Catalyst deactivation pattern along a residue hydrotreating bench-scale reactor

Pablo Torres-Mancera*, Patricia Rayo, Jorge Ancheyta, Gustavo Marroquín, Guillermo Centeno, Fernando Alonso

Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, Col. San Bartolo Atepehuacan, Gustavo A. Madero, México, D.F. C.P. 07730, Mexico

ABSTRACT

An atmospheric residue (312 °C+) was hydrotreated in a bench-scale reactor. After shutdown, spent catalysts of the first bed of the hydrotreating reactor were sampled. A portion of the samples was regenerated. Both spent and regenerated catalysts were characterized by nitrogen physisorption and SEM-EDX. The type of coke deposited on spent catalysts was analyzed by DRIFT. The remaining catalytic activity was evaluated by thiophene HDS and cumene HDC. The profile of metals and coke depositions through the catalytic bed in fresh-basis was determined. The results showed that vanadium and nickel depositions decrease and carbon increases from top to bottom of the bed. It was found that both hard and soft coke amounts increases towards the bed outlet. A tendency of metals to deposit in pores of midsize and coke to fill big pores was observed. Around 25% of the fresh catalyst activity in thiophene HDS and cumene HDC remains in spent catalysts. These results match the values in the remaining of pore volume. Additionally, an enhancement of cumene HDC activity through the regeneration of spent catalysts was noticed.

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1. Introduction

Catalysts deactivation is a great concern in the hydroprocessing of heavy oils and residues [1–9]. Various causes of deactivation have been identified for hydroprocessing catalysts including metal and coke deposition, poisoning and sintering [1–12]. Deactivation extent strongly depends on feedstock properties, operating conditions, catalyst properties and type of reactor. Due to the complexity of the process, hydroprocessing is often accomplished in multistage, i.e., a series of reactor and/or several catalytic beds aiming to protect the tail-end catalysts from premature deactivation [1–3]. Through the different stages, one or several specific goals are aimed; diminish metal content, transform asphaltenes and resins, extinguish metal-containing molecules, lessen sulfur and nitrogen content, achieve ultra-deep sulfur levels. Therefore, the mechanism and extent of catalytic deactivation depends on the hydroprocessing stage. In the case of the first stage of the hydroprocessing of heavy feeds, catalysts with controlled pore size in order to process big structures such as resins, metalloporphyrines or asphaltenes, are required. Whilst regarding catalytic functionalities, a precise balance among hydrocracking (HDC), hydrogenation (HYD), hydrodemetallation (HDM), hydrodeasphalthenization (HDAs), and hydrodesulfurization (HDS) is desirable. For this type of

catalysts, coke and metal depositions are the main causes of deactivation. Several studies on deactivation by metals and coke in hydroprocessing catalysts have been reported [13–28]. Nonetheless, only few studies on deactivation pattern along residue hydrotreating bench-scale reactor have been published [29–32]. In this paper, the catalyst deactivation of the first stage of a hydrotreating bench-scale reactor is analyzed. Metal and coke deposition profiles are outlined, and also the remaining HDC and HDS activity of spent and regenerated catalysts is determined.

2. Experimental

2.1. Hydrotreating conditions and catalyst sampling

An atmospheric residue 312 °C+ obtained from 13° API crude oil distillation was hydrotreated in a bench-scale reactor; $T = 360–410\,°C$, $P = 100\,kg/cm^2$, $LHSV = 0.25\,h^{-1}$, H_2/HC ratio = 5000 ft^3/bbl (826.7 Nl/l). A NiMo/γ-Al$_2$O$_3$ in tetralobular extrudate shape was packed as front-end catalyst in a fixed-bed reactor operated continuously at concurrent downflow. The reactor was shutdown after 1100 h of operation. A flow of naphtha is passed throw the spent catalysts inside the reactor. Afterwards, spent catalysts at different heights of the reactor were sampled by suction; the samples were kept in toluene to prevent oxidation. The spent samples were placed in cellulose extraction thimbles, and then they were washed with hot toluene in a soxhlet extractor during 20 h. After cooling to room temperature, the washed

* Corresponding author. Tel.: +52 55 91758422.
  E-mail address: ptorres@imp.mx (P. Torres-Mancera).

Table 1
Properties of the feedstock (atmospheric residue 312 °C+).

Property	value
Specific gravity (60/60 °F)	1.031
API gravity	5.70
Sulfur (wt.%)	5.93
Nitrogen (wt.%)	0.582
Asphaltenes (Ins. n-C7 wt.%)	22.12
Conradson carbon (wt.%)	21.48
Ni (wppm)	144
V (wppm)	549

samples were recovered, and then dried at 110 °C and atmospheric pressure during 12 h. The so treated catalysts were halved; a portion is labeled as spent catalysts; while, the other half was regenerated. The regeneration was performed by heating at 350 °C for 2 h and then at 550 °C for 8 h in presence of air using 5 °C/min as heating rate.

2.2. Feed properties

Feed properties were determined according to ASTM standard test methods: specific gravity (ASTM D70), sulfur (ASTM D4294), carbon (ASTM D5291), nitrogen (ASTM D4629), asphaltenes (ASTM D3279), and Conradson carbon (ASTM D189). Nickel (Ni) and vanadium (V) contents in the feed and also in spent catalysts were measured by flame atomic absorption spectrometry (ASTM D5863). Carbon (C) and sulfur (S) contents in the catalysts were determined by direct combustion-infrared detection methods (ASTM C1408 and ASTM D1552). The feed properties are shown in Table 1.

2.3. Characterization of catalysts

BET specific surface area (BSA), pore volume (PV), and pore size distribution (PSD) were determined in a Quantachrome Nova 4000 equipment by N_2 physisorption at temperature of liquid nitrogen. Prior to adsorption, the catalysts were pretreated in vacuum and temperature for 3 h, spent at 150 °C and regenerated at 300 °C. The composition and surface morphology of the spent catalysts were analyzed by SEM-EDX using a Nova NanoLab 200 microscope.

The spent samples were heated in flowing dry air from room temperature to 500 °C with a heating rate of 5 °C/min and ramps at room temperature, 200, 300, 400, and 500 °C. This regeneration process was monitored by DRIFT by means of a Harrick diffuse reflectance accessory model Praying Mantis equipped with KBr windows. The spectra were collected in an 8700 Nicolet FT-IR spectrophotometer with 300 scans and a resolution of $4 \, cm^{-1}$.

2.4. Catalytic activity

To explore the remaining sulfur removal capacity and acidity, in both spent and regenerated catalysts, thiophene HDS and cumene HDC were used. Both reactions were performed in a fixed-bed glass reactor operated at atmospheric pressure and temperature of 350 °C. A feed consisting of 60 mL/min of a mixture of 5 mol% thiophene in hydrogen was used for thiophene HDS, while for cumene HDC the feed was a mixture of 0.23 mol% cumene in hydrogen with a flow of 50 mL/min. Prior to activity test, the catalysts (spent and regenerated) were sulfided at 400 °C for 2 h using a flow of 40 mL/min of CS_2 and H_2 gas mixture. Catalyst particle was sized to 20–40 mesh. The progress of the reaction was monitored by online gas chromatography using a Varian 4700 gas chromatograph equipped with a FID.
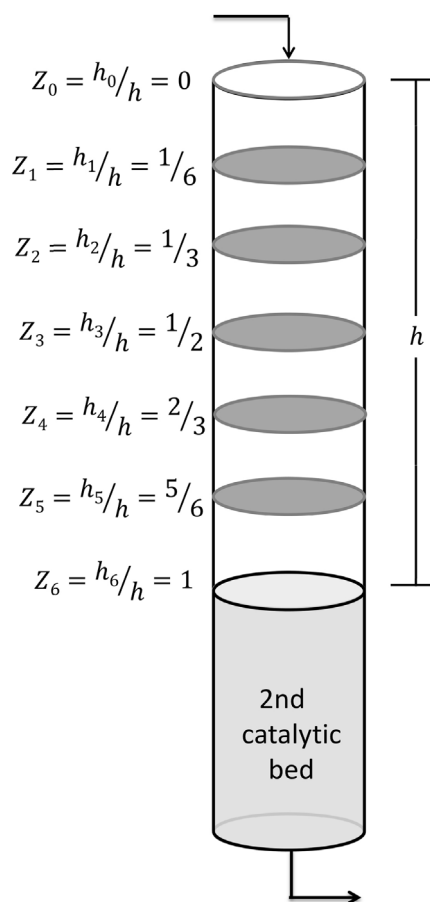
Fig. 1. Catalysts sampling.

3. Results

3.1. Feed and catalyst samples

A high amount of coke deposited on the catalyst is expected in view of the contents of asphaltenes and Conradson carbon of the feed (22.12 and 21.48 wt.%, respectively). An important contribution to catalyst deactivation by metals is also expected; as vanadium and nickel contents are also high (see Table 1).

Spent catalysts corresponding to the first bed of the hydroprocessing reactor were sampled according to Fig. 1. The bed height is normalized as $Z_i = h_i/h$, where h states for the total bed length and h_i corresponds to the height of the ith sample. Hereafter, catalysts samples are identified as their corresponding normalized height plus either "spent" or "reg" for spent and regenerated samples, respectively.

3.2. Deposition of C, S, and metals

The profiles of the amount of V, Ni, C, and S retained in the spent catalysts are plotted in Fig. 2. Clearly from top to bottom of the catalytic bed, the retained amount of V, Ni, and S decreases, whereas the C content augments. The values are expressed per gram of fresh catalyst. This fresh-basis has the advantage of rendering directly the retained amount capacity of the catalyst. As for instance, a value of 0.4 of V implies that 0.4 g of V were retained in 1 g of fresh catalyst [33]. Henceforth, the deposition is discussed in terms of the amount retained per gram of fresh catalyst. Near the entrance of the reactor (Z_1), the V retained in the catalyst almost reaches 0.5 g and then this amount decreases to 0.2 g at Z_5. The Ni retained amount is lower