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Full Length Article

Catalyst used in fluid catalytic cracking (FCC) unit as a support of NiMoP catalyst for light cycle oil hydroprocessing

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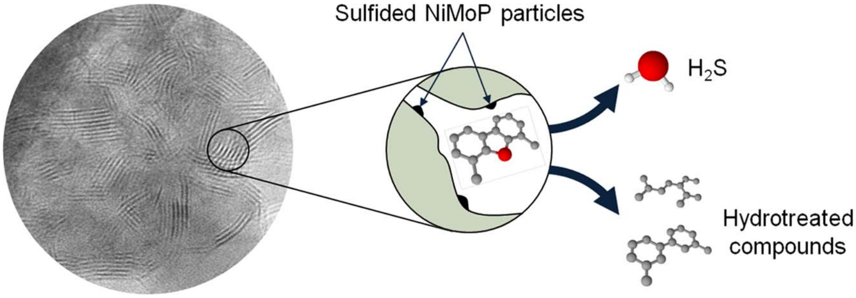
GRAPHICAL ABSTRACT



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ABSTRACT

The behavior of the NiMoP catalysts prepared by means of impregnation of different supports (MCM-41, SBA-15, catalyst used in FCC unit) has been studied, using them in the hydroprocessing of Light Cycle Oil (LCO) with the aim of maximizing the sulfur removal and reduce polyaromatics content; so the hydroprocessed LCO can be hydrocracked in another unit with metal noble catalysts.

Catalysts have been characterized through several techniques: N_2 adsorption–desorption, elemental analysis (ICP-AES), X-ray diffraction (XRD), acidity measurement by temperature programmed desorption (TPD) of *tert*-butylamine, temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), UV–Vis spectroscopy, transmission electron microscopy (TEM), and temperature programmed oxidation (TPO) (spent catalysts). The hydroprocessing runs have been carried out in a fixed bed reactor working in trickle bed regime at 320–400 °C; 80 bar; H_2:LCO ratio, 1000 $mLN_{H_2}\ mL_{LCO}^{-1}$; space time, 0.2 h, and time on stream (TOS), 8 h.

The catalyst NiMoP/HY-Al_2O_3 (spent FCC catalyst) stands out due to its high hydrodesulfurization activity attributable to the ease of impregnation of metals over FCC catalyst and the accessibility of the components of the LCO to the hierarchical porous structure. Its activity for reducing polyaromatics compounds of LCO is also remarkable, without diminishing the diesel fraction content by overcracking. Besides, the deposition of coke over this catalyst is scarce, since the retention of the high molecular weight molecules of LCO in its porous structure is minimized.

1. Introduction

The petroleum industry has to meet the growing demand of fuels solving the inherent difficulties of the lower quality of the crude and of the increasingly strict policies about fuel composition [1]. In this scenario, refineries have to steadily adapt their units for the processing, in the medium and long term, of the non-conventional crudes (heavy-oil, extra-heavy oil, oil sands). Besides, the incorporation of new feeds

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derived from biomass (bio-refinery) [2–4] and residua from consumer society, such as plastics and tires (waste-refinery) [5–7] is being studied with the aim of obtaining fuels and raw materials for the petrochemical industry (such as olefins and BTX aromatics).

Currently, a technological effort in industrial development is being done to intensify the valorization of petroleum, by means of the adaptation (revamping) of the units to co-feed refinery secondary streams. Due to its high capacity and versatility, the catalytic cracking units (FCC) are receiving great attention for the co-feeding of non-usual streams [2,4,8,9]. Nevertheless, within the scheme of a conventional refinery, best prospects are focused in the usage of hydroprocessing units [10], even though this process shows several limitations, such as the high deactivation of the catalyst [11].

Among the refinery streams that potentially can be valorized, the light cycle oil (LCO) awakens great interest as its conversion into fuels has a high economic incidence. The LCO is produced in FCC units with a high yield (15–20%) but its composition, with high content of aromatics (75–90 wt%), sulfur (0.2–1.5 wt%) and low cetane number (CN 15-25), limit its inclusion into refinery diesel pool [12]. The LCO can be valorized both via cracking [13,14] and hydroprocessing [15–18], being the latest the most effective and versatile route to achieve the sulfur (hydrodesulfurization) and aromatics (hydrodearomatization) content values demanded for gasoline and diesel pools. Although noble metal catalysts are very active not only for the hydrodesulfurization reactions, but also for the ring opening reactions implied in the LCO hydrocracking, they suffer from a fast deactivation caused by sulfur poisoning and coke deposition [19,20]. Consequently, the most appropriate strategy for LCO and another residual streams valorization (*REVAHS*, ***RE***sidua ***VA***lorization by means of ***H***ydrogen ***S***urplus) consists on the hydrotreating of LCO in two stages [21] i) hydroprocessing which is generally considered as the process to perform hydrogenation and hydrogenolysis reactions; i.e. the removal of C = C and C–X bonds (where X = C, S, N, metals…), using low cost catalysts based on transition metals (Co, Ni, Mo, W) [15,16]; and; ii) hydrocracking, using more severe conditions and noble metal based catalysts with acidic supports, which are able to achieve high dearomatization yields by means of ring opening [22]. These catalysts show a moderate deactivation when are used in the hydrocracking of the hydroprocessed streams obtained in the first stage (low content of sulfur and polyaromatics) [23].

In this work, the influence of the support in the first stage of the *REVAHS* process for LCO valorization has been studied. For this purpose, three NiMoP catalysts prepared with different acidic supports have been used. MCM-41 and SBA-15 are mesoporous silica, with unimodal and bimodal structures, respectively; and hexagonal and round porous shapes, respectively; having the MCM-41 support a higher acidity. The usage of discarded FCC catalyst as a support is a promising strategy due to its porous structure designed for easing the access of high molecular weight molecules, such as those present in LCO [24], since the catalyst particles are prepared with a combination of HY zeolite and a meso and macroporous matrix aluminas (HY-Al_2O_3) [25]. Furthermore, as the spent FCC catalyst is a residue highly available in refineries, if it is used in the first stage of the *REVAHS* process for LCO valorization, its lifespan will be extended.

The main objective of the first stage of the *REVAHS* process for LCO is achieving the maximum conversion of the sulfur compounds (hydrodesulfurization) with a remarkable removal of the polyaromatics (hydrodearomatization), but without significantly diminishing the boiling point range of its components. For this purpose, the spent FCC (HY-Al_2O_3) catalyst is a suitable support, since it has a limited acidity, as a consequence of the severe dealumination suffered in the consecutive reaction-regeneration cycles, providing to it a low activity for the cracking of the aliphatic chains of LCO.

2. Experimental

2.1. Catalysts preparation

For LCO hydroprocessing three NiMoP catalysts have been used with the same nominal content of Ni, Mo and P, of 3, 8 and 1 wt%, respectively. Three different acidic materials, with different porous structure, have been used as support. Discarded FCC catalyst (referred as HY-Al_2O_3 from now on), being its composition: 53.79 wt% alumina, 13.8 wt% zeolite, 4 wt% metals (Cu, Ni, V, Fe, Na, REO) and binder, has been removed from the catalytic cracking unit of the Petronor S.A. refinery (Somorrostro, Biscay, Spain) and prior to its usage as support, it has been regenerated for about 12 h in oxidizing atmosphere at 550 °C, in order to remove the residual coke. MCM-41 mesoporous support has been synthesized from a sodium silicate solution using $C_nH_{2n+1}N(CH_3)_3Br$ as surfactant [26]. The SBA-15 silicate has been prepared from triblock amphiphilic copolymers (polyethylene and polypropylene oxides) in acidic medium, with the aim of producing highly ordered bidimensional mesophases of hexagonal silica [27].

The incorporation of Ni, Mo and P has been carried out by means of consecutive wet impregnations with aqueous solutions (water solution ratio, 20:1) of H_3PO_4, then $(NH_4)_6Mo_7O_2\cdot4H_2O$ and, finally, Ni$(NO_3)\cdot6H_2O$, being the following stages: (i) stabilization via stirring for 24 h; (ii) drying with air at 110 °C during 12 h, and; (iii) calcination at 500 °C in N_2 atmosphere during 2 h. Afterwards, catalysts have been tableted and sieved (150–300 µm). Phosphorus has been incorporated due to following benefits: (i) metal-support interaction decrease; (ii) ease Ni and Mo metals impregnation on the support; (iii) inhibition the formation of inactive $NiAl_2O_4$ species; (iv) act as a second promoter; and (v) improve the formation of type (II) Ni–Mo–S structures [28].

2.2. Catalysts characterization

The surface properties of the catalysts have been determined from the N_2 adsorption-desorption isotherms obtained with Micromeritics ASAP 2010 equipment. The specific surfaces of the samples have been determined according to BET procedure using the data in the relative pressure range of 0.05 to 0.2. Average pore sizes have been calculated by means of BJH method.

The acidity has been determined by temperature programmed desorption (TPD) of *tert*-butylamine (t-BA) adsorbed at 100 °C, using a thermogravimetric-calorimetric analyzer Setaram DSC coupled in line to a mass spectrometer Balzers Quadstar 422, for the monitoring of the formed butenes as a result of t-BA cracking [29].

The amount of coke deposited on the spent catalysts has been determined by temperature programmed oxidation (TPO), by means of air combustion in a TA Instruments TGA Q5000 IR thermogravimetric apparatus, coupled in line to a mass spectrometer Balzers Quadstar 422 to monitor the CO_2 formed in the coke combustion [30]. Previous to the combustion, an initial sweeping with N_2 was carried out to quantify the content of the retained compounds in the porous structure (possible coke precursors). In this stage, once the sample was stabilized at 100 °C, the temperature was raised up to 450 °C with a heating rate of 5 °C min^{-1} under a N_2 flow of 50 mL min^{-1}. Temperature was held for 30 min and then the sample was cooled down again to 100 °C. Afterwards, the gas was switched to air (50 mL min^{-1}) and stabilized for 5 min. Then, to carry out the coke combustion, the sample was heated following a ramp of 5 °C min^{-1} up to 550 °C, holding that temperature for 2 h with the aim of obtaining complete coke combustion. Finally, the sample was cooled down to room temperature.

Coke content (C_c, wt%) is defined from the mass of spent catalyst (m_0) and the mass of remaining catalyst after coke is burned (m_{cat}):

$$C_c = \frac{m_0 - m_{cat}}{m_{cat}}\cdot100 \qquad (1)$$