

SELECTIVE LEACHING DURING REJUVENATION OF SPENT CATALYSTS FROM H-OIL™ PROCESS

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Introduction

The rejuvenation of catalysts is an alternative for the recovery of the catalytic activity of spent catalysts that are considered industrial wastes and highly pollutants (1).

The rejuvenation of spent catalyst includes solvent wash, leaching with inorganic and organic acids, and an oxidative regeneration usually in air (2-4). We included, during the leaching step, the addition of a complex that increases the selectivity of removal of foul and metal due to the effects of the synergy of oxidizing and complexing reactions

In this work we present results of characterization of an industrial spent catalyst from the H-Oil™ Process and a modified rejuvenation process. Characterizations were made by Raman and atomic absorption spectroscopies in conjunction with X-ray diffraction and N₂ adsorption and scanning electronic microscopy (SEM). Our results clearly show that the deactivation of catalyst during H-Oil Process occurred by the formation of a coke core around the pellet, where preferably Ni and V were deposited. After the rejuvenation process we recover physical and chemical properties and catalytic activity in HDS from gas-oil.

Materials and Methods

We used fresh (Sample M0) and spent commercial NiMo/Al₂O₃ catalysts and were obtained from Petroleos Mexicanos (PEMEX) in form of cylindrical pellets of 1 mm of diameter and 3.8 mm of longitude. The rejuvenation process comprised the following steps:

- The spent catalyst was washed with naphtha in a Soxhlet extraction system to remove any residual oil (Sample M1).
- Selective acid leaching of Ni and V from the washed spent catalyst: a) With H₂SO₄, HNO₃ and HCl (10% in vol.) (Sample M2), and b) With acid solution (10% in vol) + complex salt (0.015 M) (Sample M3).
- Oxidative regeneration of leached catalysts in order to remove the coke (Sample M4 proceed from acid leaching (a), and Sample M5 from (b)).
- The effectiveness of each step during rejuvenation processes was tested by evaluating the catalytic activity of all samples submitted to rejuvenation in the HDS of a real feedstock (straight-run gas oil, S = 22,492 ppm) in a trickle bed high-pressure flow-reactor.

Results and Discussion

To preserve physical, chemical and catalytic characteristics of the fresh catalysts against Naphtha washing and acid leaching processes, the oxidative regeneration was carried out as the final step, i.e. the core of coke was maintained during leaching to preserve the catalytic active phases. The XRD patterns of the all samples show that both the crystalline structure of the support and the active metals (NiMo) were preserved during rejuvenation processes.

SEM results of the original spent catalysts indicated that the core of coke is rich in C and Ni. After treatment C content in the core decreased in 99.5 %. Ni and V concentrations were reduced gradually as to go away from surface catalyst. With respect Mo, SEM results show that this active element was uniformly dispersed over the support. The Al, Mo and Ni contents on the catalyst are practically the same after rejuvenation process and V and Ni metals from petroleum molecules deposited on the catalyst were selective eliminated until 50 %.

The Raman spectroscopy of spent catalysts during the rejuvenation process show two main characteristic bands at 1350 and 1600 cm⁻¹, and other less intense bands at 975 cm⁻¹, that correspond to octahedral surface species (Mo—O—Mo linkages). The first bands corresponding to carbonaceous Raman response and correspond to the presence of different carbon types on the surface of spent catalyst and is attributed to the stretching mode of the individual sheets in graphite (E_{2g} mode, called G band of graphite). Several aromatic systems and polynuclear aromatics with aliphatic and alicyclic appendages interconnected to form a pseudo graphitic structure with different crystallinity and cross linking. The band around 1380 cm⁻¹ is assigned to an A_{1g} type mode called the disorder band (D band) (5). The side reactions by which coke is formed do not necessarily take place on the same active sites as the main reactions. So it is possible that this coke was formed the side of the alumina.

The decrease in surface area was apparently caused by partial blocking of the cannels with V, Ni species and coke specially.

The elimination of C, N, Ni and V allowed to obtain the catalytic activity during HDS at T=350 °C, P=70 kg/cm² in HDS % as follow 69.64, 26.96 and 25.36 for samples M0, M4 and M5 respectively.

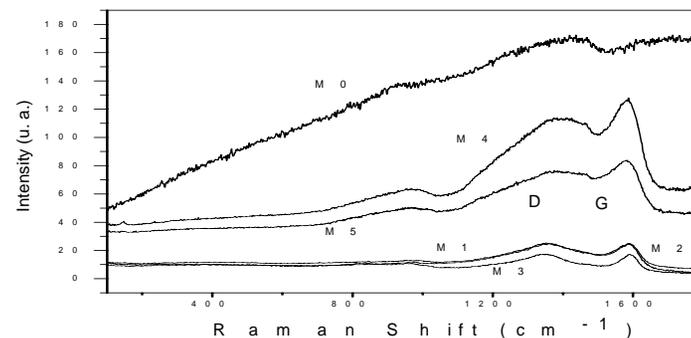


Figure 1. Raman spectra collected from: a) M0, b)M1, c)M2, d)M3, e)M4, f)M5

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