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On the effect of reaction conditions on liquid phase sulfiding of a NiMo HDS catalyst

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Abstract

Various experimental tests were conducted in a fixed-bed pilot plant in order to study the liquid phase sulfiding of a NiMo commercial catalyst. Four sulfiding feeds were employed in the present work: SRGO, SRGO + 1 wt.% sulfur DMDS, HDS-SRGO + 1 wt.% sulfur DMDS, and HDS-SRGO + 1.7 wt.% sulfur DMDS. Three sulfiding temperatures were evaluated: 290, 320, and 350 °C. Drying and soaking of the catalyst were carried out before presulfiding. Each sulfided catalyst was evaluated in the hydrotreating of SRGO at the following conditions: 54 kg/cm^2 pressure, 2.0 h^{-1} LHSV, 2000 ft^3/bbl H_2-to-oil ratio, and temperature of 340–380 °C. SRGO + 1 wt.% sulfur DMDS was the best sulfiding feed. The catalyst sulfided at high temperature exhibited better activity.

It was found that about 50% of the carbon on the catalyst after reaction is deposited during sulfiding step.

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1. Introduction

Presulfiding has been used for many years in refinery operations to obtain the maximum activity of hydrodesulfurization (HDS) catalysts. During this step, the metal oxides, i.e. NiO or CoMo in combination with MoO_3, are transformed into the active metal sulfides. Three different routes are commonly used for presulfiding of HDS catalysts [1]: (1) with non-spiked feedstock, in which sulfiding is conducted with the same sulfur from the normal feedstock, (2) with a H_2/H_2S mixture, carried out in gas phase and most practiced in laboratory experiments, and (3) with spiked feedstock, in which sulfiding is mainly done by the sulfur of the spiking agent.

In recent years, ex situ sulfided catalysts have been commercially employed and good or better activity and stability have been reported compared with catalysts sulfided commercially by spiking agents or by the feed in situ. Since ex situ sulfiding has shown some advantages during commercial operation of HDS catalyst compared with in situ sulfiding, in the near future all HDS units will use this method for activation of hydrodesulfurization catalysts [2–5]. However, when new formulations are prepared and tested in laboratory against commercial catalysts, it is mandatory to sulfide the sample in situ at the same conditions. Hence, in situ catalyst sulfiding will continue being and important step at least in the first stages of catalyst development.

Liquid-phase sulfiding is recognized in the literature to be more efficient than gas-phase procedure [6]. In the case of liquid phase sulfiding, the hydrocarbon carrier aids in wetting and hence in providing a better distribution of sulfur across the bed and evenly sulfiding the catalyst. The hydrocarbon also serves as a sink of heat generated allowing for better control of the exothermic reaction between sulfur and the metal of the catalyst. This allows for a more rapid presulfiding [7]. Between the two types of liquid-phase sulfiding procedures, the spiked one has shown to achieve maximum activity 7–8% higher that non-spiked presulfiding [1].

It should be remembered that a spiking agent is a sulfur-containing organic compound which releases H_2S at a much lower temperature than the sulfur compounds present in the

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normal feedstocks. There are various spiking agents reported in the literature and frequently used for activation of HDS catalysts, such as carbon disulfide (CS_2), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), butanethiol, ditertiary nonyl polysulfide (TNPS), ethyl mercaptan (EM), dimethyl sulfoxide (DMSO), n-buthyl mercaptan (NBM). Among them, DMDS has demonstrated better behavior during laboratory and commercial presulfiding [1,8].

It has been reported that the presulfiding agent should begin at a rate sufficient to produce a sulfur content of 0.5–2 wt.% in the feedstock. The sulfur content of the spiked-feed should be kept at or below 1 wt.%. This is done to moderate the exothermality of the reaction observed as the catalyst is sulfided. During the initial sulfiding, the bed temperature should not be allowed to exceed 260–315 °C. This minimizes coking and metal oxide reduction before sulfiding is complete. After this the bed temperature can be then slowly raised to 315–330 °C [7].

One of the scarcest detailed reports in the literature about commercial level sulfiding indicates that DMDS is employed as spiking agent with gas oil to produce a total feed sulfur content of at least 1 wt.%. A final catalyst sulfiding is also reported to be carried out at a reactor outlet temperature of 350 °C to ensure optimal activation [8,9].

Before sulfiding itself, two main steps are recommended to achieve the optimal catalyst activity [1]: (1) catalyst drying, because due to the hygroscopic nature of the alumina carrier the catalyst can take up water, and when heating up in wet conditions with oil, the catalyst can be mechanically damaged, and (2) catalyst soaking, which is done to wet the catalyst particles properly to prevent the presence of dry areas in the catalyst bed, which eventually lower the overall activity.

In the reports of the literature related to the study of sulfiding of catalyst, temperature has been the most studied parameter, which has been reported in the range of 22–350 °C [6,10,11]. However, most of the published work has been conducted with model molecules and not too much attention has been put in the behavior of the presulfided catalyst with real feeds.

To get more knowledge about the effect of reaction conditions on catalyst activation, in this work we carried out sulfiding of a NiMo commercial catalyst with different feeds and temperatures, which were further evaluated at commercial conditions in the HDS of straight-run gas oil.

2. Experimental

2.1. Catalyst preparation and presulfiding

The hydrotreating catalyst used in all sulfiding and activity experiments was a commercial NiMo/γ-Al_2O_3 sample. Its main properties are presented in Table 1.

Based on the findings and experiences reported in the literature, the following assumptions were taken into account for achieving the optimal presulfiding of the catalyst:

Table 1
Properties of the commercial catalyst

Physical properties	
Shape	Extrudate trilobe
Diameter (mm)	2.3
Specific surface area (m^2/g)	204
Pore volume (mL/g)	0.50
Bulk density (g/mL)	0.78
Chemical properties	
Mo (wt.%)	9.5
Ni (wt.%)	2.4
P (wt.%)	1.6

(1) Sulfiding was carried out in liquid phase,
(2) Liquid hydrocarbon was the same feed employed for HDS activity tests,
(3) DMDS was utilized as spiking agent,
(4) When using DMDS 1 wt.% sulfur content was employed,
(5) Drying and soaking of the catalyst were carried out before presulfiding itself,
(6) Maximum sulfiding temperature was fixed at 350 °C,
(7) Two temperatures were considered for sulfiding, keeping maximum values at 260 and 350 °C in the first and second temperature levels, respectively.

Once these conditions have been chosen, the catalyst sulfiding tests were started. The catalyst was first loaded to the reactor. The reactor was the same employed for further activity studies, which operates at steady-state and is part of a fixed-bed hydrotreating pilot plant. A detailed description of the pilot plant and the isothermal reactor was presented elsewhere [12].

Briefly, the isothermal reactor is designed as a tube with an inside diameter of 2.54 cm and a total length of 143 cm. The length of reactor is subdivided in three sections. The first section was packed with inert particles and was used to heat up the mixture to the desired temperature and to provide a uniform feedstock distribution. The following section contained the commercial catalyst mixed with a diluent. The exit section was also packed with inert particles. Between each section a wool glass plug was inserted in order to improve oil distribution.

The inert used for diluting the catalyst was silicon carbide with an average particle size of 1.4 mm. The inert particle size is lower than that of the catalyst. The catalyst (75 mL) was diluted with equal volume of inert in order to maintain a ratio of the volume of catalyst to that of diluent at a constant value of 1.0. The inert material was employed to minimize the problems when testing catalyst having commercially applied size and shape. Therefore, the hydrodynamics of the flowing fluids will be mainly dictated by the packing of small inert particles, whereas the catalytic conversion behavior is that of the catalyst in the actual size [13].

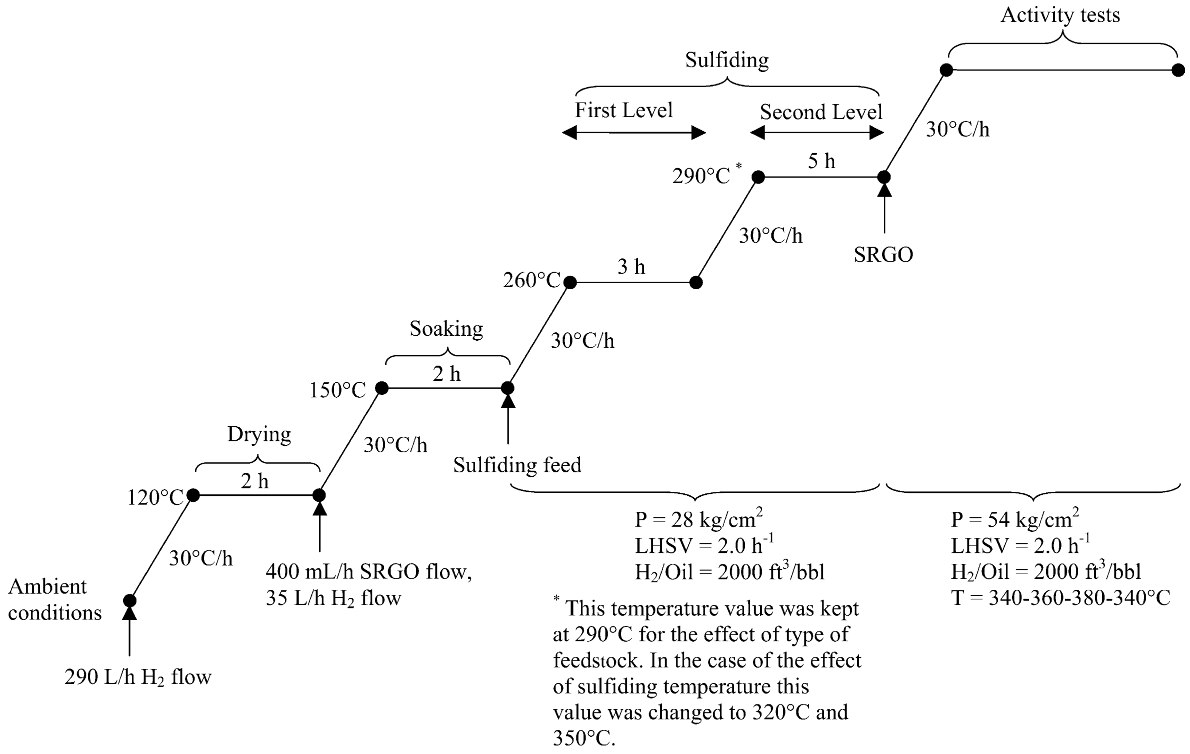

Fig. 1. Operating conditions during sulfiding of catalyst and activity tests.

After catalyst loading, drying and soaking were carried out according to the following conditions:

1. *Drying:* The catalyst was dried with high hydrogen flow (290 L/h) at 120 °C and atmospheric pressure during 2 h.
2. *Soaking:* The catalyst was soaked with high straight-run gas oil flow (400 mL/h) and low hydrogen flow (35 L/h) at 150 °C and atmospheric pressure during 2 h.

Maximum and minimum flows of hydrogen and liquid hydrocarbon were established according to operating limits of equipments and instruments of the pilot plant.

After drying and soaking, presulfiding of catalyst was carried out at two temperatures. The first temperature level was kept as constant at a value of 260 °C and this condition was maintained 3 h with flow of sulfiding feed. This value is high enough for decomposing DMDS, which has a thermal decomposition temperature of 200 °C. For studying the effect of sulfiding feed the second temperature level was maintained 3 h at 290 °C with liquid flow. The other sulfiding conditions were 28 kg/cm^2 of pressure, LHSV of 2.0 h^{-1}, 2000 ft^3/bbl of H_2/Oil ratio. Fig. 1 clearly shows schematically the changes in operating conditions for better reference.

2.2. Activity tests

Once the sulfiding conditions have been set, the first evaluation consisted of studying the type of feed on activation of catalyst. For this, four streams were evaluated:

1. Straight-run gas oil (SRGO),
2. SRGO + 1 wt.% sulfur DMDS (SRGO-1),
3. Hydrodesulfurized-SRGO + 1 wt.% sulfur DMDS (HDS-SRGO-1),
4. Hydrodesulfurized -SRGO + 1.7 wt.% sulfur DMDS (HDS-SRGO-1.7).

The main properties of these feeds are given in Table 2.

The best sulfiding feedstock was used for studying the effect of the activation temperatures. For this case only the second temperature level was modified at the following values: (a) 290 °C, (b) 320 °C, and (c) 350 °C, according also to the operating conditions given in Fig. 1.

After catalyst sulfiding, activity tests were carried out in the hydrotreating of SRGO (Table 2). The reaction condition were maintained constant at 54 kg/cm^2, 2.0 h^{-1} and 2000 ft^3/bbl, and the temperature was varied in the range

Table 2
Main properties of sulfiding feedstocks

Properties	SRGO[a]	HDS-SRGO
Specific gravity at 20/4 °C	0.8733	0.8536
API gravity	29.99	33.71
Sulfur (wt.%)	1.70	0.023
Total aromatics (wt.%)	44.50	28.98
Mono- (wt.%)	20.38	20.41
Di- (wt.%)	12.65	8.14
Tri- (wt.%)	10.31	0.37
Tetra- (wt.%)	1.16	0.06

[a] This feed was also used for activity tests.

of 340–380 °C. For verifying the stability of the catalyst, the test at 340 °C was repeated after 66 h of time-on-stream.

In all HDT experiments pure hydrogen was used in a once-through mode. Product samples were collected at 9 h intervals after allowing a 4 h stabilization period. Two experiments were done at each reaction temperature, and the reported values are the average of the two analyses. Sulfur and aromatics contents in the products were analyzed by X-ray fluorescence following the ASTM D-4294 method and by Supercritical Fluid Chromatography according to the ASTM D-5186 method, respectively.

It should be mentioned that sulfiding and activity tests were carried out separately. That is that we conducted one test only for sulfiding after which the catalyst was unloaded from the reactor and then characterized, and with a new sample of fresh catalyst we did again the sulfiding and without unloading the catalyst the activity tests were performed. In both cases, sulfiding and activity test, the catalyst was unloaded according to the following procedure:

- Reactor temperature is reduced from operating value to 200 °C at a rate of 30 °C/h. When 200 °C temperature is achieved, the sulfiding or activity test feedstocks were changed to a lighter feed (desulfirized naphtha) without stopping hydrogen flow. It is very important that the catalyst never operates without liquid flow.
- Reactor cooling is continued from 200 to 40 °C at a rate of 20 °C/h. When temperature is of 40 °C, naphtha flow is stopped and at the same time hydrogen is changed to nitrogen to have the catalysts in an inert atmosphere.
- Pressure is then reduced from operating value to atmospheric pressure and temperature is decreased from 40 °C to ambient.
- When these conditions are reached, catalyst is unloaded and immediately transferred to a clean and dry vessel. The vessel has to be with nitrogen bubbling before and after catalyst unloading. Finally, the vessel is hermetically closed.

The sulfided and spent catalysts were washed with toluene by Soxhlet process and dried at 110 °C before characterization. Carbon and sulfur contents were measured by combustion with an infrared detector.

3. Results and discussion

3.1. *Effect of the type of sulfiding feed*

In this part of the study, four feeds were chosen in order to observe the effect of the nature and concentration of the sulfur compounds on catalyst sulfiding. Catalyst activity

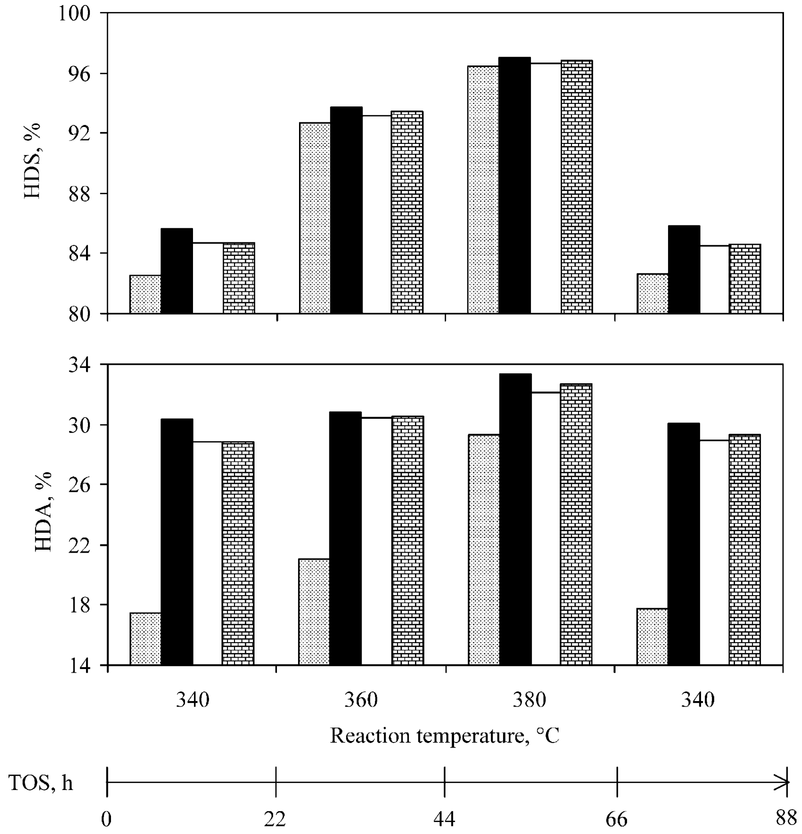

Fig. 2. Effect of type of sulfiding feed on activity of catalyst (▨) SRGO, (■) SRGO-1, (□) HDS-SRGO-1, (▦) HDS-SRGO-1.7.

results (HDS: hydrodesulfurization, HDA: hydrogenation of total aromatics) of the catalyst sulfided with different feeds are shown in Fig. 2. Two general observations can be drawn from this figure:

(1) Both HDS and HDA reactions have identical behavior with respect to which feed yields better catalyst activity, and
(2) The differences in activities among the four feeds are better appreciated at low temperature (340 °C).

Other interesting conclusions can also be pointed out from the comparison of results of each sulfiding feed shown in Fig. 2:

(1) SRGO and HDS-SRGO-1.7 sulfiding feeds have the same sulfur content. The difference is that the former has the common sulfur compounds present in petroleum and the latter has DMDS. It is then clearly observed that DMDS added to the HDS SRGO gives better activity than SRGO.
(2) HDS-SRGO-1.7 feed has more sulfur content than HDS-SRGO-1 feed (1.7 wt.% versus 1 wt.%), and in both cases the sulfur is mainly that from DMDS. However, no important differences in activities were observed when the catalyst was sulfided with these two feeds, which means that 1 wt.% of sulfur as DMDS is enough for achieving optimal catalyst activities. Of course it may be possible that less than 1 wt.% sulfur added as DMDS could be only necessary for optimal behavior of the catalyst, however in our present investigation we did not try with lesser sulfur contents.
(3) SRGO-1 yielded the highest activity values. This means that the combination of the sulfur compounds commonly present in petroleum and DMDS helps in achieving the optimal catalyst activity.
(4) At high temperature all the feeds seem to give the same HDS activity. This similarity in activities could be attributed to the high reaction rate observed at high temperature compared with low temperature, since at 380 °C the conversion is probably close to the maximum sulfur removal. HDA does not follow this behavior, which may be due to the thermodynamic equilibrium commonly found at these conditions [14]. If we see the high temperature experiments we can notice that they were done at 44–66 h time-on-stream and those at low temperature at 0–22 h. One can think here that at long time-on-stream no matter the sulfiding feed the catalyst has continued being sulfided by the same feed until complete sulfiding. However, the repetition of the 340 °C temperate experiments, which were carried out at 66–88 h time-on-stream, contradicts this because the differences in activities obtained with the four reactions are again evident.

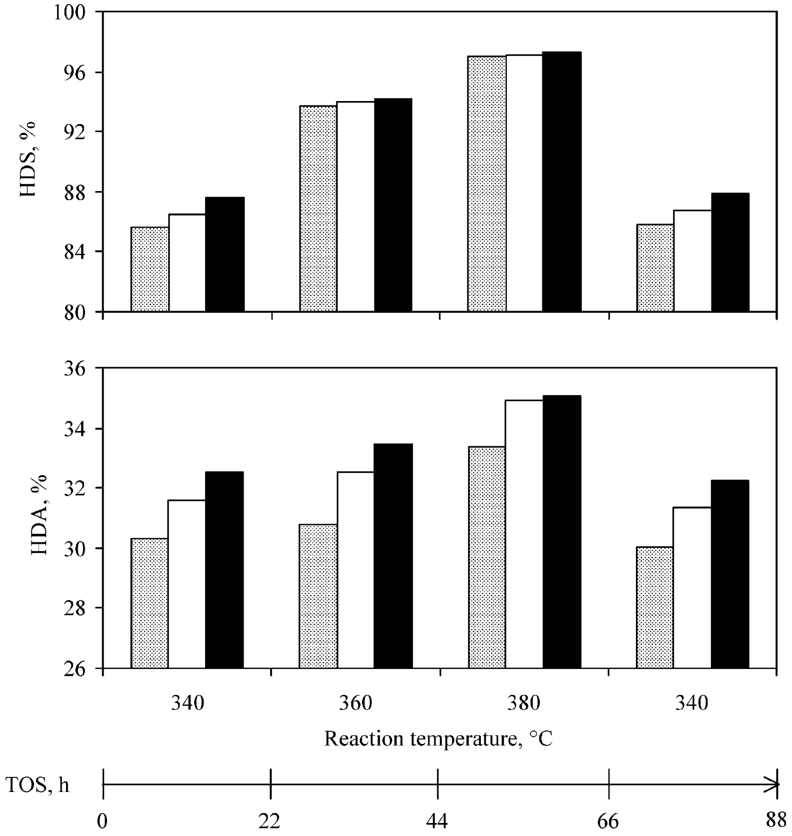

Fig. 3. Effect of sulfiding temperature on activity of catalyst (▨) 290 °C, (□) 320 °C, (■) 350 °C.

From the above observations, it is then concluded that SRGO plus 1 wt.% sulfur (DMDS) is the best sulfiding feed. This is a confirmation of earlier works as reported by Speight [15]. The better activity of the catalyst sulfided with SRGO-1 is probably due to the simultaneous decomposition of the low molecular weight sulfur compounds present in the SRGO with the DMDS which consequently transforms the metallic oxides more efficiently into the sulfide form. This better behavior of SRGO-1 feed is clearer at low temperature in which short time-on-stream is also present. This is an important fact, since most of the experimental work reported by others is carried out at these conditions in order to magnify differences in activity of laboratory and commercial catalysts.

3.2. Effect of sulfiding temperature

Once the best sulfiding feed was defined the temperature effect was studied. Only the second sulfiding temperature level was modified in the range of 290–350 °C, and the first temperature level was kept constant at 260 °C. Results of HDS and HDA are given in Fig. 3. From this figure, the following observations can be made:

(1) HDS and HDA catalytic activities increase with sulfiding temperature. This behavior has been reported by others [10], who also found that after 400 °C HDS of thiophene and hydrogenation of tetralin activities of a $CoMo/Al_2O_3$ catalyst remain constant. The catalyst sulfiding in this study was done in gas phase with a mixture of H_2/H_2S and temperature was varied from 22 up to 500 °C.
(2) The differences in HDS activities among the three sulfiding temperatures are better appreciated at low reaction temperature (340 °C). In the case of HDA activities, the differences are clearly seen at all reaction temperatures.

From these results, it is then observed that 350 °C sulfiding temperature may be the optimal value for achieving better catalyst activity. We did not try with higher temperature values since coking and metal oxide reduction is surely present before completing sulfiding of catalyst. In fact, at 350 °C this coke and metal oxide reduction may appear, therefore, 320 °C sulfiding temperature may be more convenient.

3.3. Characterization of sulfided and spent catalysts

The deposits of sulfur on the sulfided catalysts as function of sulfiding temperature expressed as S/(Ni + Mo) atomic ratios are shown in Fig. 4. It is seen that the higher the temperature the higher the sulfur deposit. Similar behavior has been reported in the literature for a CoMo catalyst [10] (shown also in Fig. 4) in which no increases in sulfur deposits were found after 350 °C sulfiding temperature.

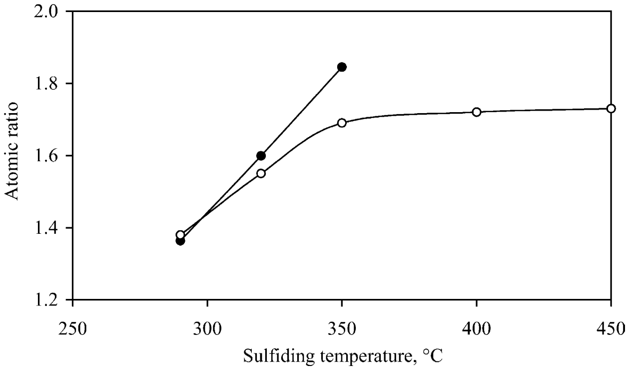

Fig. 4. S/(Ni + Mo) atomic ratio of sulfided catalysts at different sulfiding temperatures (●) this work, (○) data of S/(Co + Mo) taken from Ref. [10].

The deposition of carbon and sulfur on the catalyst leads to an apparent decrease in metals loadings. Hence, we have recalculated the catalyst composition on carbon and sulfur-free basis, i.e. g of S (C)/100 g fresh catalyst. It was supposed that fresh catalyst exhibits a marginal amount of carbon as contaminant.

Carbon and sulfur deposits on the catalyst calculated by this way before and after reaction are shown in Fig. 5. What is very clear from these results is that more than 50% of the carbon on the catalyst after reaction is deposited during sulfiding step, and this deposition increases with sulfiding temperature. In the case of sulfur, it is observed that independently of the temperature, the catalyst continues being sulfided during the HDS reaction. At high temperature, it seems that the catalyst sulfiding is almost completed, since the difference between sulfur in sulfided and spent catalysts is minimal.

According to this, sulfiding temperature has an important effect on carbon and sulfur deposited on the catalyst and of course on the behavior of the catalyst during HDS reaction. Carbon deposition is inevitable during this step and it may delay the transformation of the Ni and Mo oxides into the corresponding sulfides. Carbon deposit is known to be one cause of catalyst deactivation, which is more critical when hydrotreating of heavy feeds. However, for hydrotreating of

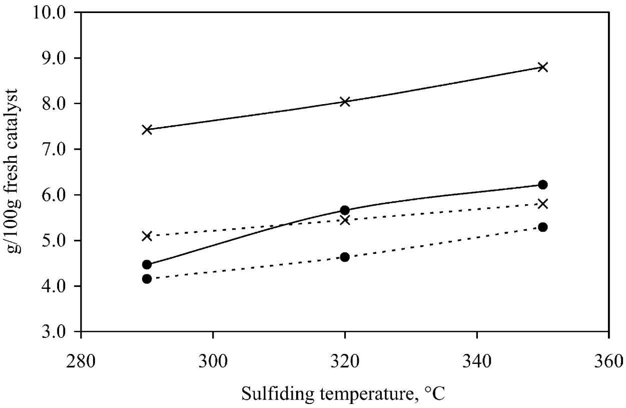

Fig. 5. Carbon and sulfur contents of catalysts at different sulfiding temperatures (●) sulfided catalyst, (×) spent catalyst, (– – –) sulfur, (—) carbon.

light feeds, such as the one employed in the present work, catalysts deactivation is minimal. In recent literature reports, it has been found that the carbon deposited during the sulfiding step has a beneficial effect in the stability and activity on the HDS catalysts [6], hence this is probably the reason that in our experiments we obtained greater activities in both HDS and HDA reactions when the catalyst was sulfided at high temperature.

4. Conclusions

The selection of sulfiding feed and temperature is very crucial for achieving the optimal hydrotreating catalyst activities. For liquid phase sulfiding it was demonstrated here that the combination of sulfur compounds present in straight-run gas oil with DMDS (1 wt.%) yields the best behavior of a NiMo HDS catalyst.

The catalyst sulfided at high temperature (320–350 °C) exhibited better activity on the HDS and HDA reactions of a SRGO compared with lower sulfiding temperatures.

Characterization of sulfided and spent catalysts showed that about 50% of the carbon found on the catalyst after reaction is deposited during sulfiding step. Sulfur deposits on the catalyst were higher at elevated sulfiding temperature.

At higher sulfiding temperature small differences between sulfur contents in sulfided and spent catalysts were found indicating that most of the sulfur was deposited during sulfiding step.

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