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Study of accelerated deactivation of hydrotreating catalysts by vanadium impregnation method

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Abstract

The main causes of catalysts deactivation for hydrotreating are coking and metals deposition. In this present work, accelerated deactivation of hydrotreating catalysts was studied. In this respect, vanadium which is deposited with nickel during hydrotreating reaction was impregnated into the fresh hydrotreating catalyst. Different percentage of vanadium was impregnated and their hydrodemetalization (HDM) and hydrodesulfurization (HDS) activities were studied in bench-scale reactor of heavy crude oil. Accelerated deactivations for both HDM and HDS were observed on vanadium impregnated catalysts. The rate of HDS deactivation was faster than that of HDM reaction. The rapid deactivation of HDS may be due to the coverage of active sites by impregnated vanadium atom. The deactivation is slower when the V loading is low; but above 10 wt% loading a rapid deactivation is observed. A comparison of deactivation is made in between normal deactivation and the deactivation by vanadium impregnation. It was found that deactivation by vanadium impregnation is lower than that of normal deactivation. It suggests that at initial stage the formation of coke causes deactivation of the catalyst whereas at later stage when metals sulfides deposition is quite high, these sulfides take part in deactivation.

Keywords: Accelerated deactivation; Heavy crude oil; Vanadium; HDS; HDM

1. Introduction

Deactivation of hydroprocessing catalysts occurs time-on-stream. Activity changes rapidly during first few hours of run and then activity becomes stable. It is generally practiced in refinery that catalyst is allowed to deactivate to a certain level and then the reaction temperature is increased to compensate activity [1–3]. The principal causes of catalyst deactivation are deposition of carbonaceous species (coke) [4,5] and formation of metal sulfide on the catalyst [6]. Coke is deposited very rapidly within a few hours of run and then gets a steady-state in later stage of run. Whereas coke deposition under sufficient high hydrogen pressure reaches a steady-state level, the amount of metal deposited on the catalyst does not reach a steady-state. It is continuously deposited on the catalyst during run [7].

The presence of vanadium and nickel is of particular concern because of the poisoning effect during the hydrodesulfurization and cracking of the feeds. The metals are usually distributed between porphyrin and nonpophyrin type of structures [8–11]. These metal containing compounds are deposited on the catalyst during hydrotreating. These metals compounds are accumulated as metal sulfides into the pore mouth or into the pore cavity depending on the pore diameter of the catalyst. These sulfides can block the way to the entrance of reactants or cover the active sites and it causes deactivation of catalyst.

Aldag [12] has studied the aging test of the hydrotreating catalyst by using Hondo and Maya heavy hydrocarbon fractions. The catalyst was exposed to the mentioned heavy oil for several days so that the metals contained in the feeds were deposited into the catalyst. The author observed normal deactivation of exposed catalyst and it was concluded that accelerated deactivation of HDS was not possible by using such type of heavy crude for aging catalyst. If the catalyst was first impregnated by metals (nickel and/or vanadium) the accelerated HDS deactivation was possible. It was also noted that the Hondo heavy crude was more suitable for simulation of HDM activity compared to Maya crude.

The effect of vanadium poisoning on thiophene HDS activity was studied by Ledoux and Hantzer [13]. A series of catalysts were prepared by wetness impregnation of a water

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solution of ammonium vanadate. The oxide form of NiMo catalysts was used for the impregnation of vanadate. The maximum of vanadium used in this study was about 10 wt%. The thiophene hydrodesulfurization activity of these impregnated catalysts was studied. It was observed that HDS activity decreases with increasing concentration of vanadium on catalyst. The fresh catalyst (0 wt% V) has very high HDS activity. Addition of 0.87 wt% of V, causes a drastically decreases in the HDS activity.

The studies of accelerated deactivation on hydrotreating catalysts are very rare in the literature. Therefore, in this present work, the accelerated deactivation was performed on different hydrotreating catalysts, prepared by impregnating of vanadium salt. Their hydrotreating activities were measured using heavy crude oil as reactant.

2. Experimental

2.1. Preparation of vanadium solution

The solubility of the vanadium compounds is very low. To make a vanadium solution, severe conditions were used. Vanadium pentoxide was dissolved in concentrated HCL at 150 °C and 26 kg/cm^2. Even at these conditions a solution of a maximum 10 wt% of vanadium (on catalyst weight basis) can be prepared. The required amount of vanadium pentoxide was dissolved into the predetermined HCl solution which is measured by just pore filling of catalyst. The micro-oven of atomic absorption unit was used to reach the above said temperature and pressure. At first, the vanadium solution was kept one week to confirm that there was no precipitation of vanadium species in the solution.

2.2. Preparation of catalysts

The catalysts were prepared by impregnation of the vanadium solution on a hydrotreating catalyst (10.7 wt% of MoO_3, 2.88 wt% of NiO and 3.73 wt% of TiO_2 and gamma alumina). To impregnate more than 10 wt% vanadium, multiple impregnations technique were performed. Once the first 10 wt% V was impregnated, the sample was dried at 120 °C for 7 h following a second impregnation. In the end, all impregnated samples were dried at 120 °C for 12 h and then calcined at 500 °C for 5 h.

2.3. Characterization of catalysts

BET specific surface area, pore volume and pore size distribution of the catalysts were measured by nitrogen adsorption at 77 K (Quantachrome Nova 2000). The transversal concentration of vanadium in the catalysts was measured by scanning electron microscope, model XL30 ESEM, Philips. X-ray diffractograms were recorded on a SIEMENS D-500 model using a Cu Kα radiation.

2.4. Presulfiding of catalyst

Oxide catalyst was sulfided *in situ* before the run. Hundred milliliter of oxide catalyst was loaded into the reactor and treated in a flow of hydrogen for 2 h at atmospheric pressure at

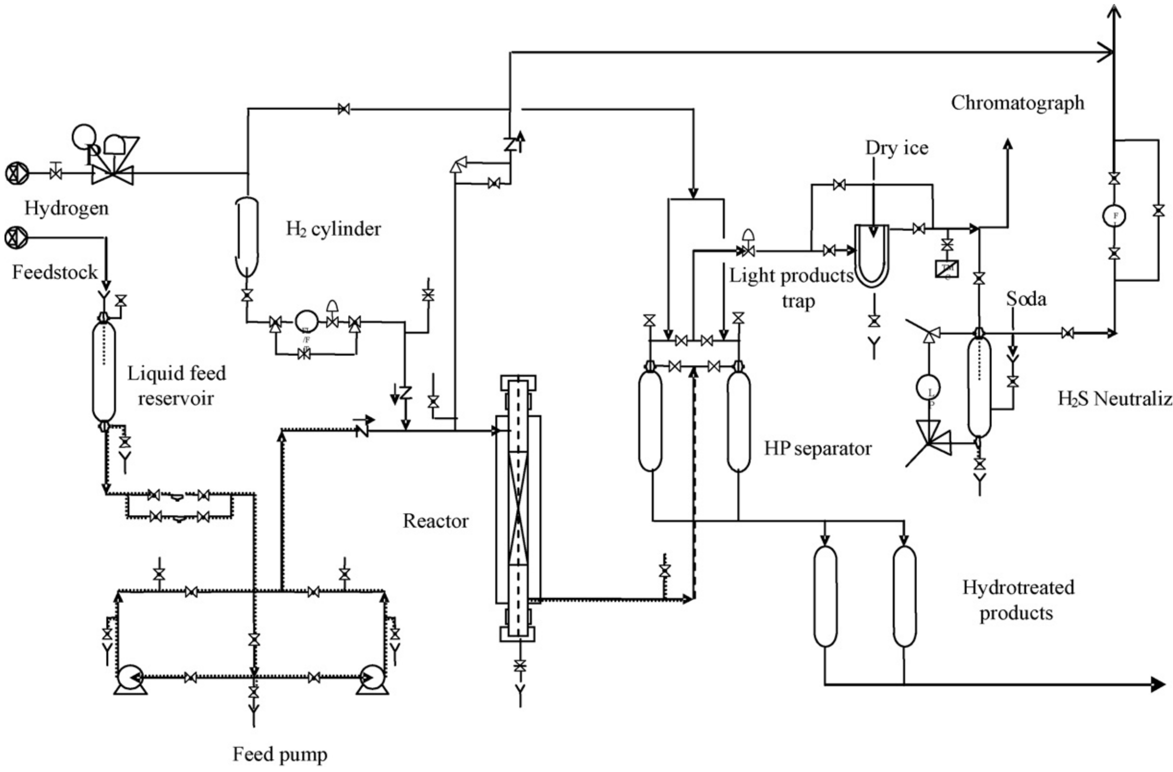

Fig. 1. Flow diagram of a bench-scale reactor.

Table 1
Characteristics of feed

Properties	Value
Specific gravity at 20/4 °C	0.9787
API gravity	12.67
Ramsbottom carbon (wt%)	15.99
Conradson carbon (wt%)	16.25
Sulfur (wt%)	5.25
Nitrogen (wppm)	4890
Asphaltene in $n\mathrm{C}_7$ (wt%)	21.83
Vanadium (wppm)	448.34
Nickel (wppm)	87.11

120 °C. After drying, catalyst was allowed for soaking during 2 h at 150 °C. Light gas oil (LGO) was used for soaking. This LGO contains 1.7 wt% of sulfur. After soaking LGO with dimethyl disulfide (DMDS, 1 wt%) was introduced in the system as a sulfiding agent. Sulfidation was performed at 28 kg/cm^2 at 260 °C for 3 h and finally at 320 °C for 10 h.

2.5. Catalyst activity test

Catalyst tests were performed in a fixed-bed bench-scale reactor in down flow mode. The flow diagram of this unit is given in Fig. 1. The experimental conditions employed for catalysts test are: pressure, 100 kg/cm^2; temperature, 400 °C; LHSV, 1.0 h^{-1}; and H_2/HC, 356 m^3/m^3. Heavy crude was used as a feed and the characteristics of this feed are given in Table 1.

2.6. Analysis of feed and products

The total metals in the feed and products were measured by atomic absorption (Thermoelectron model Solaar AA). Sulfur was analyzed by X-ray fluorescence (HORIBA model SLFA-2100).

3. Results and discussion

3.1. Characterization of catalysts

A reference catalyst (BET specific surface area, 138 m^2/g, total pore volume 0.53 ml/g and average pore diameter, 155 Å) was used for impregnation of vanadium compound. Several vanadium containing catalysts were prepared and the percentage of the vanadium contained is given in Table 2. The percentage of V in the catalyst was measured by atomic absorption unit. The pore size distributions of the reference catalyst and vanadium impregnated catalysts are presented in Fig. 2. It shows that the reference catalyst has wide range of pore. Total pore volume and pore size distribution of vanadium containing catalysts decrease with increasing V loading into the catalyst. It is also observed from the figure that the pore volume in micropore region decreases with increasing V loading. In Table 3, the pore volume having different pore diameter is calculated. It is clearly noted from the table that the pore volume of pores having diameter below 100 Å decreases with increasing concentration of vanadium into the catalyst.

Table 2
Percentage of vanadium loading

Catalysts	V loading (wt%)
V0	0
V5	4.46
V8	8.43
V9	9.3
V12	11.69
V15	15.07

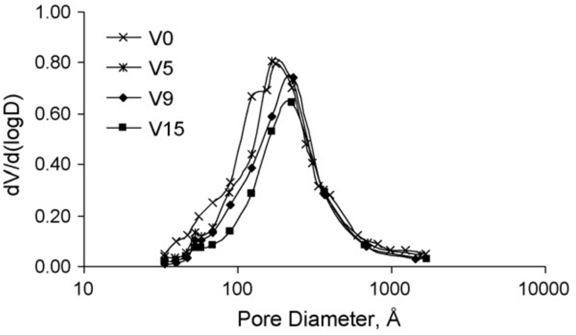

Fig. 2. Pore size distribution of vanadium free and vanadium loaded catalysts.

Table 3
Pore size distribution (PSD) of vanadium free and vanadium loaded catalysts

PSD (vol%)	Catalyst			
	V0	V5	V9	V15
>1000	1.17	2.1	1.54	2.82
1000–500	6.06	5.09	4.36	5.1
500–200	28.96	29.66	32.69	36
200–100	37.7	42.82	42.65	41.01
<100	26.11	23.07	18.76	15.07

The transversal mapping of V15 catalyst is measured by SEM and is presented in Fig. 3. It shows that the vanadium pentoxide which is used for vanadium impregnation deeply enters into the catalyst pore cavity and it is distributed homogeneously. The vanadium concentrations (transversal) of different catalysts are also measured and results are given in

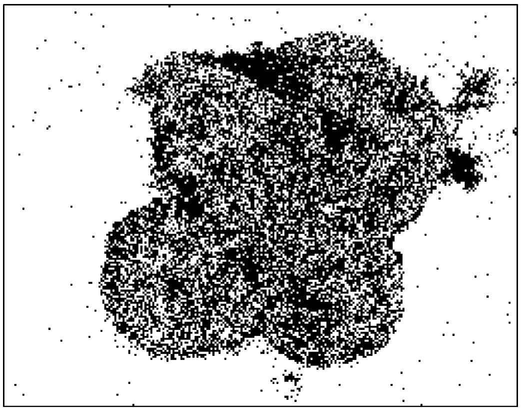

Fig. 3. SEM transversal vanadium distribution of V15 catalyst.

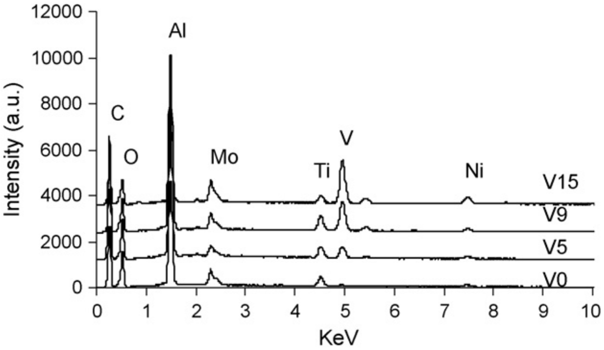

Fig. 4. Transversal vanadium concentration of V free and V loaded catalyst.

Fig. 4. It also shows that vanadium concentration increases with increasing vanadium loading. Both SEM and pore size distribution results indicate that the vanadium pentoxide enters deeply into the catalyst pore and mainly micropores of the catalysts are covered by impregnated vanadium. In our earlier studies [14], it was also observed that the vanadium sulfides deposited from feed was generally distributed through out the catalyst particle. Depending on the pore diameter of the catalyst, profiles of vanadium-deposition are of two types, it is either U shape or M shape. In U shape more vanadium atoms are concentrated into the periphery of catalyst particle and in M shape comparatively vanadium atoms are distributed all over the particle. The U shape profile is found when the pore diameter of the catalyst is narrow whereas M shape profile is observed if the pore diameter is bigger. In this case, average pore diameter of the catalyst is around 155 Å which is quite large and therefore, vanadium pentoxide is distributed all over the catalyst particle.

X-ray diffractograms of vanadium free and vanadium loaded catalysts are presented in Fig. 5. The most of the vanadium oxide peaks appear at 2θ of 20–30°. However, the most of XRD peaks are observed in this region on V0 (vanadium free) catalyst. Therefore, XRD peaks of vanadium containing catalysts appeared in this region is difficult to distinguish from vanadium free catalyst. However, we have seen a distinct peak hump in the 2θ of 25–26° in the 15 wt% vanadium loaded catalyst. These peaks may be due to the presence of crystalline vanadium pentoxide or aluminum vanadium oxide ($AlVO_4$). The formation of crystalline vanadium pentoxide is less probable since the more intensity peak at 2θ of 20.16 is not found. Therefore, at higher loading, vanadium may interact with bare surface of alumina and forms aluminum vanadium oxide. It is also confirmed that the average peak intensity of alumina is reduced on the catalyst having 15 wt% vanadium. It may be concluded that at higher loading vanadium dispersed all over the alumina surface and some of the dispersed vanadium interact strongly with surface alumina during calcinations and as a result formation of $AlVO_4$ is observed.

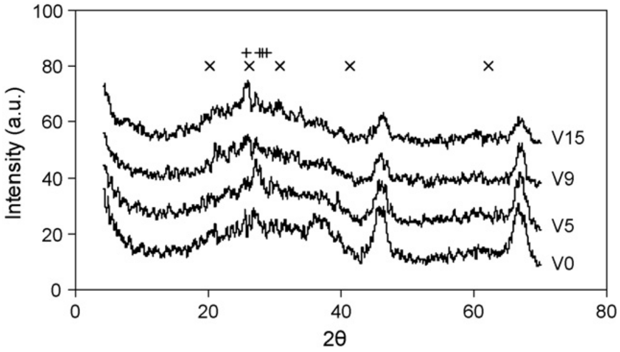

Fig. 5. X-ray diffractograms of vanadium free and vanadium loaded catalysts (×, V_2O_5; +, $AlVO_4$).

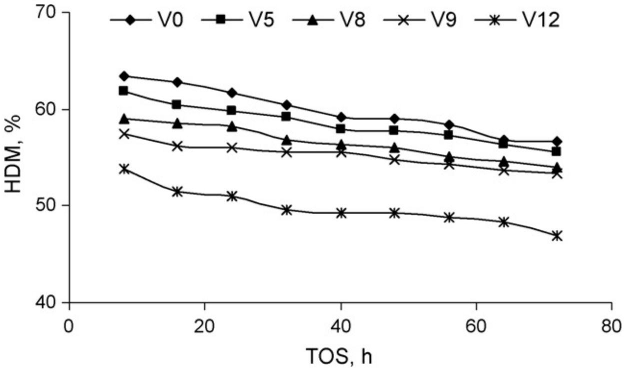

Fig. 6. Hydrodemetalization of different catalysts with time-on-stream.

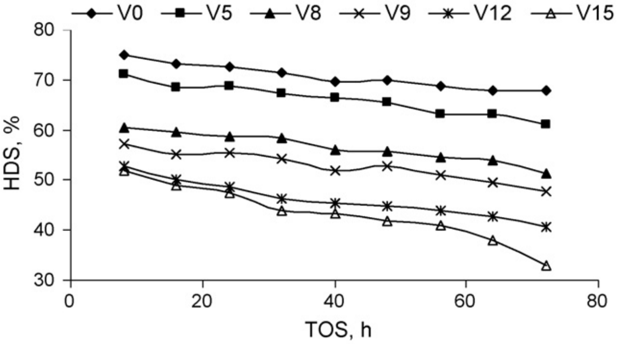

Fig. 7. Hydrodesulfurization of different catalysts with time-on-stream.

3.2. Activities study

The catalyst activity is studied on vanadium loaded catalysts in bench-scale reactor. Hydrodemetalization (HDM) and hydrodesulfurization (HDS) of fresh catalyst and vanadium loaded catalysts were studied with time-on-stream (TOS) and the results are given in Figs. 6 and 7, respectively.

In Fig. 6, the percentage of HDM activities of reference catalyst as well as V loaded catalysts are presented against TOS. The figure shows that HDM activity of fresh catalyst (V0) is higher than those of V containing catalysts. It is also noticed that with increasing V loading HDM activity decreases. It also reveals that the activity decreases with TOS which may be caused by coke and metals deposition on the catalyst-pore-mouth or pore plugging.

The HDS activities of the fresh and V loaded catalysts are presented in Fig. 7. It shows that HDS activity has also similar

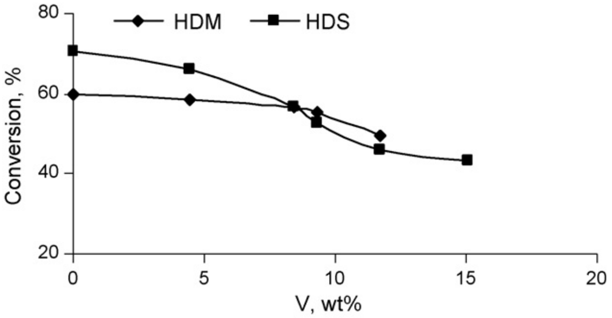

Fig. 8. Effect of vanadium loading on HDM and HDS activities.

trend as HDM does. It means that HDS activity decreases with increasing concentration of vanadium compound in the catalysts.

To see more inside to the deactivation due to vanadium metal, time weight mean conversion (TWMC) of HDM and HDS reactions are calculated according to the following equation:

$$\text{TWMC} = \frac{\sum_{i=1}^{N} x_i t_i}{\sum_{i=1}^{N} t_i}$$

where x is the conversion, t is the time (duration of balance), and N is the number of balances. Although initial conversions of the catalysts are high, they decrease with time. Therefore, TWMC is more appropriate to discuss these results, since it takes an account of the time factor into the conversion. This approach has two benefits: it allows the averaging of variable data over a number of balances to obtain a more real performance, and it gives less weight to the initial conversion.

The TWMC(s) are plotted against the weight percentage of vanadium contained in the catalysts in Fig. 8. This figure shows that both HDM and HDS activities decrease with increasing V loading. Therefore, it is indeed that vanadium causes deactivation of hydrotreating catalysts. However, the loss of HDM and HDS activities is not same with the impregnation at the same amount of vanadium. It is found that the loss of HDS activity due to impregnation of V is more rapid compared with that of HDM activity. The loss of HDM and HDS activities is also slow at lower loading of V, but it becomes rapid above 10 wt% loading.

During hydrotreating vanadium and nickel sulfides are deposited with coke into the catalyst. Vanadium can decorate the edge of a molybdenum disulfide slab just as nickel or cobalt does. However, vanadium displaces nickel from the edge sites on the molybdenum slab and then becomes a source of deactivation since promotion by vanadium is less than by nickel. Moreover at higher concentration, the vanadium sulfides grow and these may cover the edge sites instead of edge decoration. Hence rapid fall of activities are observed. From our characterization techniques we have observed that the impregnated vanadium pentoxide enters into the pore interior of the catalyst. During sulfidation, these oxides are converted into the sulfides. These sulfides can block the pore or cover the active sites as explained above. In this study as well as in our earlier study [14] we have observed that metal deposition has more adverse effect on HDS than on HDM. It indicates that the mechanism of removal of metals and sulfur from heavy crude oil is not similar in manner. In general, metal containing compounds are bigger in size, whereas sulfur compounds in heavy crude are of two types: one attached with asphaltene structure and the other like benzo-thiophene structure. Therefore, removal of sulfur compounds from heavy crude not only depends on pore size of the catalyst but also active sites. The vanadium sulfide may cover the active sites so that it hinders direct interaction of sulfur compounds with active sites.

A comparison was also made in between the normal deactivation with TOS and accelerated deactivation by V impregnation. Around 10.5% loss of HDM activity occurs at 72 h of TOS in normal deactivation (V0 catalyst in Fig. 6). During this period, maximum 2 wt% of metals (calculated from metal on catalyst (MOC) value) can be deposited. On the other hand, by impregnation of 4.5 wt% V, only around 2.2% loss of HDM activity (in Fig. 8, comparison of TWMC of the catalysts V0 and V5) is observed. In the case of HDS reaction, loss of activity is around 9.5% and 6.4% by normal and accelerated deactivation, respectively. So in both cases, we have observed that normal deactivation is rapid though the metals deposition in normal deactivation is almost half of the accelerated deactivation by V. It suggests that the deactivation by coke is also quite important when catalyst is treated with heavy crude oils in normal deactivation. In normal deactivation carbon is deposited very rapidly within a few hours of run and then it gets a steady-state. But, metals are progressively deposited throughout the hydrotreating process. In this study, it was also observed that at initial when the metal loading is low, the deactivation by V impregnation is slow, but above certain concentration of V rapid deactivation occurs in both HDM and HDS reactions.

4. Conclusions

The hydrotreating catalysts for heavy crude oils are deactivated by coke and metal sulfides deposition and there are several research papers on this subject. However, accelerated deactivation by vanadium loaded catalysts is very rare in the literature. The main objective of this investigation is to study the deactivation caused by vanadium loaded catalyst. Both HDS and HDM activities were decreased with increasing V loading. It was found that at lower V loading decreasing trend is slower compared with at higher vanadium loading. Deactivation of HDS activity by V impregnation was faster than that of HDM activity. It may be due to the fact that vanadium atom enters into the pore and covers active sites. It was also observed that the deactivation by vanadium impregnation is lower than that of normal deactivation with time-on-stream at least at initial stage. Therefore, it suggests that at initial stage the formation of coke causes deactivation of the catalyst whereas at later stage when metals sulfides deposition is quite high, these sulfides take part in deactivation.

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