (2)$$

As shown in Fig. 3a, and according to the bifunctional catalyst mechanism [22], 1 and 2-ring aromatics hydrogenate on the metallic sites of the catalyst to form naphthenes, which subsequently suffer ring opening to form paraffins and isoparaffins on the acid sites of the activated carbon. The first hydrogenation is a reversible exothermic reaction, so if the cracking activity is not dominant, the yield of aromatics increases with temperature (400–440 °C), as a consequence of the thermodynamic equilibrium of hydrogenation being disfavored. At temperatures of 480 °C and above, cracking and ring opening are more dominant and naphthenes are easily converted into paraffins and isoparaffins. In these conditions, paraffins and isoparaffins are the most abundant components, up to 50 wt%.

In Fig. 3b, it is observed that, as a consequence of deactivation, X_{HDS} decreases from almost complete conversion down to values between 65

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