



# NiMo supported acidic catalysts for heavy oil hydroprocessing<sup>☆</sup>

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## ABSTRACT

Large pore diameter Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> acidic mixed oxide supports were prepared by using homogeneous co-precipitation method. The acidic properties of supports (oxide) and supported catalysts (sulfided) were chemically probed with cumene cracking (HCR) into propane and benzene at atmospheric pressure and 400 °C. NiMo supported hydroprocessing catalysts activities were also evaluated with heavy Maya crude oil. The use of acidic support is to optimize yield of high octane gasoline components, *i.e.* selective cracking of complex crude oil molecule. The supported fresh and spent catalysts were characterized by means of N<sub>2</sub> adsorption-desorption and SEM-EDX spectroscopic techniques. The results point out that deactivation takes place mainly at the entrance of pore due to coke deposition, while the depositions of vanadium and nickel sulfides mainly depend on the diameter of the pores. The results also indicated that the deactivation due to carbon deposition is carried out at initial hours of the crude oil processing. The large pore diameter catalyst contains higher amounts of deposited species, which are distributed proportionally along the extrudate radius, while for smaller pore diameter catalyst the deposition mainly occurs on the extrudate surface.

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## 1. Introduction

The petroleum industry is increasingly concerned about heavy and extra-heavy oil processing. These crudes are also being considered as a future option for fuel production using different processes. In general crude oils are composed by virtually infinite number of different complex hydrocarbons containing large amounts of sulfur, nitrogen and metals. On the contrary, the increasing demand for middle distillate fuels with improved quality, which have limited reserves in the nature, has been requested by the market due to stricter environmental legislations. To achieve such specifications refiners need to look for improved or new catalysts technologies, which must be able to satisfy the middle distillate yield as well as remove inorganic contaminants (S, N, Ni, V, Fe, Ca, etc.) from the heavy crude oil. However, the direct hydroprocessing of virgin heavy crude oil will not produce commercial fuels rather it is a primary process to reduce metals and asphaltene content in heavy oil, which will be effectively used as FCC and hydrocracking feedstock or for synthetic crude oil production [1].

Mixed oxides have some acid sites which demonstrated to possess notable activity for hydrodemetallization (HDM) and cracking reactions. [2,3]. Also in order to improve both hydrodesulfurization (HDS) and hydrogenation activity, nickel is included in the catalyst formulation. On the other hand, the relative contributions of the catalytic reaction and thermal cracking on the hydrocracking of heavy oil have been evaluated in detail and it is reported that asphaltenes conversion into light oil fractions is mainly due to thermal cracking [4] and the main role of the catalyst is to supply hydrogen to the cracked fraction and prevent its carbonization. Moreover, catalyst deactivation can be partially avoided by using high hydrogen pressure, in which multifaceted heterolytic dissociative role of hydrogen is expected during the hydroprocessing of heavy oil (i) to regenerate Brønsted acid sites, ability to break C–C bonds and produce carbocations; (ii) to terminate radicals formed by C–C bond breaking; and (iii) to hydrogenate C=C bond and decrease carbonaceous material, but the investment of the process increases proportionally, thus, increasing the hydrogen pressure is not a solution.

The hydroprocessing of heavy oils is a complex task due to the presence of high contaminants content, particularly metals (Ni and V) and Conradson carbon, which cause poisoning and rapid deactivation of the catalysts commonly used for hydroprocessing. Asphaltene is the most difficult molecule to be processed in the

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