



Carbon and metal deposition during the hydroprocessing of Maya crude oil



Mohan S. Rana^{a,*}, J. Ancheyta^a, Sangram K. Sahoo^{b,1}, P. Rayo^a

^a Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, Mexico, DF 07730, Mexico

^b Department of Chemistry, University of Akron, Akron, OH 44325-3601, USA

ARTICLE INFO

Article history:

Received 22 April 2013

Received in revised form 26 August 2013

Accepted 15 September 2013

Available online 20 October 2013

Keywords:

Hydroprocessing

Heavy oil

Residue

Deactivation

Coke and metal deposition

ABSTRACT

During the heavy oil hydroprocessing, a decrease in catalytic activity with time-on-stream (TOS), is due to the metal and carbon deposition on the catalysts. In this investigation, spent catalysts were obtained from the Maya heavy crude hydrotreating unit, as the processing conditions were close to the industrial practice. The catalysts were unloaded after considerable activity decrease, considering the initial activity as base activity. The spent catalysts were characterized by pore size distribution, SEM-EDS, TEM and ¹³C solid state NMR. Results indicate that catalysts were deactivated mainly due to the deposition of metal and carbon. The sources of deactivation were identified along with the location of foreign species by analyzing the deposited species on the spent catalysts. The nature of the coke and its compositions were derived from ¹³C CP/MAS and CP/MAS with dipolar dephasing NMR experiments. The wide range of analysis of spent catalysts specify that the catalyst pores were plugged during the heavy oil processing. The deactivation of catalysts were not only due to the carbon deposition but also due to the deposited metal sulfide (V_xS_y, Ni_xS_y) over the existing (CoMoS) active sites. It appear from the results that considerable amount of deactivation is irreversible and non-regeneratable (i.e., metal deposition). Hence catalyst deactivation during heavy oil hydrotreating (HDT) is a function of metal and carbon deposition during time-on-stream. The metal deposition on spent catalysts, e.g. vanadium is on the surface, while Ni distributed deeper into the pore of the catalysts. The removal of Ni and V showed different behavior, which was attributed to an oxygen atom presence to vanadium and its influence on the vanadium porphyrin structure.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The worldwide crude oil production scenario is changing toward heavier crudes, which is expected to play an increasing role in order to accomplish world demand for hydrocarbon fuels. The heavy oil contain more metals (Ni+V), sulfur, nitrogen and has low API gravity. In order to obtain clean fuel almost all petroleum streams are required to pass through the various catalytic processes where the catalyst decreases their activity with time-on-stream (TOS). Thus, in catalytic processes the key problem is related to the loss of catalyst activity with TOS, i.e. “deactivation”. The deactivation occurrence involved both chemical and physical changes

in the catalyst nature along with the catalytic reaction. Therefore, deactivation is an inevitable phenomenon, but it can be slowed or prevented and some of its consequences can be avoided, if the exact cause of deactivation is known.

Heavy crude oil have complex composition that is delicately balanced system, which depends upon the relationship of the different constituent fractions to each other and the relationships are dictated by molecular interactions. The oil components and their compatibility (physical properties) are the principal cause for the asphaltene instability or coke type species formation. It has also been found that asphaltenes are the most complex molecule present in crude oil or its residues fractions, which chemistry play further role to generate more complex coke-like hydrocarbon (i.e., sediment or coke) during the hydroprocessing reaction. The heavier crude oils contain large amounts of contaminants and produce large fractions of bottom of the barrel (residue) after distillation. Crude quality is vital not just from the refiner's interest for refining yields and environment-friendly products, but also determines the value of a crude oil. Since complex hydrocarbon molecules also contain hetero-atoms (S, N, O, etc.,) that require catalyst in order

* Corresponding author. Current address: Kuwait Institute for Scientific Research (KISR), Petroleum Center, Ahmadi, P.O. Box 24885, Safat 13109, Ahmadi, Kuwait, Kuwait. Tel.: +965 24956890; fax: +965 23980445.

E-mail addresses: mrana@kISR.edu.kw, mohan.rana@gmail.com (M.S. Rana).

¹ Current address: Ashland Specialty Ingredients, Ashland Inc., 500 Hercules Road, Wilmington, DE 19808, USA.

to upgrade or refine the bottoms of barrel or crude oils. The major problems arising for catalytic processes due to the catalyst deactivation, which is mainly classified into three basic types such as mechanical, thermal and chemical [1]. During the hydroprocessing, deactivation is either due to the metal or coke deposition [2–7]. The deactivation at the initial stage in which carbon deposition may occur due to the acid sites while at the later stage deactivation is due to the hard coke or sediments formation [8–13]. In fixed bed units catalyst deactivation during the run is compensated by a progressive increase in bed temperature. Each degree increase in temperature will add on the severity of process condition. Therefore, deactivation is due to three main causes: carbon lay down (step I), slow metal deposition on active phase (step II) and diffusion limitation into the pores (step III). The coke/metal deposition is associated with the loss of activity, due to the decrease in catalytic sites as well as textural properties [14,15].

Since refineries are forced to process crude oil and its residue, more effectively in order to produce clean fuel products and persuade market demand. Processing of these crude oils either with thermal or catalytic processes, have been widely used in the past to convert it into valuable products [5,7]. Thermal processing usually produce low quality distillates, which need further upgrading by hydroprocessing to improve fuel quality. Thus, alternative approach is hydroprocessing which provides a high yield of middle distillate, and produces high-quality (low sulfur, nitrogen) products. Although, hydroprocessing also has some limitations such as catalyst deactivation (metals and coke deposition). Usually, heavy oil feedstock that are rich in asphaltenes, which has stoichiometric relation in the crude and if this ratio changes, asphaltene will get precipitated by itself [14], which leads to catalyst deactivation as well as pressure drop by blocking the reactor and its tubing. Hence deactivation usually correspond to asphaltene instability during the catalytic reaction. However, well deign (mainly large pore diameter) catalyst and moderate conversion can prevent the foresaid problems. In general, deactivation on supported catalysts involve complex physical and chemical occurrences, which varies with the nature and type of foreign species (metal and coke) deposition on the surface of catalyst [8,16,17]. Previous studies have reported that metals removed from residue were deposited on the catalyst in the form of metal sulfides during hydrotreating [18–22].

The consequence of deposited coke and metals on the deactivation pattern are due to different reasons because position of coke and metal deposition on catalysts are different. Thus, it is an important cause to study the deactivation behavior of heavy crude oil hydrotreating catalyst by investigating deposited species, state and distribution of coke and metals on catalyst. The catalysts were tested against the industrial feedstock and spent hydroprocessing catalyst was characterized for physico-chemically techniques. The results of these characterization techniques are discussed in view of the activity and the composition of the fresh catalysts.

2. Experimental

2.1. Catalyst preparation and activity

Prototype alumina support and CoMo/NiMo supported catalysts were prepared. The molybdenum-supported catalysts were prepared by the incipient wetness impregnation method. The promoted (Co and Ni) Mo catalysts were also prepared by using co-impregnation procedure. The final catalysts were dried in the presence of air at 120 °C overnight and calcined at 450 °C for 4 h.

The sulfide catalyst activity tests were carried out in a high pressure fixed-bed up flow reactor. The catalyst was sulfided in situ with a mixture of dimethyldisulfide, straight run gas oil and H₂. The reactor was loaded with oxidic catalyst with 3–5 mm

Table 1
Physico-chemical characterization of feed for different plants.

Properties	Feed pilot-plant	
	Maya crude	HDM (Maya + Diesel, 50/50, w/w)
Elemental analysis		
C (wt.%)	86.9	84.2
H (wt.%)	5.3	8.8
N (wt.%)	0.3	0.184
S (wt.%)	3.52	2.21
Metal (wppm)		
Ni	49.5	26.21
V	273.0	124.78
(Ni + V)	322.5	150.99
Ca	11.26	5.0
Mg	2.04	1.01
Na	44.83	21.2
K	20.25	10.2
Fe	2.16	1.02
Asphaltene (wt.%) (n-C ₇ insol.)	12.7	8.43
Physical properties		
Density, 20/4 °C	0.9251	0.88
Pour point (°C)	−30	−15
Ramscarbon (wt.%)	10.87	5.45
API gravity	21.31	37.09
Catalyst	CoMo/Al ₂ O ₃ (PP)	CoMo/Al ₂ O ₃ (MP), NiMo/Al ₂ O ₃ (MP)

extrudate size diluted with equal volume of SiC. The final temperature of sulfidation was 320 °C, which was stabilized for 5 h at 2.8 MPa. After sulfidation, the flow was switched to feed (Table 1) and the operating conditions were adjusted accordingly. The catalyst activity was measured using a diluted Maya crude with diesel (50/50 wt%) and virgin Maya crude oil feeds at 380 °C and 400 °C temperature, respectively. The properties of the feedstocks are presented in Table 1. The feed and products analysis were analyzed using flame atomic adsorption spectrometry for metals (Ni, V), ultra-violet fluorescence for S while nitrogen was measured by oxidative combustion and chemiluminescence method. Asphaltene is defined as the insoluble fraction in n-pentane. The catalyst tested in micro-flow reactor is indicated with the MP while catalyst tested in pilot-plant is known as PP. The relative activity (R_x) is defined as the ratio of the conversion with time and initial activity at a given time, which can be expressed as: Relative activity (R_x) = X_{TOS}/X_i , where x = HDS, HDM and HDAs conversion, X_{TOS} is a conversion with time-on-stream (TOS) at 0–200 h, while X_i is an initial conversion of HDS, HDM and HDAs.

2.2. Catalyst characterization

Fresh, spent and regenerated catalysts surface areas, total pore volumes and pore size distribution were measured by N₂ adsorption–desorption at −196 °C using a Quantachrome Nova 2000 equipment. The spent catalyst carbon (coke) analysis was carried out with toluene washed samples in a Leco SC-444 instrument using ASTM: C 1408-98 method by direct combustion–infrared detection. The chemical analysis of the fresh and spent catalysts were carried out in order to determine the concentrations of V, Ni, Mo, etc., by using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The surface morphology of catalysts were studied by means of elemental analysis with the SEM-EDS analytical instrument xT Nova NanoLab 200 (FEI Schottky FEG, 30-1 keV). The samples were deposited on a carbon holder and evacuated at high vacuum (10^{−5} Torr) before images were taken. The analysis was made across the radial line of the extrudate in order to obtain metals, sulfur, and carbon distribution profiles.

Download English Version:

<https://daneshyari.com/en/article/54393>

Download Persian Version:

<https://daneshyari.com/article/54393>

[Daneshyari.com](https://daneshyari.com)