



Deactivation of hydrotreating catalyst by metals in resin and asphaltene parts of heavy oil and residues



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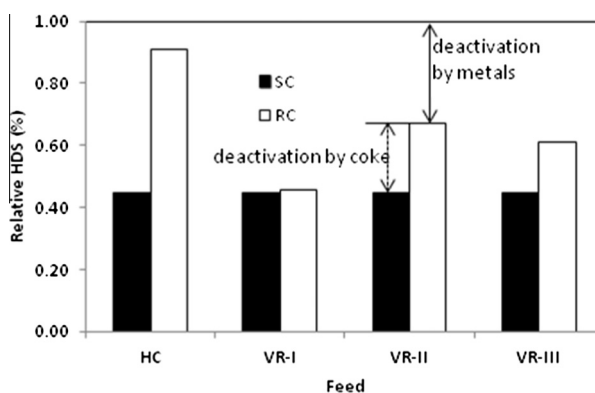
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HIGHLIGHTS

- Deactivation by metals in resin is less adverse than that in asphaltene.
- Nickel deactivates HDS active sites to a lesser extent than that done by vanadium.
- The feed having high concentration of wax materials can deactivate a catalyst rapidly.

GRAPHICAL ABSTRACT

Comparison of HDS activity of spent (SC) and regenerated (RC) catalysts using LCO as feed.



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ABSTRACT

The degree of deactivation was studied on the hydrotreating catalyst by using four different feed stocks. This work demonstrated that the deactivation by metals in resin and asphaltene parts of the heavy crude oil and residues was different. The degree of deactivation by metals does not always depend on the concentration of these, but also the nature of the metals. Firstly, the metals in resin part may not have as adverse effect on deactivation as the metals in asphaltene part have. It may possible that these metals in resin may deposit on the bare alumina surface, not on the active sites. Secondly, the nickel containing compounds in the feed deactivate the HDS active sites in lesser extent than that done by vanadium compounds. The deactivation by heavy crude having high concentration of wax materials suggests that long paraffinic or naphthene/aromatic substituted paraffinic chains may take part in coke formation during hydroprocessing reaction conditions. This coke mostly covers the HDS active sites of the catalyst; but does not precipitate as solid coke. The formation of solid coke is observed for the feeds having high percentage of asphaltene content.

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1. Introduction

Residue conversion is becoming one of the important process in the refinery. It becomes more essential when most of the refinery

goes for zero fuel oil configuration. Hydroprocessing of residues or heavy oils is used to upgrade residues or heavy oils to the more valuable products. However, the catalytic process i.e. hydroprocessing of residue is not a simple process like hydroprocessing of lighter fractions. Residues and heavy oils contain high concentration of contaminants and these contaminants have an adverse

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effect on catalyst. These heavy ends have a high percentage of asphaltene. During hydroprocessing reactions at high temperature, mostly these asphaltene molecules are converted into coke [1–3]. Moreover, residue and heavy oils also consist of metals, mainly vanadium and nickel. These metals also deactivate the catalyst in due course of the reaction. Furthermore, the deactivation by metals is irreversible. It is reported in literature that the deactivation of catalyst depends on the metal content in the feeds. The catalyst is more rapidly deactivated by the feed containing more metals compared to the feed containing less metal [4–6].

In the recent past, the study on deactivation by coke and metals during hydroprocessing of heavy crude and residue became an important topic for researchers. In this context, the catalyst deactivation during hydrotreating of Maya heavy crude was extensively studied by Maity et al. [7–10]. The results of activities of spent and regenerated catalysts were compared and it was established that both coke and metals contributed to the loss of HDM activity, whereas the loss of HDS activity only occurred by metals deposition. It was also said that the mechanism for metal and sulfur removal did not follow the same course. It is well understood from the literature that the principle cause for initial deactivation of the hydrotreating catalyst is rapid coke deposition and deactivation by metals becomes prominent at the later stage of the reaction. It was reported by Zeuthen et al. [11] that the HDS activity of benzothiophene was unchanged up to 4 wt% of coke deposition. The same HDS activity was then drastically decreasing with further increase of coke deposits. Gualda and Katsztelan [5] reported that deactivation by metals was prominent even at the initial stage of operation. The degree of deactivation depends on the properties of feed, operating conditions and the type of catalyst used for this reaction. Maity et al. [9] reported that alumina supported catalyst was deactivated faster by coke deposition whereas both metal sulfides and coke deposits were responsible for deactivation of alumina–titania and alumina–silica supported CoMo catalysts.

To better understand the deactivation process, the activity of a spent catalyst was also studied by investigators. The spent catalyst deactivated by coke deposit can be reused by decoking of the spent catalyst. However, the metal deposition on a spent catalyst is an irreversible process and the spent catalyst in general is not used, particularly after processing of a feed having high concentration of metals. But the usefulness of the spent catalyst having high contaminants from the feed was reported by some researchers [12]. If the spent catalyst was decoked and mixed with the fresh boehmite, this mixed catalyst showed not only high HDS activity, but also showed good HDM activity [12]. Some researcher also assumed that at high concentration of V in spent catalyst, V–Mo–S phase was formed and it governed the catalyst activity [13].

The effect of vanadium poisoning on thiophene HDS activity was studied by Ledoux and Hantzer [14]. A series of catalysts were prepared by wetness impregnation of a water solution of ammonium vanadate. The oxide form of NiMo catalysts was used for the impregnation of vanadate. In this method authors only impregnated around maximum 10 wt% of vanadium. It was reported that HDS activity decreased with increasing concentration of vanadium on the catalyst. The fresh catalyst (0 wt% V) had very high HDS activity. In impregnation of only 0.87 wt% of V, HDS activity drastically decreased to almost less than a half. Different percentage of vanadium was impregnated into the hydrotreating catalysts and their HDM and HDS activities were studied by using Maya crude as feed [8]. It was noticed that the rate of HDS deactivation was faster than that of HDM activity. It was concluded that the faster deactivation of HDS activity was due to the coverage of active sites by impregnated vanadium. Koyama et al. [15] also reported the adverse effect of metal deposit on the hydrotreating catalyst. The relative HDS activities of dibenzothiophene were investigated on the spent and regenerated catalysts. It was found that the

relative HDS activity of a regenerated catalyst was very low even when metals deposit on the catalyst below 7 wt%.

The activity of a spent catalyst can also regain to some extent by leaching out the deposited metals from the spent catalyst. Oxalic acid in the presence of H_2O_2 was found to be the best leaching agent where the spent catalyst (after removal of metals by leaching) showed almost the same HDS activity as a fresh catalyst did [16].

The activity studies on the spent catalyst can give better idea how the catalyst is deactivated during hydroprocessing of heavy oil and residue. Though there are several studies on the deactivation, however activity studies on the spent catalyst is very limited in the literature. Therefore in this investigation different feeds are used to obtain the spent catalysts. The hydrodesulfurization activity of light cyclic oil (LCO) on these spent catalysts was investigated. The same HDS activity was also compared with the regenerated and fresh catalysts. The basic idea of this work is to investigate the effect of metals as a whole and the nature of metals on the catalyst deactivation.

2. Experimental

2.1. Preparation of catalyst

The NiMo catalyst supported on commercial alumina was prepared by the sequential incipient wetness impregnation method. An appropriate amount of ammonium heptamolybdate (Alfa Aesar) and nickel nitrate (Alfa Aesar) salts were used to prepare aqueous solutions. The prepared solutions were impregnated into the dry support. The molybdenum/nickel promoted catalysts were dried in the presence of air at 110 °C for 6 h and calcined at 450 °C for 4 h. This catalyst contains 10 wt% of MoO_3 and 3 wt% of NiO on the catalyst basis.

2.2. Characterisation of fresh and spent catalysts

BET specific surface area, pore volume and pore size distribution of support and supported catalyst were measured by nitrogen adsorption–desorption analysis at 77K (BEL MAXSORP). Prior to the analysis, the samples were degassed for 2 h at 300 °C.

TPR analysis (Micromeritics 2920) was carried out using 10% H_2 in argon. Reducing gas mixture was purified by molecular sieves. Before each run, the baseline was stabilized at room temperature by passing gas mixture at a flow of 25 mL/min. After stabilization the sample was heated at 10 °C/min from room temperature to 1000 °C.

X-ray diffractogram of the fresh catalyst $\text{NiMo}/\text{Al}_2\text{O}_3$ were recorded on a Bruker AXZ GMBH using a $\text{Cu K}\alpha$ radiation ($k = 0.15418$ nm).

Weight loss due to combustion of the spent catalysts has been measured by thermogravimetric (Perkin Elmer TGA4000) analysis. For this analysis, 10 mg of the sample was placed in a platinum crucible and heated from ambient temperature to 900 °C at a rate of 10 °C/min in the presence of air (flow rate 50 mL/min). The surface morphology and composition of the spent catalysts were also studied by SEM-EDX (Quanta200F).

2.3. Catalyst activation and activity studies

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 with hydrogen was passed

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