



Research article

Petcoke-derived functionalized activated carbon as support in a bifunctional catalyst for tire oil hydroprocessing



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ABSTRACT

The catalytic performance of three NiMo catalysts supported on tailored activated carbon (AC) supports has been studied for the hydroprocessing of tire oil for sulfur removal and conversion of heavier fractions towards lighter naphtha and diesel production. The supports have been obtained through physical activation of petcoke for different times, and in some cases functionalized via acid treatment with HNO₃. The hydroprocessing runs have been carried out in a fixed bed reactor working in trickle bed regime at 275–375 °C, 65 bar and a space time of 0.16 h. The catalyst properties have been measured by ICP-AES, N₂ adsorption–desorption isotherms, TPR, and *tert*-butylamine adsorption–desorption (TPD). A preliminary catalyst screening using a synthetic mixture of model compounds of tire oil was used to select the most active catalyst. This catalyst, which contained a support activated for 9 h and functionalized with HNO₃, had an HDS conversion of up to 99.9%. In the hydroprocessing of real tire oil, the same NiMo/AC catalyst reached a steady sulfur removal of 96.3% and a heavy gasoil lump removal higher than 11 wt%, with complete olefin hydrogenation and a decreased content of naphthenes and aromatics in the products. The cetane number of the diesel fraction was also enhanced with this catalyst.

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1. Introduction

Recently, increasing interest is being paid to waste tire processing and valorization because of the growing accumulation of dumped tires - annually, approximately 7 million tons of waste tires are disposed worldwide, accounting for 2% of the total waste [1]. The inappropriate disposal of these tires results in environmental damage caused by uncontrolled dumping and non-biodegradability of this type of plastic waste, and a loss of a potential feed to satisfy the increasing demand for hydrocarbon fuels [2]. Retreading, incineration and/or grinding have all been considered as alternative management processes. These methods, however, have significant drawbacks, including emissions of dioxins, particulates, SO₂ and NO_x. Thus, the development of a more sustainable, efficient and environmentally friendly recycling process for waste tires is required [3].

Pyrolysis of waste tires has been widely studied in the literature [2,4] and has proven to be a valid alternative, with more energetic efficiency (70%) and reduced harmful emissions compared to direct combustion processes. Pyrolysis also allows scrap tires to be co-processed with other types of waste (plastics, biomass) [5,6] or coal [7,8], using various technologies from fixed bed reactors or rotary kilns to conventional fluidized beds (moving or bubbling). The conical spouted bed reactor (CSBR) has been successfully used for the fast pyrolysis of tires and

other types of residue, such as biomass or plastics [9–12]. This reactor offers interesting features for waste pyrolysis, such as (i) suitability for handling particles with irregular texture and D-group particles (according to the Geldart classification), (ii) isothermicity and good heat transfer, favored by counter-current gas–solid contact in most of the bed, (iii) low segregation and (iv) vigorous gas–solid contact.

Pyrolysis produces a liquid fraction known as tire oil [13,14], which is a potential combustion fuel [15,16]. Indeed, we have recently reviewed the pathways for obtaining fuels from tires indicating the potentiality of using its tire oil [1]. The disadvantage to this liquid product is its high content of contaminants, particularly sulfur, which may vary between 0.5–3 wt% depending on the technology that has been used to produce the tire oil. This high level necessitates subsequent processing within the standard scheme of a refinery to reduce the sulfur content in order to comply with the increasingly strict environmental protection policies. Refiners are pushing catalytic hydrotreaters to their limits [17–19], demonstrating the challenges facing waste refineries [20]. NiMo/Al₂O₃ [21] and CoMo/Al₂O₃ [22] are the classic catalyst formulations for hydrodesulfurization (HDS) of petroleum derived feedstock. The HDS activity of these types of catalysts is highly dependent on the features of the support, as demonstrated in previous studies [23,24]. Recent efforts have been focused towards developing and improving kinetic models [25] and new types of supports for HDS catalysts such as (i) zeolites, (ii) mesoporous materials (MCM-41, SBA-15, etc.) and (iii) activated carbon (AC). AC is of special interest not only due to its suitability to be used as a catalytic support but also due to its stability

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in basic and acidic media, possibility for reuse, and flexibility to tailor its physical and chemical properties according to specific aims [26].

Several agricultural (i.e. fruit stones, nutshells) and petroleum-derived wastes and by-products can serve as AC precursors. In particular, petroleum coke (petcoke) is a by-product of the upgrading of bitumen and heavy oil and produced at over 140 refineries and upgraders worldwide. The global annual production is expected to be 170 million tonnes by 2016 [27,28] and, unless new markets are discovered, 20% of this amount will remain unused in stockpiles near the refining facilities [29]. Given its abundance, petcoke can be partially activated (via chemical or physical activation) and converted into AC, which can be used as a catalytic support itself. The carbon atoms located on the surface of the AC act as active centers, and chemisorb elements like oxygen, hydrogen, nitrogen or sulfur, which form surface complexes that are responsible for most of the physico-chemical properties of the solid material. Oxygen complexes (i.e. carboxyls, lactones and phenols) are particularly important [30] and can be added during the AC preparation using oxidizing agents such as O₂ or air [31], and chemical treatment with different acids (HNO₃, HCl, H₂SO₄, etc.) [32–35] to improve catalyst performance. HNO₃, with low cost and easy application can be a valid candidate for surface modification of catalysts on an industrial scale [36,37].

In this work, AC-based hydroprocessing NiMo catalysts were developed for reducing sulfur content and obtaining lighter fractions (naphtha, diesel) over the heavier gasoil fraction (>350 °C) of tire oil, for automotive fuel production.

2. Experimental

2.1. Catalysts preparation

Three different NiMo catalysts have been used in this work. The carbon-based catalytic support was prepared through the physical activation of petcoke (oil sands delayed coke, Suncor Energy Inc., Canada). The petcoke was activated with CO₂ (150 mL min⁻¹) in a tubular quartz reactor by heating to 950 °C at a rate of 7.5 °C min⁻¹, and maintaining this temperature for activation times of 9 h and 13 h. Prior to activation, the petcoke was ball milled, dried and sieved to the desired particle size (90–150 μm). Acid treatment was carried out after activation, impregnating HNO₃ (5 wt%) by boiling at 85 °C for 6 h, washing until pH 4 was reached, and finally vacuum drying at 80 °C for 12 h. Wet impregnation of the supports was carried out using aqueous solutions of (NH₄)₆Mo₇O₂₁·4H₂O and Ni(NO₃)₂·6H₂O as precursors, to add Mo and Ni, respectively. The required amount of solution (water:precursor ratio of 20:1) was added drop wise, and after every salt was impregnated, stages of (i) 24 h stirring, (ii) 12 h of drying in air at 110 °C, and (iii) 2 h calcination in N₂ at 500 °C were performed. Three batches of each catalyst were prepared and mixed after being characterized separately for ensuring reproducibility. Therefore, the results of the measurements given for each catalyst are the average corresponding to the three samples. The catalysts are named according to the length (h) of activation of the support and whether the support was acid-treated. That is, catalyst NiMo/AC₉ has a support activated for 9 h without acid treatment, catalyst NiMo/AC_{9A} has a support activated for 9 h with acid treatment, and catalyst NiMo/AC_{13A} has a support activated for 13 h with acid treatment.

2.2. Characterization techniques

The metal content of the catalysts was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) with an X7-II Thermo quadrupolar mass spectrometer (Q-ICP-MS). The fresh catalysts were acid digested with hydrofluoric acid (Merck) at 90 °C.

Surface area, pore volume and pore size distribution of the fresh catalysts have been measured by N₂ adsorption-desorption isotherms at -196 °C using a Micromeritics ASAP 2010 apparatus. All

catalysts were degassed at 150 °C for 8 h prior to N₂ adsorption. Surface area was determined using the BET equation whereas pore size distribution and average pore diameter were determined with the BJH equation.

Catalyst acidity was determined by isothermal adsorption of *tert*-butylamine (*t*-BA) at 150 °C, using a Setaram DSC-111 calorimeter. After saturation of the catalyst, physisorbed *t*-BA was removed by He stripping. Then, temperature-programmed desorption (TPD) was performed by raising the temperature at 5 °C min⁻¹ up to 550 °C, in a He flow of 50 mL min⁻¹, and recording the signal of the *t*-BA cracking products in a mass spectrometer. The main cracking product was *n*-butene (*m/z* = 56).

Metal reducibility was studied with temperature-programmed reduction (TPR), in a Micromeritics AutoChem 2920 apparatus. Previous to metal reduction, impurities were removed from the sample in a He flow for 1 h at 300 °C. Then, the sample was cooled to room temperature, and the gas switched to H₂:Ar mixture (10 vol%) before heating the metal to 550 °C at a rate of 10 °C min⁻¹, and holding at this temperature for 4 h.

X-Ray photoelectronic spectroscopy (XPS) measurements were carried out in a SPECS system equipped with Phoibos 150 1D-DLD analyzer and Al Kα (1486.6 eV) monochromatic radiation source. An initial scan was performed (wide scan: step energy 1 eV, dwell time 0.1 s, pass energy 40 eV) and then a detailed analysis of the elements present was performed (detail scan: step energy 0.1 eV, dwell time 0.1 s, pass energy 20 eV) with an electron outcome angle of 90°. The C 1 s peak was established at 284.6 eV to correct possible charge effects and the spectrometer was previously calibrated with the Ag 3d 5/2 peak (368.28 eV). The spectra were adjusted by CasaXPS 2.3.16 software, modeling the Gauss-Lorentzian contributions after background subtraction.

2.3. Reaction equipment

Tire oil was obtained at 500 °C in a spouted bed reactor located within a pilot plant unit schematically shown in Fig. 1a and previously described by Lopez et al. [10]. The grinding rate of scrap tires was 3 g min⁻¹. To ensure stable spouting, the N₂ flow rate was set at 1.2 times the minimum spouting velocity (9.5 L min⁻¹). A bed of 35 g of sand (0.63–1 mm) was used to guarantee good heat transfer and isothermicity during the continuous operation.

The tire oil hydroprocessing was carried out in a laboratory scaled fixed bed reactor working in trickle bed regime (Fig. 1b), under the following experimental conditions: 275–375 °C, 65 bar, H₂:Oil ratio of 1000:1 in volume, space time of 0.16 h, and time on stream (TOS) of 24 h. Prior to the reaction, the catalysts were sulfided in-situ with 50 mL min⁻¹ of a H₂S:H₂ mixture (10 vol%) heating at 5 °C min⁻¹ to 400 °C and maintaining that temperature for 4 h. The catalyst diluted in CSi was loaded in the reactor following the procedure described by van Herk et al. [38]. To avoid gas bypassing and heat losses, CSi layers of approximately 20 mm thickness were placed above and below the catalyst bed. The reaction products were sent to a gas-liquid separator, analyzing the gases online in a Varian CP-4900 microGC. The feedstock was diluted to 50 vol% in *n*-decane (Alfa Aesar, 99%) so that the general properties of the feed could be considered to be similar to those of *n*-decane.

2.4. Analysis of products

Two-dimensional gas chromatography (GCxGC) coupled with mass spectrometry (MS) was used for analyzing the feed and the reaction liquid products. The analysis equipment used was an Agilent 7890A Gas Chromatographer coupled in line with an Agilent 5975C series MS, and consisted of two columns of different polarities which were connected through a flow modulator [39]. The first column was a non-polar DB-5MS (length, 30 m; internal diameter, 0.25 mm), whereas the second column was a polar TRB-50 HT (length, 6 m; internal

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