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Long-term evaluation of NiMo/alumina–carbon black composite catalysts in hydroconversion of Mexican 538 °C+ vacuum residue

E. López-Salinas [*], J.G. Espinosa, J.G. Hernández-Cortez, J. Sánchez-Valente, J. Nagira

Instituto Mexicano del Petróleo, Eje Central 152, G.A. Madero, México 07730 D.F., Mexico

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Abstract

Alumina with (8–18 wt.%) carbon black composite (AMAC) supports was prepared as bimodal extrudates, containing 11–20% of total pore volume as macropores (i.e. >1000 Å). These supports, in spite of containing carbon black and macropores, showed good side crushing strength (0.67–1.19 kg/mm) after pyrolysis in 6% O_2/N_2. AMAC-catalysts were obtained after impregnating these alumina–carbon black supports with Ni and Mo, to obtain 3.5 wt.% NiO and 15 wt.% MoO_3. These catalysts were evaluated for about 700 h in the hydroconversion of a Mexican vacuum residue (538 °C+) at 415 °C, 200 kg/cm^2, H_2/HC = 6000 ft^3/barrel in a pilot plant equipped with a Robinson–Mahoney reactor. In comparison with a commercial bimodal alumina-based catalyst (ComCat), AMAC catalysts showed much fewer sediments and less Conradson carbon formation. Initial HDS in AMAC containing macropores can be as high as 92%, while that in a ComCat is 86%. On average, yields of naphtha and kerosene were 2.6 and 1.34 times higher with AMAC catalysts than those with ComCat, while diesel yields were similar.

Keywords: Hydroconversion; Hydrodesulfurization; Hydrodenitrogenation; Vacuum residue; H-oil; Carbon-black; Alumina support; Macropores

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1. Introduction

Petroleum residues are the heavy fraction remaining after distilling petroleum crudes at atmospheric pressure (atmospheric residue) or at reduced pressure of 25–100 mmHg (vacuum residue). Residues have high molecular weight ($\gg$1000 amu number average for vacuum residue) and contain polynuclear aromatics, also termed asphaltenes. Because of their high thermal stability, asphaltenes having 3–4 rings provide the greatest limitation to the conversion of residue. In addition, the high concentrations of heteroatoms (sulfur, nitrogen, vanadium, and nickel) in petroleum residue act along with asphaltenes to poison catalysts. No matter which type of process is used, a substantial fraction of residue molecules can be cracked off as fragments to become liquids in the transportation fuel and vacuum gasoil boiling ranges. However, one should not try to overly convert residues because asphaltene content can force the selectivity to go to the thermodynamically favored, but lower valued, products: coke and/or sediments and/or hydrocarbon gases. One of the processes designed to convert heavy oil residue to lighter fractions is the so-called H-Oil^{TM}, which typically operates at 410–420 °C, 120 kg/cm^2, LHSV: 0.5 h^{-1}, H_2/HC: 3500 ft^3/barrel, and uses an ebullated bed reactor.

Maya crude oil is classified as heavy oil, and it accounts for more than 50% of the total crude oil production in Mexico. In terms of environmental problems, catalytic hydrodesulfurization (HDS) and hydrocracking (HC) technologies are important to produce low sulfur fuel oils by upgrading residues from Mexican crude oil which contain not only high concentrations of sulfur compounds (around 4.5 wt.%), and catalyst-deactivating vanadium compounds (around 400 ppm), but also asphaltenes. At present, Mexican refineries operate with crude oil blends, that is, 55–60% Isthmus (e.g., the Mexican light blend), and 45–40% Maya (e.g., the Mexican heavy blend) crude oils; but since heavy oils tend to become relatively abundant, an unavoidable situation for the Mexican oil industry in the near future will be to refine Maya crude oil richer blends. Two H-Oil^{TM} plants, which have been operating for more than 30 years in the Salamanca, Gto. refinery (18,500 BPD designed capacity), and more recently in the Tula, Hgo. refinery (50,000 BPD designed capacity), transform Mexican heavy vacuum residue into more valuable oil fractions, such as gasoil and diesel, removing great amounts

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[*] Corresponding author. Fax: +52 55 9175 8429.
E-mail address: esalinas@imp.mx (E. López-Salinas).

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of polluting sulfur compounds. Nonetheless, the H-Oil^{TM} process is frequently hampered by the formation of high-molecular weight compounds, called sediments, which cause many downstream operational problems, especially by blocking valves, pumps, flow-control devices, and hot and cold separators. Sediments are polynuclear aromatics which result from complex cracking, recombination, and nucleation reactions among asphaltenes [1]. H-Oil^{TM} plants cannot operate at high conversion levels since sediment yields rise, particularly when using heavy residue from heavy crude oils [2]. Thus, sediment yields above 1 wt.% render H-Oil^{TM} plant operation anywhere from troublesome to inoperable. Taking into account these drawbacks, new catalyst designs must offer: (1) accessibility to large asphaltene agglomerates in order to increase their diffusion and transformation, and (2) catalytic active sites or support adsorption sites that are less favorable to sediment formation.

In the first approach, and to overcome the difficulty of asphaltene diffusion through small pores, an appropriate porous structure can be obviously rationalized in terms of creating macropores (>1000 Å) in the shaped support or catalyst. However, not that many macropores (ca. above 30% of total pore volume) should be created, since shaped particles could turn fragile. The formation of macropores in extrudates is a direct consequence of support or catalyst formulation when making extrudates. In fact, new generation commercial catalysts developed for the H-Oil^{TM} process contain macropores [3]. The second approach deals with the catalyst support's intrinsic acid sites (e.g., γ-Al_2O_3) [4], which are believed to participate in sediment formation.

In this study, an alumina–carbon black composite support was developed with the aim of diminishing either the strength, and/or number of acid sites. Carbon black: (i) is cheap, (ii) has a low tendency to form coke-related compounds (e.g., very weak acid sites), (iii) has an affinity for V and Ni porphyrine-like compounds, which could be refrained from attacking catalytic active sites, (iv) has high hydrodesulfurization (HDS) [5,6] and hydrodenitrogenation (HDN) [6–8] activity, and (v) has no micropores below 30 Å which could be easily occluded, therefore turning active Ni and Mo metals into inactive ones. In earlier works, microporous activated carbon was used as a support, despite the fact that micropores are of little use for catalytic reactions involving large molecules [9], and it is more expensive than carbon black. Unfortunately, carbon or carbon black supports are known for their low mechanical resistance; this physical property being of the utmost importance since shaped catalyst particles will be colliding among themselves and against reactor walls in the ebullated bed reactor. On the other hand, pyrolyzed carbon, or pyrolyzed carbon black, has good mechanical properties. Very little work has been reported on the hydroconvertion of heavy residues on NiMo- or CoMo- catalysts based on carbon supports. For instance, Segawa et al. used NiMo on active carbon as a catalyst for the hydrogenation of an Arabian vacuum residue, and they found that coke formation was considerably suppressed [10].

One of the challenges of this study is to achieve an intimate and homogeneous mixture of Al_2O_3 and carbon black in an extrudable paste, which could eventually result in macropore-containing, mechanically resistant, Al_2O_3–carbon black extrudates. In order to record deactivation, using near real-operation conditions, selected catalysts, obtained from impregnating these prospective supports simultaneously with Ni and Mo, were evaluated and monitored continually for about 700 h on the run. A bimodal alumina-based NiMo commercial catalyst was used as a comparison.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Support preparation

Catalysts were prepared by closely following the preparation procedure shown in Fig. 1. Commercial boehmite-phase alumina (325 m^2/g; acid dispersability index: 30%; loose bulk density: 192–224 kg/m^3; $Na_2O < 0.01$ wt.%), dried at 110 °C, was used throughout the study. This alumina (200 g) was kneaded with 1–1.5vol.% acetic acid (280–320 cm^3) for about 30 min. Then, 15 g of carbon black #970 (particle size: 16 nm, specific surface area: 260 m^2/g), from Mitsubishi Chemicals, and sucrose (15 g), used as a binder, were poured in, after which kneading continued for about 15 min. The black wet paste obtained was kept in a closed plastic vessel for 12 h at room temperature, in order to maintain moisture and allow homogenization of the mixture. Then, the paste was extruded in a Brabender mechanical extruder at a constant speed (30 rpm), using 1/16 in. dice. Wet extrudates were

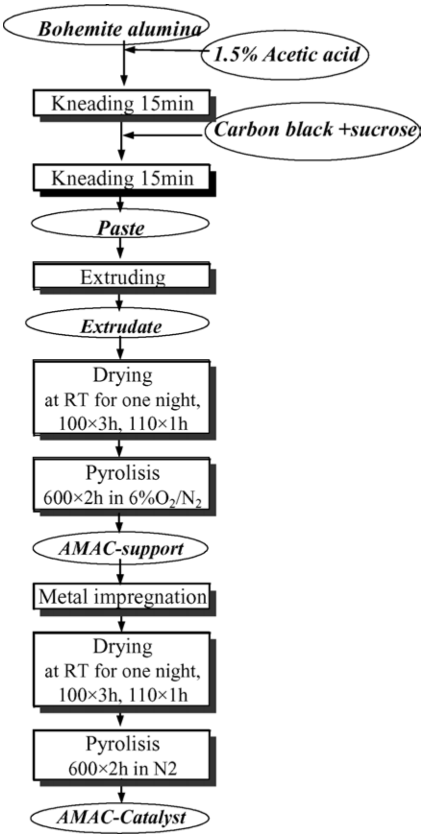

Fig. 1. Preparation scheme of AMAC supports and catalysts.