Full Length Article

Coking propensity during hydroprocessing of vacuum residues, deasphalted oils, and asphaltenes

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ABSTRACT

Residue hydroprocessing is one of the important processes in refinery to get maximum benefit. Coke deposition on the catalyst and on the interior of parts of the unit is a major challenge to process the residue having high concentration of metals and micro carbon residues. In this regard, three vacuum residues of different refineries are used to study the hydroprocessing activities on $NiMo/Al_2O_3$ catalyst. Asphaltenes and deasphalted oils are extracted and their hydroprocessing activities are compared with that of vacuum residues. It is noticed that the hydrocracking activity of the deasphalted oil is easier than that of the respective vacuum residue. The result also shows that the hydrocracking of asphaltene is very difficult particularly at low temperature like 410 °C. However, this temperature is sufficient for coke formation by free radical mechanism. It is also observed that the deasphalted oils also yield coke though the feeds do not content asphaltene. It suggests that resin and aromatic hydrocarbons contribute microcarbon residue and hence finally to coke formation. Microcarbon residue of a feed is a very important factor to determine the coking tendency of a feed. The combustion property of coke measured by TGA shows that the cokes deposited on spent catalysts have similar combustion property irrespective of the origin: whether it is from aromatic, resin or asphaltene.

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1. Introduction

Residue hydroprocessing is one of the important processes in refinery to get maximum benefit. In this process, residue is converted to more valuable products like transportation fuels. In early days, the residues produced by refinery were used as fuel oil or as bitumen for road construction. The price of these two materials (fuel oil or bitumen) is very low compared to the price of transportation fuels. However, the hydroprocessing of residue is not a simple process due to rapid coke deposition on the catalyst. The rate of coking increases with increasing molecular weight or boiling point of the feed. The feed containing high aromatic and heterocyclic hydrocarbons shows higher coking tendency. It is believed that due to the higher interaction of aromatic hydrocarbons with catalyst surface facilitates conversion of these aromatic molecules to higher molecular weight compounds [1,2]. These molecules are further converted to coke if sufficient active hydrogen is not available into the reaction mixture. Residue contains saturates, aromatics, resin and asphaltene. It is an established fact that coking tendency of asphaltene is much higher than that of resin [3]. Coking process increases with increasing concentration of asphaltene

in a feed [4]. It was reported that the rate of catalyst deactivation depends upon quality of asphaltene rather than quantity [5]. Asphaltene in a residue is dissolved into the resin and aromatic hydrocarbons. Asphaltene may come out as sediment from the oil-asphaltene matrix if colloid stability is disturbed during hydroprocessing reaction. Therefore, resin plays an important role to stabilize the asphaltene or to minimize the sediment formation in a residue during reaction [6]. The conversion of resin and asphaltene with similar rate is always expected for the smooth running of the hydroprocessing unit. The catalyst deactivation during hydroprocessing of Maya heavy crude, extra heavy crude and their residues was elaborately studied by Ancheyta and his group [7–12]. The HDM and HDS activities of both spent and regenerated catalysts have been compared with that of fresh catalysts. It was concluded that coke and metals contributed to the loss of HDM activity, whereas the loss of HDS activity occurred by metals deposit [7]. The structural change during hydrotreating of Maya heavy crude was studied at different temperature [8]. It was noticed that a drastic structural changes of asphaltene occurred at temperature of 440 °C. It was also reported that aromaticity of asphaltene increased with increasing reaction temperature. It was noticed that both the amount of asphaltene and its properties were responsible for the catalyst deactivation [12]. Zeuthen et al. [13] reported that upto 4 wt% of coke deposition on the catalysts

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did not affect the HDS activity; however, this activity decreased with further increase of coke deposition. Diez et al. [14] reported that HDS, HYD and HDN activities decreased to around 20% with a coke deposit of 3 wt% and then the same activities decreased to 75% with the 10.6 wt% of coke deposit. The effect of feed properties on the deactivation was also reported [15]. Around 23 wt% of hydrogenation activity was lost when the NiMo/Al$_2$O$_3$ catalyst was treated with a feed of having −290 °C. But no loss of HDS activity was observed. When the same catalyst was treated with a feed having −454 °C material, 82% of hydrogenation and 70% of HDS activities were lost.

The degree of deactivation does not always depend on the amount of metals present in the feed [16]. It also depends on the nature of metals. The metals in asphaltene part have more severe effect on the deactivation than the metals in resin part. It was reported by author that the heavy crude oil having very low concentration of asphaltene can also deactivate the catalyst. It was found that the wax materials consisting of paraffinic/naphthene or aromatic substituted paraffinic chains yielded the coke deposit on the catalyst surface. The thermal and catalytic conversions of asphaltene were extensively studied by Zhao et al. [17–19]. More liquid yield and less coke were formed during hydrocracking of residue than that by thermal cracking. It was also reported that at low reaction temperature mostly C-S bond breaking dominated and hence more gas and liquid were produced whereas more coke was yielded at higher reaction temperature. Sun et al. [20] reported that asphaltene having higher sulphur content was easily converted than those with lower content of sulphur. It was mentioned that it was due to weaker C-S bond compared with C-C bond. And therefore, the asphaltene having higher concentration of sulphur was easy to convert into lighter hydrocarbons. The hydrotreating of asphaltene was carried out using decaline as solvent and it was observed that with increasing reaction severity more gas, gasoline and coke [21] were produced. Thermal cracking of asphaltene at 440 °C in presence of different solvents was studied by Raimi et al. [22] and it was observed that the amount of coke deposit depends on the type of solvent and concentration of asphaltene. Usui et al. [23] had drawn a correlation between molecular weight of asphaltene with its conversion. It was noticed that the hydrocracking activity of asphaltene decreased with the increasing molecular weight of asphaltene as well as nitrogen content in asphaltene.

A large number of literatures regarding the catalyst deactivation during hydrotreating of residue and asphaltene have been discussed. However, a comparison of hydroprocessing activities of residue, deasphalted oil and asphaltene in one place is rare in the literature. Therefore, in this study, three different residues were used to extract DAO(s) and asphaltenes. Their hydroprocessing activities on NiMo/Al$_2$O$_3$ catalyst were compared with that of whole residue. Three vacuum residues were collected from three different refineries so that the deactivation or coking tendency can be investigated depending on the nature of the feeds.

2. Experimental

In this work, to understand the role of asphaltene in hydrocracking of residue, high asphaltene containing vacuum residues were used to separate deasphalted oil and asphaltenes. The hydrocracking of VR, DAO and asphaltenes were carried out with same catalytic reaction conditions.

2.1. Catalyst synthesis and characterisation

One NiMo catalyst was prepared by sequential incipient wetness technique. An appropriate amount of ammonium hepta-

molybdate (AHM, Aldrich) salt was dissolved into distilled water. The solution was impregnated on the dry support and the impregnated samples were allowed to stay overnight at room temperature and then dried for 7 h at 120 °C and calcined at 450 °C for 3 h. Nickel promoter was also impregnated over the Mo-loaded catalysts and dried and calcined in a similar procedure as mentioned above. Final catalyst contains 10 wt% of MoO$_3$ and 3 wt% of NiO as on catalyst basis. Gamma alumina was used as support and the physical properties of this support are: – surface area 259 m^2/g, pore volume 0.91 cm^3/g and average pore diameter 13.98 nm. BET specific surface area and pore size distribution of supported NiMo/Al$_2$O$_3$ catalyst was measured by nitrogen adsorption-desorption analysis at 77 K (BEL MAXSORP). Prior to the analysis, the samples were degassed for 2 h at 300 °C. X-ray diffractogram of catalyst was recorded on a Bruker AXZ GMBH using a Cu Kα radiation (k = 0.15418 nm).

2.2. Preparation of feeds (deasphalted oil and asphaltene)

Three different vacuum residues (VR-1, VR-2 and VR-3) were used to study the hydroprocessing activity on NiMo/Al$_2$O$_3$ catalyst. Asphaltene was extracted from these residues by using n-heptane as solvent. Initially, 300 g of residue was dissolved in 1.5 litres of n-heptane and the mixture was heated to 80–90 °C for a period of 1.5 h with continuous stirring. After the reaction, the mixture was kept in a dark place for 2 days and then filtered. The asphaltene part was then dried and used for physical characterization and catalyst activity test. An appropriate amount of asphaltene (equivalent amount of 200 g of vacuum residue) was dissolved in toluene to make the feedstock. From the liquid refinate, the solvent (n-heptane) was removed. The deasphalted oils obtained from VR-1, VR-2 and VR-3 are named as DAO-1, DAO-2 and DAO-3 respectively. Similarly the asphaltene extracted from these three residues are designated as ASP-1, ASP-2 and ASP-3.

2.3. Activation of catalyst

To evaluate the catalytic behaviour with different industrial feedstocks, the catalyst was tested in the high pressure batch reactor. Five grams of a fresh catalyst was sulfided ex-situ for each experiment. An atmospheric unit was used for this sulfidation. In this unit, hydrogen was passed through a container having CS$_2$, and then the saturated mixture of CS$_2$ and hydrogen was passed through the reactor. The sulfiding conditions are as follows: – temperature-400 °C, pressure –atmospheric and duration of sulfidation-4 h.

2.4. Catalyst activity test

For each experiment, 200 g of feed was taken into the reactor vessel (1 L capacity). The sulfided catalyst was transferred into the reactor in nitrogen atmosphere very quickly so that catalyst would not come in contact with air for long time. The reactor vessel was sealed properly and checked for leakage. The reactor vessel was then purged two/three times with hydrogen gas so that there was no air left inside the reactor. An appropriate amount of hydrogen was added into the reactor so that the final pressure can reached to 100 kg/cm^2 at reaction temperature. Heating was started from room temperature to the required temperature at the rate of 3 K/min. Stirring was started when temperature reached the set point (reaction temperature) and the time was noted as the beginning of the reaction at this point. Hydrotreated products were collected at end of the reaction. Catalyst was separated from products after reaction and metals and sulfur contents of the products were analyzed. The experimental conditions used for batch reactor are: reaction temperature, 410 °C; reaction pressure, 100 kg/cm^2; total reaction time, 4 h and stirring rate, 750 rpm. A systematic