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Characterization and controlled combustion of carbonaceous deactivating species deposited on an activated carbon-based catalyst

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HIGHLIGHTS

- Acid carbon is an attractive alternative for hydrocracking catalyst supports.
- High reaction temperature attenuates catalyst deactivation but favors coke aging.
- TPO reveals the presence of light deactivating species on the catalyst surface.
- LDI/MS uncovers the nature of deactivating species deposited on carbon.
- Catalyst properties are partially recovered through controlled-combustion.

GRAPHICAL ABSTRACT

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ABSTRACT

The composition of the carbonaceous deactivating species (coke) deposited on a Pt and Pd supported P-containing activated carbon catalyst has been studied. These deactivating species were deposited on the catalyst during the hydrocracking of scrap tire pyrolysis oil at 400–500 °C, and it has been selectively characterized by means of temperature-programmed oxidation (TPO), temperature-programmed desorption/gas chromatography (TPD/GC) and laser desorption-ionization/mass spectroscopy (LDI/MS). In addition, the evolution of the textural properties and the acidity of the deactivated catalysts have been evaluated. The high thermal and oxidation resistance of the catalytic support has allowed to combust the coke in the TPO and calculate its intrinsic activation energy as a function of the extent of the combustion. Combined TPO and LDI/MS results have shown that an increase in the hydrocracking temperature attenuates the catalyst deactivation due to the hydrocracking of coke precursors. Coke aging, by evolving

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towards a more condensed structure, is also favored at higher hydrocracking temperatures. The combustion of the most condensed coke requires of higher temperatures than 375 °C, which hinders the complete regeneration of the activated carbon-based catalyst.

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1. Introduction

Activated carbon-based materials are obtained from a wide range of renewable sources, like biomass or wastes (as plastics and tires), and have shown promising performance as catalysts or catalyst supports and adsorbents for renewable feed processing [1–3], capable of substituting the commonly used inorganic materials (i.e. alumina or zeolites) in some applications [4–7].

Regardless of their organic or inorganic nature, heterogeneous catalysts deactivate due to organic species fouling or being trapped in their porous structure [8,9]. Inorganic heterogeneous catalysts are usually regenerated by the combustion of these species (coke), ensuring that the support properties remain practically unaltered after combustion at relatively high temperatures (normally above 500 °C) [10]. Nevertheless, commonly used activated carbons show low combustion temperatures and tend to easily oxidize their surface due to the affinity of carbon towards O₂ [11,12]. Consequently, the challenging regeneration of activated carbons through coke combustion restricts their use as support in those applications in which deactivation is fast. Moreover, the low combustion temperature of activated carbon hinders the use of temperature-programmed oxidation (TPO) technique, frequently used for analyzing the nature and location of coke deposited on inorganic catalysts [13].

Making these materials thermally stable in oxidizing atmospheres represents a challenge for the application of activated carbons in environmental engineering processes and sustainable production of fuels. By achieving this, spent carbon-based catalysts could be analyzed by TPO and regenerated through a controlled combustion of the deposited coke. For this reason, activated carbons obtained by chemical activation of biomass wastes with H₃PO₄ (ACPs) have an outstanding potential as catalyst supports since they combine the benefits of activated carbons (low price, very high surface area and porosity), with their noticeable acidity and hydrothermal resistance [12,14–16]. These properties are associated with the presence of thermally stable C–O–P surface groups, which decompose at temperatures higher than 700 °C [12].

Pt-supported catalysts present high activity in the hydrocracking of heavy feeds, as those derived from the Fischer-Tropsch process, for the sustainable production of fuels [17,18]. In previous works, the performance of a bifunctional Pt–Pd catalyst supported on ACP was studied in the hydroprocessing of pyrolysis oil from biomass (bio-oil) [19] and scrap tire pyrolysis oil (STPO) [20]. The presence of the aforementioned phosphorus acid sites in the bifunctional catalyst, and its cracking capability, lead to a synergistic effect with the metallic Pt and Pd sites, which favors the hydrogenation of the oxygenated compounds of bio-oil and the unsaturated hydrocarbons of STPO. However, the deposition of carbonaceous deactivating species (coke) is inevitable in both cases, causing catalyst activity decay with time on stream as commonly occurs in hydroprocessing reactions [21]. Consequently, advances in the understanding of coke formation mechanisms are important for considering this deactivation stage in the kinetic models for hydroprocessing reactions [22].

In this work, the carbonaceous species deposited on a deactivated Pt–Pd/ACP bifunctional catalyst used for STPO hydroprocessing have been characterized. Gathering insights into the species deposited on the catalyst support and enhancing the activated

carbon stability are the main challenges in order to use activated carbon for this applications. These species have similar nature than those of the ACP support itself, and therefore combining different characterization techniques is required for a proper characterization of the deactivated catalysts. The content and location of deactivating species have been studied by temperature-programmed oxidation, estimating the activation energy by isoconversional methods and varying the O₂ partial pressures. More details about the nature of deactivating species have been obtained through LDI/MS and TPD/GC. Besides, the potential of the catalyst for being regenerated by controlled combustion has been studied. The regenerated catalyst has been characterized, comparing its properties with those of the fresh and deactivated catalyst.

2. Materials and methods

2.1. Catalyst preparation

The P-containing activated carbon support (ACP) was prepared using olive stone as precursor. Olive stone was chemically activated using an aqueous solution of H₃PO₄ (85 wt%, mass ratio H₃PO₄/olive stone = 3) at room temperature and dried at 60 °C for 24 h. The impregnated precursor was activated in a tubular furnace under a continuous N₂ flow (150 mL min^{−1}), raising the temperature at a rate of 10 °C min^{−1} up to 500 °C and maintaining it for 2 h. Then, the catalyst was cooled inside the furnace under a N₂ flow and washed with distilled water at 60 °C until constant pH was reached and negative phosphate presence in the eluent was achieved [23]. The obtained activated carbon was dried in a vacuum drier at 100 °C and subsequently, it was sieved to a particle size of 100–300 µm.

Pt and Pd were incorporated on the support by simultaneous incipient wetting impregnation using an aqueous solution of H₂PtCl₆·6HCl and PdCl₂, slightly acidified with HCl. The impregnated support was calcined at 400 °C for 4 h under a N₂ flow of 150 mL min^{−1} in a tubular furnace to yield a supported catalyst with 0.5 wt% Pd and 1 wt% Pt. This Pt:Pd ratio has proven to be suitable for providing a stable catalyst against sulfur poisoning [24].

2.2. Catalyst characterization

The porous texture of the catalyst was studied by means of N₂ adsorption-desorption at −196 °C and CO₂ adsorption at 0 °C, using a Micromeritics ASAP2020 apparatus. All catalysts were degassed at 150 °C for 8 h prior to analysis to remove impurities. From N₂ isotherms, specific surface area was determined using the Brunauer-Emmett-Teller (S_{BET}) equation, whereas micropore volume (V_{micropore}) was determined with the *t*-method, based on the Harkins-Jura equation. Mesopore volume (V_{mesopore}) was computed as the difference between total pore volume and micropore volume. The narrow micropore volume (V_{DR}) and the narrow micropore area (S_{DR}) were estimated by applying the expression of Dubinin-Radushkevich from the CO₂ adsorption isotherm.

Catalyst acidity was determined by isothermal adsorption of *tert*-butylamine (*t*-BA) at 100 °C, using a Setaram DSC-111 calorimeter. After saturation of the catalyst occurred, physisorbed

t-BA was removed by He stripping at the same temperature. Then, a temperature-programmed desorption (TPD) was performed by raising the temperature at a 5 °C min⁻¹ rate up to 500 °C in a He flow of 50 mL min⁻¹, and recording the signal of the *t*-BA cracking products in a mass spectrometer, with butene being the main product, (*m/z* = 56) [25].

X-ray photoelectron spectroscopy (XPS) was carried out in a 5700 C model Physical Electronic apparatus for studying the surface chemical composition of the catalysts. The C1s carbon peak was established at 284.5 eV [26] and taken as reference for locating in the spectra the rest of the studied elements. The different species, functional groups, and binding energies were established based on the literature [27].

2.3. Hydroprocessing runs and product characterization

The tire oil was produced in a pyrolysis pilot plant using a conical spouted bed reactor at 500 °C [28], and hydrotreated for the removal of sulfur using Ni-Mo catalysts in a laboratory scale fixed bed reactor that has been described elsewhere [29]. The same experimental unit was used for carrying out the hydrocracking of the previously treated tire oil under the following conditions: space time, 0.16 g_{cat} h g_{feed}⁻¹; 400–500 °C; 65 bar; H₂/oil ratio of 1000 vol(STD)/vol; and time on stream (TOS) of 0–6 h. Prior to the reaction, the catalyst (diluted in 1 g of CSi) was reduced under atmospheric pressure in a stream of H₂:N₂ (30 mL min⁻¹ H₂, 50 mL min⁻¹ N₂). Temperature was raised at a rate of 5 °C min⁻¹ from room temperature up to 400 °C, and then maintained for 4 h. The feed was diluted (50 vol%) in *n*-decane.

The feed and reaction products were analyzed offline by means of comprehensive gas chromatography (GC × GC) coupled in line with mass spectrometry (MS) using an Agilent 7890A GC apparatus coupled with an Agilent 5975C series MS, and consisting of two columns of different polarities connected through a flow modulator. The first column is a non-polar DB-5 ms J&W 122-5532 (length, 30 m; internal diameter, 0.25 mm), and the second one is a polar TRB-50 HT (length, 6 m; internal diameter, 0.25 mm). The outlet flow goes through both a flame ionization detector (FID) and a mass selective detector (MSD). The chromatograms of both products and feed were analyzed by means of an analytical MATLAB routine [29], that discretizes the molecular pool into different lumps based on their boiling point. The composition of the STPO was: 27.9 wt% naphtha (35–216 °C, C₅–C₁₂), 50.3 wt% diesel (216–350 °C, C₁₃–C₂₀), and 21.8 wt% gasoil (>350 °C, C₂₁₊). Hydrocracking conversion (*X*_{HC}) was defined as the fraction of gasoil reacted:

$$X_{HC} = \frac{X_{Gasoil|STPO} - X_{Gasoil|prod}}{X_{Gasoil|STPO}} 100 \quad (1)$$

The nomenclature used for deactivated catalysts was based on the reaction temperature of each catalyst sample. In this way, the catalyst used at 400 °C was designated as T400, and so on. The catalyst deactivated at 440 °C and subsequently regenerated was named T440R.

2.4. Characterization of deactivating species

The nature of coke species, which leads to catalyst deactivation, was determined by a combination of different techniques: (i) temperature-programmed oxidation (TPO); (ii) temperature-programmed desorption/gas chromatography (TPD/GC); and (iii) laser desorption-ionization/mass spectrometry (LDI/MS).

TPO analyses were carried out using a TA Instruments TGA Q5000 IR apparatus. Prior to analysis, the catalyst was subjected to a N₂ stream followed by one of air (100 mL min⁻¹) at 50 °C.

Then, in the combustion experiments, the temperature was raised up to 900 °C using a heating rate of 5 °C min⁻¹. From TPO results, combustion kinetics were modeled for correlating the combustion of the deactivating species with their activation energy. This activation energy was calculated using the following equation:

$$\frac{d\alpha}{dt} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (2)$$

Where α is the extent of the combustion of the carbonaceous material (deactivating species and ACP support, $0 < \alpha < 1$), t is time, A is the pre-exponential factor, β is the heating rate, E_a is the activation energy, R is the ideal gas constant, T is the temperature and $f(\alpha)$ is the combustion kinetic model, which is considered to be constant for constant values of α [30]. The heating rates (β) used were 2, 5, 10 and 15 °C min⁻¹. Additionally, an isoconversional method [31] was applied for estimating the evolution of the activation energy with the extent of the combustion reaction using the same results obtained before. The calculation, using a MATLAB routine, allows for determining the E_a for different α values.

TPD/GC analyses were performed in a Pyroprobe AS2500 microreactor provided with an automated feeder and connected in line with a gas chromatograph (Agilent Technologies 7890 B provided with a J&W LTM Column) for analyzing the evolved products, as described in more detail elsewhere [32,33]. The reactor consists of a quartz tube located inside a reaction chamber and heated by means of a coiled platinum filament. The catalyst is instantaneously heated at a rate of 10,000 °C s⁻¹ up to 500 °C under a continuous He flux (the maximum hydrocracking temperature in a continuous setup and also the maximum to ensure that carbon degradation does not take place) and the reaction temperature is maintained for 20 min.

LDI/MS measurements were carried out on a Bruker Autoflex Speed instrument (Bruker, Germany) equipped with a 355 nm Nd:YAG laser. All spectra were acquired in the positive-ion reflection mode (accelerating voltage 20 kV, pressure 5 · 10⁻⁶ mbar). Each catalyst was immersed in an acetonitrile solution (1% trifluoroacetic acid), and prepared according to the “dry droplet” method using a polished steel target. LDI analyses were carried out without using any matrix because of the high intensity of the matrix peaks, which might distort the results. LDI technique is particularly suitable for characterizing compounds with π -electrons, such as the ones of aromatic coke [34].

2.5. Catalyst regeneration

The catalyst regeneration was performed in the aforementioned TG equipment, recording the weight loss of deactivated catalyst. Each regeneration run consist of a two-stage controlled combustion treatment under a continuous air flow (100 mL min⁻¹): (i) a heating stage at a rate of 10 °C min⁻¹ up to the final temperature, and; (ii) a 4 h isothermal step. The final combustion temperatures were in the 325–425 °C range.

3. Results and discussion

3.1. Catalyst deactivation

The effect of reaction temperature on the evolution with time on stream of the hydrocracking conversion (*X*_{HC}) is depicted in Fig. 1. As observed, at 500 °C the conversion is practically complete (99.8 wt%), and it remains almost constant after 6 h of reaction (94.4 wt%). However, lower reaction temperatures lead to a notable activity loss, with decreases in the conversion of 44 and 55 % at 440 °C and 400 °C, respectively. The evolution of the product yields with time on stream is detailed in a previous work [20]. A

Fig. 1. Evolution of the hydrocracking conversion with time on stream ($0.16 \text{ g}_{\text{cat}} \text{ h g}_{\text{feed}}^{-1}$; 65 bar).

similar effect with temperature was reported by Hita et al. [35] for the same process using a Pt-Pd/SiO₂-Al₂O₃ catalyst in the 440–500 °C range. In that case, a decrease of 40 % of the initial activity was observed at 440 °C. Temperature plays an important role in the evolution with time on stream of hydrocracking conversion and product distribution, which could be related to the effect of temperature on the coke formation and the catalyst deactivation.

The main physicochemical properties of the fresh and deactivated catalysts at different temperatures (T440 and T500 catalyst) are summarized in Table 1. The fresh catalyst shows a specific surface area (S_{BET}) of $1305 \text{ m}^2 \text{ g}^{-1}$, with a relatively high porosity. The existence of phosphate groups on the fresh catalyst surface resulting from the chemical activation with H₃PO₄ is proven by the P:O ratio measured through XPS [36]. This P-containing groups, with acidic character, provide the catalyst with a total acidity comparable to that of a silica-alumina support [35]. Regarding deactivated catalysts, a remarkable drop of surface area (ca. 90 % of S_{BET}) is observed, with a very significant decrease in micropore volume ($V_{\text{micropore}}$, only measurable with CO₂ adsorption) and in mesopore volume (ca. 50 % drop of V_{mesopore}), which leads to an increase in the average pore diameter. This way, T440 catalyst exhibits lower narrow micropore area and volume (S_{DR} and V_{DR} , respectively), and higher average pore diameter than those of T500 catalyst.

Table 1
Physicochemical properties of the fresh and deactivated catalysts.

	Fresh	T440	T500
Porous texture (N₂)			
S_{BET} ($\text{m}^2 \text{ g}_{\text{cat}}^{-1}$)	1305	145	155
$V_{\text{micropore}}$ ($\text{cm}^3 \text{ g}_{\text{cat}}^{-1}$)	0.512	–	–
V_{mesopore} ($\text{cm}^3 \text{ g}_{\text{cat}}^{-1}$)	0.829	0.449	0.386
Average pore diameter (Å)	52	106	85
Porous texture (CO₂)			
S_{DR} ($\text{m}^2 \text{ g}_{\text{cat}}^{-1}$)	493	73	92
V_{DR} ($\text{cm}^3 \text{ g}_{\text{cat}}^{-1}$)	0.198	0.029	0.037
Surface chemistry (XPS)			
C1s (wt%)	88.4	91.7	91.6
O1s (wt%)	8.17	6.52	6.83
P2p (wt%)	2.18	1.02	1.00
Pd3d (wt%)	0.45	0.32	0.28
Pt4f (wt%)	0.8	0.43	0.31
Total acidity ($\text{mmol}_{\text{tBA}} \text{ g}_{\text{cat}}^{-1}$)	0.29	0.06	0.08

Compared to the fresh catalyst, a clear decrease in the metallic phase concentrations of Pd and Pt on the catalyst surface is observed in Table 1 for the deactivated catalysts (Pt decreasing nearly 50 wt%, and Pd decreasing ca. 34 wt%). At the same time, a decrease of ca. 50 wt% in the surface P-groups (related with the acid sites) is observed, which suggests that both metallic and acid sites are being blocked by the carbonaceous species. Indeed, the total acidity of the deactivated catalysts decrease to 0.06 and 0.08 $\text{mmol}_{\text{tBA}} \text{ g}_{\text{cat}}^{-1}$ for the T440 and T500 catalysts, respectively (from an initial acidity of 0.29 $\text{mmol}_{\text{tBA}} \text{ g}_{\text{cat}}^{-1}$ for the fresh catalyst). These results highlight that the effect of the reaction temperature on the catalyst properties deterioration is consistent with the aforementioned effect on the conversion drop (Fig. 1).

3.2. Coke nature characterization

3.2.1. TPO analysis

Fig. 2a shows the TPO profiles for the fresh and deactivated catalysts at different reaction temperatures. Two clearly separated combustion zones can be defined: (i) a zone at 200–400 °C corresponding to the combustion of deactivating species, and; (ii) a zone at 450–620 °C assigned to the combustion of the carbon catalyst

Fig. 2. (a) Effect of the reaction temperature on the TPO profiles of the deactivated catalysts, and (b) evolution of the DTG curves with the extent of the combustion (as calculated from isoconversional method).

support (ACP). Focusing on the first combustion zone, two peaks are observed, corresponding to two types of deactivating species with different composition or location on the catalyst surface. The first type of deactivating species (DS1) burns at 200–310 °C with a combustion maximum at 275 °C. DS1 are presumably species with high H/C ratio and/or located on the external catalyst surface [37] or on the metallic sites (combustion catalysts) [38–40]. The second group of deactivated species (DS2) burns at higher temperatures of 310–400 °C with a maximum at 360 °C. DS2 are species with higher condensation degree and/or deposited on the micropores of the catalyst.

Coke content (DS1 + DS2), as measured by the TPO profiles in Fig. 2a, decreases upon increasing the reaction temperature, from 25 wt% for T400 to 5 wt% for T500. These results support the deactivation trends in Fig. 1 and suggest that the increase in the reaction temperature favors the hydrocracking of the coke precursor intermediates. Consequently, reaction temperature plays an important role in the nature of the coke deposited on the catalyst. Thus, T400 catalyst shows an important fraction of DS1 species, while T500 catalyst only presents DS2 species. Furthermore, a slight shift towards higher temperatures (ca. +10 °C) is observed in the DS2 peak of the T500 catalyst, proving that the condensation of these species is favored by rising the reaction temperature. Therefore, the total amount of coke decreases upon increasing the reaction temperature, but this coke is of a more condensed nature. Regarding the combustion peak of the ACP in the fresh catalyst (450–620 °C), the maximum is at 575 °C, 100 °C higher than the combustion temperature reported for chars or physically activated carbons [12]. This shift is attributed to the modification of the oxidation mechanism in the presence of phosphorus surface groups and different hypothesis have been reported regarding this effect: (i) phosphorus groups could act as a physical barrier for O atoms, keeping them from approaching the active carbon sites [12,16]; (ii) phosphorus are more likely to bond with oxygen rather than carbon, forming thermally stable C–O–P groups instead of forming CO₂ at moderate temperatures (450 °C) [12,14,15,41]; and (iii) carbon takes oxygen from a O–P bond breakage, and thus P-groups act as oxygen carrier in the oxidation mechanism [12]. This delay in the combustion temperature prompted by P can also be achieved by modifying the carbonization treatment of the precursor (i.e. increasing the carbonization temperature) [42]. However, this harsher carbonization condition leads to a shrinking of the carbon particles, decreasing the specific surface area and therefore, decreasing the catalyst activity. Fig. 2a also shows a slight shift towards lower temperatures (–10 °C) and a peak widening for the combustion of the support (ACP) in deactivated catalysts. This phenomenon is due to the presence of very condensed deactivating species whose combustion temperature is overlapped with that of the carbon support. The presence of these species of similar nature to that of the support leads to an acceleration of the support combustion, which burns at lower temperature due to an inertial combustion effect.

From the TG-TPO analyses, the evolution of the DTG curve with the extent of the combustion reaction (α) was studied by means of isoconversional methods, using both linear and non-linear mathematical approaches to simulate the non-isothermal process behavior (Fig. 2b). Note that $\alpha = 0$ corresponds to a situation where no combustion has taken place yet, and $\alpha = 1$ represents for total combustion of both deactivating species and ACP support. In Fig. 2b, it is possible to observe a peak at $\alpha = 0.8$ for the fresh catalyst, which could be attributed to the aforementioned characteristic combustion mechanism of this activated carbon [12]. This additional peak is also observed in the TPO profile (Fig. 2a) at ca. 590 °C. The evolution of the DTG curve with α is quite different for the deactivated catalysts due to the combustion of the deactivating species. Three peaks are observed for the T400 deactivated catalyst, with maxima

at $\alpha = 0.1$ and $\alpha = 0.2$ (attributed to the combustion of DS1 and DS2 species, respectively) and $\alpha = 0.7$ (attributed to ACP support). For T440 and T500 catalysts only two peaks are identified, at $\alpha = 0.07$ (DS2) and at $\alpha = 0.6$ (ACP). Besides, at $\alpha = 0.27$, DS1 and DS2 species are completely burned in T400 catalyst, whereas DS2 burns at $\alpha = 0.15$ and 0.1 in T440 and T500 catalysts, respectively. On the other hand, it is noteworthy that the peak at $\alpha = 0.8$, associated with the ACP combustion mechanism, is not observed for the three deactivated catalysts.

The evolution of the activation energy with the extent of the reaction was determined from DTG data (Fig. 2b) using the Eq. (2). Fig. 3a displays this evolution for the fresh and the T440 catalyst and the corresponding regression coefficient (r^2). These results were obtained using the methodology proposed by Vyazovkin [31], which allows for achieving the best fitting ($r^2 > 0.99$ for all α values, Fig. 3a). It should be noted that the results obtained with this integral method are similar to those obtained applying other differential methods [30,43]. The evolution of the E_a curve for the fresh catalyst shows the typical shape of the simulated data with pseudo-Gaussian random noise. This explains the slight deviations observed at low and high combustion extent (α) [44], with activation energies between 170 and 195 kJ mol⁻¹ and an average value of ca. 190 kJ mol⁻¹, attributed to the combustion of the ACP support. Significant differences are observed for the T440 catalyst, with an E_a decrease at low α values (low combustion degree), and a minimum value of 130 kJ mol⁻¹ at $\alpha = 0.15$, which could be attributed to the combustion of the light deactivating species with high H/C ratio. This E_a drop is consistent with the combustion of

Fig. 3. (a) Evolution of the activation energy with the extent of the combustion for the T440 catalyst, and (b) effect of the reaction temperature on the activation energy of the deposited DS1 and DS2 species and the ACP support.

carbonaceous species over Pt or Pd, which are oxidation catalysts and facilitate the combustion of deactivating species [45,46].

For $\alpha > 0.2$, the E_a trend recovers the shape observed for the fresh catalyst, associated with the ACP support combustion, with an average E_a value of 176 kJ mol^{-1} for $\alpha = 0.6$. This decrease in the average E_a , compared to that of the fresh catalyst (191 kJ mol^{-1} at $\alpha = 0.5$), could be related to the 10°C shift and the widening observed in the TPO profile of the support combustion peak for the deactivated catalysts (Fig. 2a). As mentioned above, this results can be explained by the inertial combustion effects caused by deactivating species burning and inducing, in part, the combustion of the ACP support. For α values higher than that of the E_a minimum mentioned, no additional E_a minimum associated to the combustion of heavier and more condensed deactivating species is observed for the T440 catalyst. This probably occurs because these species cannot be identified with different values of E_a , due to the structural similarities between both heavy coke fraction (with high content of polyaromatics) and the support (ACP). However, the E_a decrease at $\alpha = 0.8$ for the fresh catalyst, which could be related to the combustion mechanism of the ACP support [12], disappears for the T440 catalyst. These results are consistent with the differences observed in the TPO profiles of the fresh and the deactivated catalyst (Fig. 2).

Fig. 3b shows the effect of the reaction temperature on the E_a values corresponding to the maxima observed in Fig. 2b for the fresh and the three deactivated catalysts. This way, the E_a values attributed to each carbonaceous species (DS1, DS2 and ACP) corresponds to the α values at which DTG curves show a maximum. As observed, the E_a associated with DS2 increases upon increasing the reaction temperature, which suggests that higher reaction temperatures favor the condensation of deactivating species and yield well-developed polyaromatic structures. In fact, the combustion of DS2 species deposited on T500 shows an activation energy (213 kJ mol^{-1}) higher than that of ACP (197 kJ mol^{-1}). The evolution of coke on the catalyst acid sites is well established [8,47], so the lower deactivation of acid sites at higher reaction temperatures contributes to the coke structure condensation. On the other hand, the E_a associated with the ACP support is notably lower in T400 (160 kJ mol^{-1}) than in the fresh catalyst. This could be due to a synergetic effect between the combustion of deposited species (DS1 and DS2) and the ACP support, and it is also consistent with the aforementioned inertial effect of the ACP combustion. The low E_a of DS1 and DS2 for this catalyst confirms that these species present an elevated H/C ratio.

3.2.2. TPD/GC analysis

The precursors of coke formation were identified by TPD/GC technique, thus characterizing the low molecular weight species trapped within the deactivated catalysts. These species presumably correspond to those observed in TPO profiles at low combustion temperature (Fig. 2a), which evolve to more developed coke structures. The temperature of the desorption experiments was 500°C , as it is the one used for the ACP support preparation through a carbonization treatment.

Fig. 4 shows the chromatograms obtained for T440 desorbed products, together with the one corresponding to the STPO feed. Some of the main representative compounds of STPO and desorbed products from the T440 deactivated catalyst are numbered, and their concentrations (as determined from the chromatogram area) are displayed in Table 2. The composition of the desorbed products of the T440 catalyst suggests that certain cyclic compounds present on the STPO (mostly styrene and cyclohexene-type molecules, compounds 7–9) could also act as precursors of deactivating species themselves, due to their tendency to polymerize and condense towards heavier species. These trapped species mostly correspond to the DS2 fraction identified in the TPO profile of T440 catalyst

Fig. 4. Chromatogram corresponding to the TPD/GC analyses for the STPO feed and the desorbed species at 500°C from the T440 deactivated catalyst.

(Fig. 2a). Furthermore, it is observed that some STPO compounds present a lower tendency to remain adsorbed on the catalyst surface (compounds 15 and 16), due to their high hydrocracking reactivity. As a result of hydrocracking, a noticeable decrease in the concentration of heavy compounds (ret. time $> 13 \text{ min}$) is measured for the desorbed products of the T440 deactivated catalyst compared to those of STPO.

3.2.3. LDI/MS analysis

Fig. 5 shows the mass pattern obtained from LDI/MS analyses of the fresh and deactivated catalysts (T400, T440 and T500). The presence of a large number of peaks, different of those of ACP, reveals the capacity of the LDI/MS technique in order to characterize the deposited coke. The mass pattern of the fresh ACP catalyst (Fig. 5a) shows only a few well-defined masses assigned to ionized groups of the bulk support, which is hard to ionize due to the more ordered structure. The species detected for the deactivated catalysts (Fig. 5b–d) correspond to the coke formed in the hydrotreatment reaction, with a very heterogeneous composition [48]. These species became heavier (bulkier) and discretized (decrease the peak density and increase their definition) upon increasing the hydrocracking temperature. This coke evolution during the hydrocracking reaction (aging) is consistent with the previously discussed results for the TPO analyses of the deactivated catalysts. Moreover, coke aging during a thermal treatment is a well-known phenomenon in acid zeolite catalysts deactivated during cracking reactions [49] or during acetone conversion into hydrocarbons [50]. The mass range of LDI/MS spectra ($200\text{--}1000 \text{ Da}$) in deactivated catalysts (Fig. 5) is similar to that reported by Ibarra et al. [51] for the coke deposited on a commercial FCC catalyst in the simultaneous VGO (vacuum gas oil) and bio-oil catalytic cracking. Besides, it is higher than that reported by Kim et al. [52] for a pyrolyzed fuel oil-derived pitch, and much larger than that for the coke deposited on isobutene/butene alkylation [34]. For a more detailed study, Fig. 6 shows the LDI/MS spectrum of the T440 catalyst (Fig. 6a) and the molecular weight ranges corresponding to the highest peak intensities (Fig. 6b and c). The number of species separated by 1 Da is noteworthy, which suggests an elevated

Table 2

Concentration of the main desorbed species identified in STPO and the deactivated T440 catalyst as measured by TPD/GC analyses.

Peak	Structure	Name	Concentration (wt%)	
			STPO	T440 desorbed products
1		2-Methyl-1,3-butadiene	0.93	2.94
2		Benzene	0.87	1.86
3		Toluene	0.42	1.57
4		Bicyclo(3.2.1)oct-2-ene	0.30	0.76
5		Ethylbenzene	0.08	0.39
6		Xylenes	0.10	0.76
7		Styrene	0.92	10.40
8		4-Ethenyl-1,4-dimethyl-cyclohexanes	0.25	4.61
9		<i>o</i> -Methylstyrene	0.41	2.22
10		<i>d</i> -Limonene	1.47	3.30
11		1-Ethynyl-4-methyl-benzene	0.35	1.29
12		1-Methyl-4-(1-methylethenyl)-benzene	0.44	1.38
13		1,3-Butadienyl-benzene	1.17	1.63
14		Benzothiazol	0.33	1.56
15		<i>n</i> -C ₁₅	0.78	0.23
16		<i>n</i> -C ₁₇	1.36	0.35

hydrogen presence, characteristic of aliphatic structures with a high proportion of C-H bonds. On the other hand, well-defined peaks separated by 14 Da are also observed, which are assigned to species with a difference of a CH₂ group. Fig. 6d shows a normalized distribution of the crackdown pattern summing in 50–100 counts for an easy comprehension of the nature of the deactivating species deposited on the T440 catalyst. A wide distribution of species is observed, with a maximum centered at 600 Da and an additional hump at 350 Da, evidencing the existence of two dominant types of coke species of different condensation degree. Comparing these results with those obtained from TPO analyses (Figs. 2 and 3), the existence of two main groups of deactivating species of different molecular weight ranges is confirmed by LDI/MS measurement. This result evidences the presence of heavy coke species deposited on T440 catalyst, whose combustion is presumably overlapped with the one of ACP support in the TPO profiles (Fig. 2a). For the sake of investigating the possibilities for identifying additional combustion peaks (corresponding to the heavy carbonaceous species observed by LDI/MS means), supplementary TPO runs with different heating rates and O₂ concentrations were carried out. Fig. 7a shows the DTG curves obtained for T440 at different heating rates

and, as can be seen, a decrease in the heating rate leads to a displacement of the curves to lower combustion temperatures. However, only one peak is observed for the combustion of ACP and the heavier coke fraction. On the other hand, the amount of O₂ does have a more remarkable effect on the obtained TPO profiles, as seen in Fig. 7b. In this case, a decrease in the O₂ concentration results in a delay on the combustion, and also allows for obtaining more clearly differentiated combustion zones.

The minimum O₂ concentration required for ensuring the complete combustion of the deactivated catalyst in the temperature limit range of the TG equipment is 2 vol%. This complete combustion is reached at a combustion temperature as high as 800 °C. In these conditions, the carbon combustion peak shows an important widening (500–800 °C), probably attributed to impediments on O₂ diffusion. At those conditions, the wider combustion peak of the T440 catalyst (compared to that of the fresh catalyst), and particularly the new hump at 520 °C, could probably be related to the presence of other deactivating species besides the support itself. However, its combustion is overlapped with that of ACP support, which avoids the quantification of these deactivating species.

Fig. 5. LDI/MS spectra of (a) the fresh catalyst and catalysts deactivated at (b) 400 °C, (c) 440 °C, and (d) 500 °C.

3.3. Controlled combustion and catalyst regeneration

The heavier nature of some deactivating species observed through LDI/MS analyses, with higher molecular weights than 600 Da, suggests that the catalyst regeneration requires of high combustion temperatures, whose upper limit value is conditioned by the ACP support combustion. The results illustrated in Fig. 7 indicate that there are not clear thresholds of combustion temperature, heating rate or O₂ concentration that allow the complete combustion of deposited coke without observing a certain ACP support mass loss (and probably a deterioration of its catalytic performance).

In order to estimate the optimal combustion temperature for the catalyst regeneration, different temperature values were tested for the fresh and deactivated catalysts using air as oxidant agent (Fig. S1). The fresh catalyst proved to be resistant towards oxidation in the temperature range between 325–425 °C (which is consistent with the results in Fig. 2a) and, in fact, it shows very limited mass loss after 4 h of isothermal treatment at 425 °C. However, the deactivated T440 catalyst suffers a continuous weight loss during the isothermal combustion treatment at this temperature, reaching a maximum loss of 55 wt% of the initial mass (Fig. S1). This result indicates that the combustion of the deposited deactivating species induces the combustion of the ACP support and accelerates the degradation of the catalyst at this temperature. For this reason, a lower temperature (375 °C) was chosen as the suitable combustion temperature to regenerate the T440 catalyst, because it is possible to burn the maximum amount of deactivating species without a significant combustion of the ACP support.

Fig. 8a–c shows the TPO profiles for deactivated catalysts at three temperatures (T400, T440 and T500) and also those corresponding to the same catalysts regenerated via controlled combustion at 375 °C in air (T400R, T440R and T500R). The stripped area

Fig. 6. (a) General, (b) detailed molecular weight ranges and (c) normalized LDI/MS spectrum for the deactivated T440 catalyst.

corresponds to the difference in the DTG profiles of deactivated and regenerated catalyst, which is associated to the mass of deactivating species removed in the combustion. Qualitatively, it is possible to observe that the regeneration treatment is apparently effective in all cases for removing the deactivating DS1 and DS2 species identified in TPO analyses (Fig. 2a). Moreover, the TPO profiles of the partially regenerated catalysts are quite similar to those of the fresh catalysts, with only one peak but maintaining the aforementioned -10 °C shift of the maximum peak. Textural and acid properties of the regenerated catalyst were analyzed in order to evaluate the effectiveness of the controlled combustion regeneration treatment. N₂ adsorption-desorption isotherms corresponding to the fresh, and the different deactivated and regenerated catalysts are shown in Fig. 9a. As observed, the fresh catalyst exhibits an I + IV-type isotherm typical of solids with a very well-developed micro and mesoporous structure. The isotherms corresponding to the deactivated catalysts are IV-type isotherms with a H4-type loop beyond 0.4, caused by the presence of lamellar and thin mesopores. The deposition of deactivating species during

Fig. 7. Effect of (a) the heating rate and (b) the O_2 concentration on the TPO profile of the T440 catalyst.

the hydrocracking reaction leads to a total blockage of micropores and narrow mesopores, resulting in an important decrease in the surface area. Via controlled combustion of the catalyst, the micro- and mesoporous structure becomes partially accessible again (as concluded from the difference between the slopes of the fresh and T440R isotherms). The recovered T440R catalyst shows a BET surface area of $467 \text{ m}^2 \text{ g}^{-1}$, an average diameter of 69 Å and a micropore volume of $0.117 \text{ cm}^3 \text{ g}^{-1}$. Comparing the textural properties of T440R catalyst with those of the fresh and deactivated (T440) catalysts (Table 1), a remarkable superficial recovery is observed.

On the other hand, *t*-BA TPD profiles have been obtained for studying the catalyst acidity variations (Fig. 9b). The controlled combustion of deactivating species at 375 °C allows for recovering a 60% of the initial acidity ($0.29 \text{ mmol}_{t\text{-BA}} \text{ g}^{-1}$), reaching a value of $0.16 \text{ mmol}_{t\text{-BA}} \text{ g}^{-1}$. Moreover, the TPD-curve maximum for the T440R catalyst is shifted to lower temperatures (15 °C), pointing that the average acid strength of the accessible sites is higher than that of the fresh catalyst. This result suggests a higher conversion

Fig. 8. TPO profiles for the deactivated (a) T400, (b) T440 and (c) T500 catalysts before and after regeneration through controlled combustion.

Fig. 9. (a) N_2 adsorption-desorption isotherms of the fresh, deactivated and partially regenerated catalyst and (b) *t*-BA TPD profile for the fresh, deactivated T440 and partially regenerated catalyst.

Fig. 10. LDI/MS spectra of the (a) fresh and (b) partially regenerated T440R catalysts.

in the combustion of deposited species on strong acid sites. Thereby, N_2 and *t*-BA adsorption-desorption results suggest that T440R catalyst could be used in a second reaction cycle, even though its catalytic activity will presumably be lower than in fresh conditions.

Because of the already discussed limitations (Fig. 6) for analyzing the nature of deactivating species in the catalyst, LDI/MS technique was used again for characterizing the catalyst after the regeneration treatment. Fig. 10 shows the LDI/MS crackdown patterns of the fresh (Fig. 10a) and the partially regenerated T440R catalyst (Fig. 10b). As a consequence of the combustion of the deactivating species the LDI/MS spectrum of T440R does not show the high density of peaks exhibited by the T440 catalyst (Fig. 5c) attributed to C–H bonds. In fact, the T440R spectrum is similar to that of the fresh catalyst, with a very neat pattern with well-defined peaks in the range of 300–800 Da. The T440R catalyst presents some of the same characteristic peaks of ACP support (393, 409, 684 and 702 Da), which were recovered after the regeneration treatment, but with a lower intensity. In addition, new defined peaks are observed in the T440R spectrum (439, 483 and 773 Da), which suggests the presence of a remaining coke fraction after the controlled combustion, with an ordered and condensed nature (due to the clear definition of the peaks).

These results support the hypothesis that the aging of deactivating species deposited on ACP support also occurs during the regeneration of the catalyst, leading to a catalyst state that consists in the ACP support and the carbonaceous condensed structures formed from coke deposits. This condensation of deactivating species on the catalyst surface is well-established for zeolite catalysts, observing a decrease in the H/C ratio of the remaining coke upon increasing the extent of the combustion [53].

According with the results discussed in previous sections, the performance of two techniques has been proved for analyzing the deactivating species nature on a carbonaceous support: (i) TPO analysis, calculating the evolution of the activation energy with the extent of the combustion; and (ii) LDI/MS analysis (used for identifying deactivating species of different molecular weight), based on the density and definition of the spectrum peaks. Furthermore, our results point out several factors, which should be considered for enhancing the performance of ACP as hydrocracking catalyst support. The most important are: (i) an enhancement of the thermal stability of the catalyst in order to increase the ignition temperature, avoiding the combustion overlapping with coke; (ii) a

wider investigation in the reaction conditions (increasing the reaction temperature and/or pressure to attenuate deactivation and increasing the time on stream in conditions of constant conversion); (iii) an exploration in the catalyst stability during reaction-regeneration cycles, searching for a potential recovery of constant activity after consecutive cycles.

On the other hand, the limitations for analyzing the coke deposited on carbonaceous supports with the commonly used techniques for inorganic supports has been revealed. Therefore, the results obtained in this work in the application of techniques for coke characterization (deposited on an activated carbon-based catalyst) are encouraging.

4. Conclusions

Activated carbon with phosphorus (ACP) shows an outstanding performance as acid support in a Pt–Pd bifunctional catalyst for the production of fuels through scrap tire pyrolysis oil (STPO) hydrocracking. Catalyst deactivation due to the deposition of carbonaceous species (coke), which leads to a deterioration of physical and acid properties, is attenuated upon increasing the hydrocracking temperature in the 400–500 °C range. Thus, the catalyst is practically stable at 500 °C inasmuch as the hydrocracking of the coke intermediate precursors limits their deposition. TPD/GC analyses reveal the presence of reaction medium components (from STPO and formed by hydrocracking) trapped on the catalyst surface, suggesting that they can act as coke precursors.

Methodologies for calculating the evolution of the activation energy (E_a) with the extent of the catalyst combustion (TPO analyses) offer valuable information of coke combustion, observing a decrease in the activation energy of deactivated catalysts with respect to the fresh one. This way, two coke fractions are identified, together with a change in the ACP support combustion mechanism (at high extent of the combustion) attributed to the combustion of a heavy coke fraction deposited on the ACP structure. The overlapped combustion of this coke fraction and the ACP support is not avoided by decreasing the heating rate or the O_2 concentration in TPO analyses.

LDI/MS analysis is an effective technique to study the coke-forming structures, by differentiating them from those of the ACP support. Deposited species present a heterogeneous composition, which evolves to heavier and more condensed structures upon increasing the hydrocracking temperature. Consequently, an increase in the reaction temperature attenuates the coke deposition, but also favors coke aging towards more ordered structures.

Catalyst regeneration through controlled combustion treatments evidences only a partial recovery of the textural and acid catalyst properties, since there is a certain fraction of the coke that presents a high condensation degree and forms a stable phase with ACP support. The removal of highly condensed coke requires combustion temperatures higher than 375 °C, when the ACP support combustion starts.

The using of diverse coke analysis methodologies over deactivated carbon-based catalysts and the progress towards the regeneration of activated carbons are useful for their application in sustainable fuel production processes at large scale, whose industrial implementation is still under development.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2017.06.077>.

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