FACTORS INFLUENCING THE DEACTIVATION OF INDUSTRIAL CATALYSTS

I. Co-Mo-Al$_2$O$_3$ HYDRODESULFURIZATION CATALYSTS

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ABSTRACT

The changes that occurred in the physico-chemical properties of a commercial Co-Mo-Al$_2$O$_3$ catalyst on industrial usage were examined. The catalyst under study had operated satisfactorily, meeting the full guarantes on its life, but had to be discarded after six regenerations due to shortened cycle lengths. It was observed that changes in the texture and structure of the support alumina and loss of the active components (MoO$_3$ and CoO) had occurred. Also, the spent catalyst was found to be more acidic, resulting in faster coke pick up during reaction. Some evidence for the weakening of the MoO$_3$ - Al$_2$O$_3$ interaction was also noticed. The reasons for the above changes in the physico-chemical properties, believed to be responsible for the short cycle lengths of the catalyst, are analysed.

INTRODUCTION

Hydrodesulfurization (HDS) of sulfur-containing liquids is an important catalytic process in the petroleum and fertilizer industries. Extensive research has been carried out on HDS (and hydroprocessing) catalyst systems with Mo as the major metal component and Co or Ni as the promoter supported on an active alumina. The activity-stability of these catalysts has been found to be dependent on various parameters such as the type of support used [1,2], its pore-size distribution [3], acidity characteristics [4], the nature and extent of the dispersed phase [5,6] and its reducibility [6]. Loss of desulfurization activity of the catalyst in commercial units depends on a number of other operating factors also. Using steam/ air regeneration procedure, for example, a 10% loss in activity for naphtha HDS, immediately after the first industrial regeneration could be expected [7].

In this communication, we are comparing the physico-chemical properties of a spent commercial HDS catalyst with those of a fresh sample. We will also examine how the changes in some of the properties could have led to the loss of the activity-stability of the catalyst resulting in its removal from the reactor.

TABLE 1

Background information on the process and the catalyst

Unit:	Pretreater
Duty:	To desulfurize feed to less than 1 ppm sulfur
Feed:	Naphtha, sulfur level - 200-400 ppm
Operating parameters.	
Temperature:	$320° - 360°C$
Pressure:	About 1.96 MPa
LHSV:	About 6
Gas to oil ratio:	80 v/v
Catalyst type:	$CoO-MoO_3-Al_2O_3$
Number of regenerations at the time of unloading:	6
Successive amounts of feed processed in each of the 6 cycles:	70, 59, 53, 40, 37 and 32 $m^3 kg^{-1}$ of catalyst
Product sulfur at the time of unloading:	4 - 6 ppm

EXPERIMENTAL

Catalysts

A fresh commercial Co-Mo-Al$_2$O$_3$ HDS catalyst and its spent form unloaded from a commercial installation were used in this study. The background information on the spent catalyst, the process details and the amount of feed treated in each of the six cycles are given in Table 1. Before unloading, the spent catalyst was regenerated *in situ* (air-steam regeneration) in the plant and a representative sample in its oxidic form was obtained. Pretreatment conditions were identical for both the samples.

Chemical analysis

The concentrations of Co and Mo were determined by following ASTM procedures [8].

Physical and structural properties

Surface area (BET) and pore-size distributions were obtained from N$_2$ adsorption-desorption isotherms. The total pore volumes were computed from water retention volumes. MoO$_2$ areas were determined from O$_2$ adsorption measurements at -78°C on the reduced samples [9]. Estimation of the average crystallite sizes and percent crystallinities were made from the 1.4 Å line in the XRD powder spectrum.
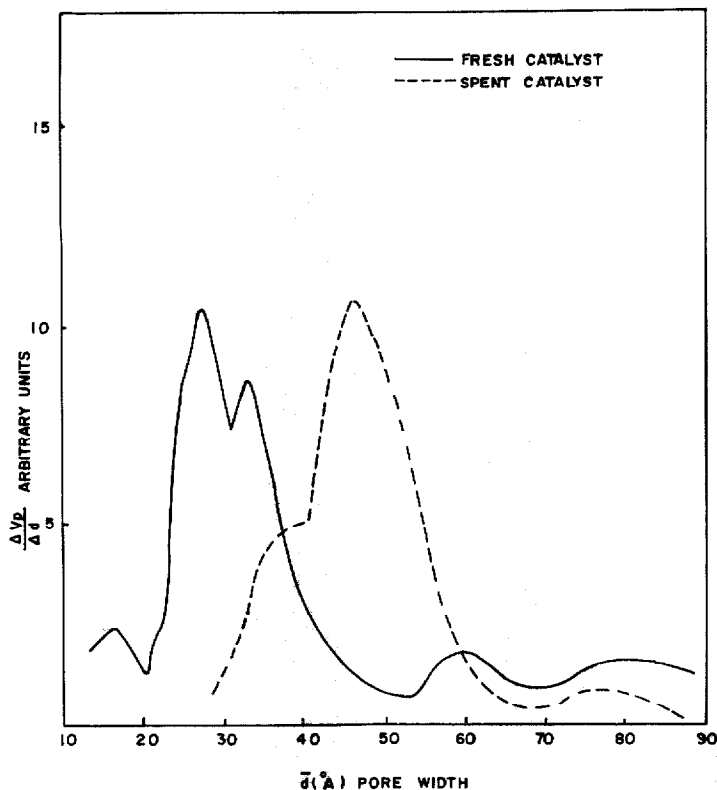
TABLE 2

Comparison of the physico-chemical properties of the fresh and the spent Co-Mo-Al_2O_3 catalysts.

Properties	Fresh catalyst	Spent catalyst
A. Composition (Wt%)		
CoO	3.0	2.2
MoO_3	12.0	8.4
B. Physical and Structural		
Surface area (BET) $(m^2\ g^{-1})$	260	150
Total pore volume $(ml\ g^{-1})$	0.55	0.39
Mean pore width (Å)	30	50
Support crystallinity (%)	67	82
Support crystallite size (Å)	46	80
Nature of cobalt	Octahedral + tetrahedral	More in tetrahedral form
C. Reducibility and activity		
Reducibility of MoO_3	slow	rapid
a) Start of reduction (°C)	240	170
b) Mo(V) signal maximum (°C)	425	300
Effective molybdenum area $(m^2\ g^{-1})$	22.3	26.4
Thiophene conversion (initial activity (wt%)	67.2	72.7
D. Acidity and coking rates		
NH_3 held $(meq\ g^{-1})$ at 300°C	0.18	0.39
at 400°C	0.05	0.26
2.6-dimethylpyridine held $(meq\ g^{-1})$		
at 300°C	0.11	0.11
at 400°C	0.06	0.06
Coke lay-down rate, relative	1.0[a]	4.0

[a]The sample after regeneration in dry air at 500°C for 2 hours had a S_{BET} of 255 $m^2\ g^{-1}$ and a pore volume of 0.53 ml g^{-1}.

Surface acidity

Surface acidity measurements were carried out gravimetrically using a Cahn electrobalance. After adsorption (of NH_3 or dimethylpyridine) at each temperature, the sample was degassed to 2.6 Pa. The amount of the base retained at this pressure is treated as being irreversibly held at the surface.

FIGURE 1   Pore-size distributions in the fresh and the spent Co-Mo-Al$_2$O$_3$ catalysts.

Magnetic measurements

A Gouy balance was used for obtaining the paramagnetic susceptibilities (due to Co) of the samples [10]. From the values of the calculated magnetic moments (μ_{eff}), the relative presence of the Co(II) in either tetrahedral or octahedral surroundings of the oxide ions was inferred [11,12].

Reducibility

The course and the extent of reduction of the samples as a function of temperature in the programmed heating mode (TPR) were followed by measuring the Mo(V) signal intensities at different intervals using Brucker E 100 D ESR spectrometer. Other details of the reduction experiments are given elsewhere [13].

Activity and coke lay-down experiments

Thiophene desulfurization activity was measured using a thiophene (2.54 wt%)-benzene feed at atmospheric pressure and at 310°C. Other details of the HDS activity measurements are given elsewhere [2]. Accelerated ageing tests were

carried out in a vertical reactor at atmospheric pressure using a benzene feed containing thiophene (2.54 wt%) and octene-2 (5 wt%). The runs were carried out at 400°C for 12 h, at a feed flow rate of 2 ml h^{-1} and a H$_2$ flow rate of 15 ml min^{-1}. The coke deposited on the samples was estimated by chemical analysis. Also, an ESR method described earlier [2], which gives the relative coke levels on the samples, was used.

RESULTS AND DISCUSSION

The various physico-chemical properties of both the fresh and the spent catalysts are reported in Table 2. These data are discussed in the same order as presented in the Table.

Composition

Chemical analysis has revealed the loss of both MoO$_3$ and CoO from the catalyst on usage. Though loss of small amounts of MoO$_3$ can be accounted for by its slight volatility, such huge losses of MoO$_3$ (30% lost) and CoO (28% lost) cannot easily be accounted for. It is possible that condensed steam during regeneration operations might have washed away the active components at the conditions of regeneration. While the loss of MoO$_3$ has a direct bearing on the long term activity, the loss of Co may lead to lower H$_2$ mobility on the catalyst surface and consequently to lower HDS activity. Also, a more rapid coke build up can occur when H$_2$ spillover is less.

Physical and structural properties

There is a large specific surface area (BET) decrease (from 260 to 150 m^2 g^{-1}) after six regenerations. Similarly, a considerable pore volume decrease accompanied by a shift in the pore-size distribution (Figure 1) has occurred. The mean pore width calculated from the surface area contribution by pores < 500 Å is about 30 Å for the fresh catalyst and about 50 Å for the spent sample (Table 2). It is likely that the changes in surface area and pore volume have occurred during the repeated regenerations (in steam). It may be mentioned here that simple laboratory regenerations of a coked and sulfided catalyst in dry air alone did not lead to any significant loss in surface area or pore volume (see Table 2, foot-note). It is hence believed that the changes in surface area and pore volume have been brought about primarily by the steam present in commercial regeneration operations.

Powder X-ray diffraction spectra show that the alumina has sintered with accompanying crystal growth (46 Å to 80 Å) on usage. Also, some decrease in the amorphous phase of alumina (33% to 18%) has occurred. Further, some transformation of the original γ-Al$_2$O$_3$ support into other forms (e.g. δ) cannot be ruled out.

Magnetic susceptibility data indicate that the used catalyst has a lower paramagnetic susceptibility (molar) for Co and a lower magnetic moment than the fresh
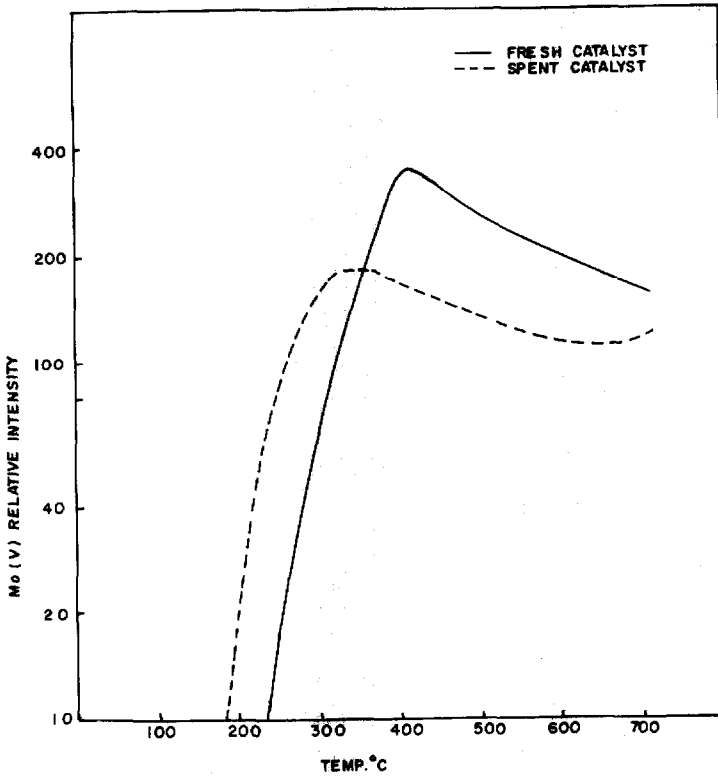
FIGURE 2 MoO_3 reduction profiles (TPR) for the fresh and the spent Co-Mo-Al_2O_3
catalysts. The extent of reduction is given in terms of Mo(V) signal intensities
observed in ESR spectra.

sample. In a tetrahedral environment of oxide ions, the observed moments for Co(I:
range between 4.2 and 4.7 B.M., and when octahedrally surrounded, the values are
in the range of 4.7 - 5.3 B.M. Comparatively, a lower value indicates the presenc<
of more Co(II) in tetrahedral environment. Although it is difficult to interpret
magnetic data unambiguously, this is an indication of the migration of some
'octahedral' forms of Co present over the surface alumina layer of the fresh samp
into the subsurface tetrahedral locations (in the spent catalyst) [12]. It has al:
been reported by earlier workers that Co in the tetrahedral form (in Al_2O_3 matrix
has a lower magnetic susceptibility and contributes less to the HDS reaction
[11,12].

Reducibility and activity characteristics

The reduction profiles (as seen by ESR signals of Mo(V) species) of the two
samples are presented in Figure 2. The concentration of Mo(V) increases with
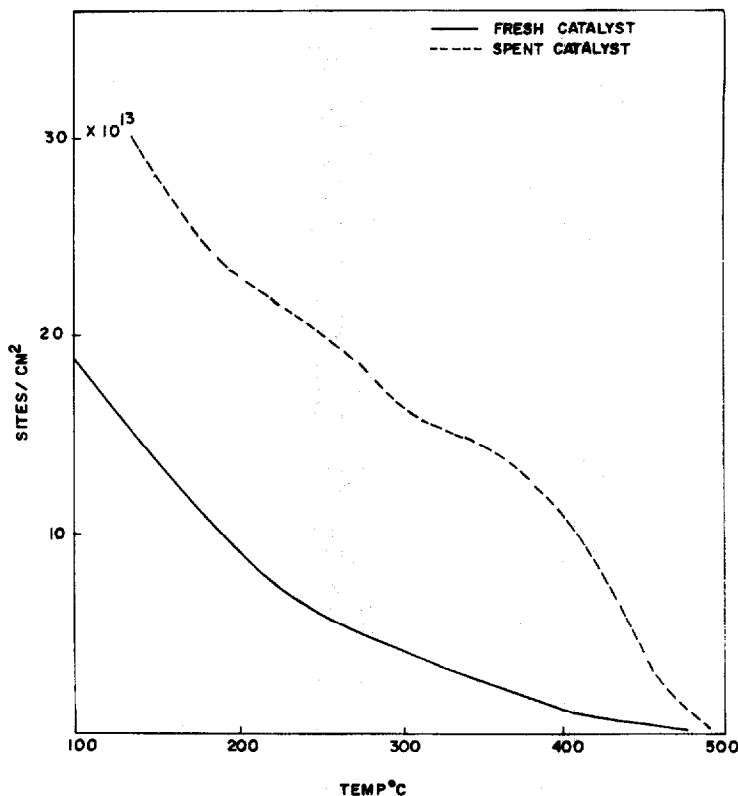
FIGURE 3 NH_3 adsorption isobars of fresh and spent $Co-Mo-Al_2O_3$ catalysts (irreversibly adsorbed at 2.6 Pa).

temperature of reduction and goes through a maximum for both the samples. However, the reduction occurs faster (as seen from the earlier start of the reduction and attainment of the maximum) on the spent catalyst than on the fresh sample. This could be due to a lower dispersion of MoO_3 and/or a poorer interaction between the MoO_3-layer and the Al_2O_3 surface, in the case of the former sample. MoO_2 area measurements on the reduced samples, however, did not show much difference, suggesting that the dispersions levels (of MoO_2) on the two samples are similar. Thus, the reducibility difference appears to be primarily due to difference in the metal-support interactions. A poor metal-support interaction can be expected to result in rapid agglomeration of the active MoS_2 crystallites leading to loss in HDS activity.

The initial activities for thiophene conversion are the same for both the samples in agreement with the similarity in MoO_2-area values. Obviously, the initial activity tests carried out in the laboratory do not throw any light on the reasons for the poor performance of the spent catalyst prior to its being un-

loaded. The slightly higher activity of the spent catalyst (72.7% against 67.2% for the fresh catalyst) could be due to its offering lower diffusion resistance to feed molecules, as a result of the larger pores present in it [2].

Acidity and coking characteristics

The number of NH_3 molecules retained irreversibly at different temperatures by both the samples are presented in Figure 3. This isobar is taken as an indication of the acid-strength distribution of the catalysts, the stronger sites being associated with the amount of base adsorbed at higher temperatures. It is seen that the spent catalyst is much more acidic than the fresh one, the difference being more marked in the stronger acidity region. For example, the ratio of the acid centers present in the two samples is: spent/fresh = 5 at 400°C and 2 at 300°C (Table 2). In order to examine the nature of the acid centers in the two samples, the adsorption of 2,6-dimethylpyridine was carried out. The adsorption of sterically hindered amines (like 2.6-DMP) has been shown by Benesi [14] to take place primarily on Brönsted sites. Our measurements using 2.6-dimethylpyridine showed about the same level of Brönsted acidity in both the samples at different temperatures. It may, therefore, be reasoned that the increased acidity in the spent samples is mostly in the form of strong Lewis centers. One of the likely reasons for the increased acidity in spent catalysts is the formation of sulfate on the support during coke burn-off operations. Other reasons which may exist are not clearly known.

Earlier reports [4] have indicated that Lewis acidity is more responsible for coke lay down on HDS catalysts than the Brönsted centers. Accelerated coking tests carried out in the laboratory at 400°C at atmospheric pressure using a benzene feed containing thiophene (2.5 wt%) and octene-2 (5 wt%) resulted in coke levels of 2.2 wt% on the fresh catalyst and 5.8 wt% on the spent catalyst. This indicates that the spent catalyst has a tendency to pick up coke many times more rapidly than the fresh sample.

CONCLUSIONS

The poor activity-stability of the $Co-Mo-Al_2O_3$ catalyst at the stage of unloading is attributed to the following reasons:
1. A physical loss of the primary active component (MoO_3) has occurred.
2. A part of the promoter Co has been physically lost, while another part has been deactivated by entering the Al_2O_3 lattice.
3. The poor interaction between the active component (Mo-species) and the support could have contributed to a more rapid loss in the active MoS_2 area through crystallite growth.
4. Rapid coke deposition attributable to the creation of strong acid sites (partly due to sulfate pick-up) in the regenerated catalyst is another major deactivating factor.

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