Deactivation of Hydrodesulfurization Catalysts in Two-stage Resid Desulfurization Process (Part 4) Deactivation in a Long-term Aging Test under Constant Reaction Temperature

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The long-term aging tests involving hydrodesulfurization catalysts were done at 380°C. The used catalysts were then characterized to investigate the deactivation mechanism. The amount of coke on the catalyst peaked around 30 days, and then decreased. This decrease in coke was due to the hydrogenation reaction with Ni-sulfide deposited on the catalyst. Elemental analysis, measurement of pore size distribution, and activity tests of the used catalysts revealed that the catalyst deactivation at start and middle of a run (MOR) was caused by coke and by metal deposits, respectively. In addition, calculations revealed plugging of pore mouths and the presence of sealed space of pores at MOR, resulting in the catalyst deactivation.

1. Introduction

Residue desulfurization (RDS) is a key process in oil refinery and is used to remove heteroatoms (S, N) and metals (Ni, V). In this process, the reaction temperature is gradually elevated to compensate for the catalyst deactivation, and thus produces oil of consistent quality. For optimum refinery operation, the catalyst life in RDS processes must be determined. To achieve an optimum catalyst life for a desired operation period, the catalyst system typically involves several different catalysts, such as hydrodemetallization (HDM) and hydrodesulfurization (HDS) catalysts.

HDM and HDS catalysts are deactivated mainly by coke and metals. It is known as a general tendency that coke formation is significant at the early stage of a run and levels off under the constant temperature. Although this coke formation is believed to be responsible for the catalyst deactivation at the start of a run (SOR), the deactivation mechanism remains unclear. Absi-Halabi and coworkers reported that pore blockage by coke occurred in smaller pores, whereas Myers et al. reported that active sites were covered by coke. Deactivation by metal deposits, on the other hand, can be simply interpreted as plugging of the pore mouth; namely, the metal deposits narrow the pore, thus obstructing reactants in their access to active sites. Deactivation by metals is predominant at the middle of a run (MOR), which is important in determining the catalyst life.

The effect of coke and that of metals on catalyst deactivation are influenced by the catalyst properties, feedstock, operating conditions, and so on. Fixed bed reactors are normally used in RDS processes. When these reactors are used, catalyst life is determined by the overall performance of the catalyst system. Recently, HDM guard processes involving an ebulliated bed and a moving bed, both of which are combined with a conventional fixed bed reactor, have been developed and commercialized. Such systems are two-stage RDS processes. The HDM activities in these guard processes are maintained by replacement of the catalyst, and thus only the catalyst life in the fixed bed reactor determines the catalyst life of the system. For such two-stage RDS processes, the catalyst life in the fixed bed reactor is affected by the operating conditions in the HDM guard process. However, there are only a few reports with respect to the effect of these operating conditions on the catalyst life.

In a previous study, we investigated the effects of HDM operating conditions and feedstock on the HDS catalyst deactivation in a two-stage RDS process (HDM/HDS) by doing fouling tests (under constant sulfur content operation). The results for the fouling rate at MOR showed that the severity of HDM operation changed the asphaltene quality, and consequently affected the deactivation of HDS catalyst. Furthermore, under constant HDM operating conditions, asphaltene quantity significantly affected the HDS catalyst deactivation.

In the present study, we did long-term aging tests of HDS catalyst under constant temperature (380°C) with
HDM oils prepared by HDM reaction at 380°C. Based on the results, we determined the deactivation mechanism of HDS catalyst at SOR and MOR.

2. Experimental

2.1. Materials

Arabian heavy atmospheric residue (AH-AR) was used as feedstock in the hydrotreatment. The feedstock contains 4.2 wt% of sulfur and 116 ppm of metals (Ni + V). Table 1 lists other properties of the feed.

HDM catalyst contains MoO3 (4.2 wt%) on alumina support and has a surface area (SA) of 200 m²/g, a pore volume (PV) of 0.85 ml/g, and an average pore radius (APR) of 8.5 nm. HDS catalyst contains MoO3 (10.5 wt%), NiO (0.7 wt%), and CoO (1.2 wt%), and has an SA of 211 m²/g, PV of 0.64 ml/g, and APR of 6.0 nm. Both HDM and HDS catalysts were donated by a Japanese manufacturer and used as received (1/22-inch trilobe extrudate).

2.2. HDM and HDS Treatment

HDM treatment of AH-AR was performed using a trickle bed down-flow reactor to obtain HDM oil, which was used as the feed in the HDS treatment. The HDM catalyst (800 ml) was loaded into the reactor and then presulfided with light gas oil (LGO) spiked with dimethyl-disulfide at 300°C for 22 h. After the presulfiding, HDM treatment was done under the following conditions: liquid hourly space velocity (LHSV) of 1.0 h⁻¹, H₂/Oil of 5000 scfb, pressure of 14 MPa, and temperature of 380°C.

For the HDS treatment, a bench-scale down-flow reactor was used with three consecutive reactors. The HDS catalyst (180 ml) was presulfided with light gas oil (LGO) spiked with dimethyl-disulfide at 300°C for 22 h. After the presulfiding, HDS treatment was done under the following conditions: liquid hourly space velocity (LHSV) of 1.0 h⁻¹, H₂/Oil of 5000 scfb, pressure of 14 MPa, and temperature of 380°C.

2.3. Preparation of Used Catalyst Samples

After the HDS treatment, the catalysts were removed from the reactor and separated into three groups, depending on their position in the reactor: so-called Top, Middle, and Bottom. Each catalyst was washed first with LGO at 350°C for 6 h in a micro flow reactor, and then with toluene in a Soxhlet apparatus. The catalysts were then dried overnight at 110°C in vacuo. In this paper, the Top and Bottom samples were mainly characterized.

2.4. Analysis of Used Catalysts

The C, H, and N contents of the used catalysts were measured by using a CHN coder (YANAKO MT-5), and the S content was determined by using the Leco method. The metal content, such as Ni and V, was measured by using an ICP-MS spectrometer. Surface area, pore volume, and pore size distribution were measured by using the N₂ adsorption-desorption method on a Micromeritics ASAP-2010. Distribution of the metals in the used catalyst pellet was determined by EPMA measurements.

Coke was isolated from the used catalysts (Middle samples) by the HF dissolution method and then characterized by using solid state ¹³C-NMR (CP/MS).

2.5. Activity Tests of Used Catalysts

HDS and hydrogenation reactions with model compounds were done to examine the remaining activity of the used catalysts. HDS activity of the used catalysts was evaluated by using thiophene pulse reaction at 275°C under 0.2 MPa with a crushed sample of the catalyst (0.05 g), and the hydrogenation activity was measured at 250°C under 5 MPa using 1-methyl-naphthalene (1-MN) with a crushed sample of the catalyst (0.2 g). For both activity tests, the used catalysts were sulfided with H₂S (5% in H₂) gas at 400°C under 0.2 MPa for 2 h prior to the reactions. Furthermore, for comparison with the results obtained with model compounds, the HDS activity of the used catalyst (5 ml) to the HDM oil was evaluated by using a micro flow reactor: temperature of 360, 380 and 400°C, LHSV of 0.4 h⁻¹, pressure of 8 MPa and H₂/Oil of 5000 scfb.

3. Results and Discussion

3.1. Long-term Aging Tests of HDS Catalysts

The HDS, HDM, and hydrodenitrogenation (HDN) activities during the long-term tests of HDS catalyst are shown in Fig. 1. The HDS and HDM activities gradually decreased with increasing run time, or aging. After a rapid decrease during the first 30 days, the HDS activity slightly increased, suggesting that hydrogenation activity was restored during the run because hydrogenation activity is essential to HDN reaction²⁰). The cause of this unusual phenomenon, namely, the restoration of hydrogenation activity, will be discussed later in the next section.

3.2. Characterization of Used Catalysts

Used catalysts were characterized to evaluate the
deactivation of HDS catalyst. Table 2 lists the elemental analyses and physical properties of the used catalysts, and Fig. 2 shows the metal content (Ni + V) and carbon content as a function of run time, or aging. The metal content of the Top and Bottom samples was relatively proportional to the run time. The metal content of the Top sample was higher than that of the Bottom sample. In contrast, the carbon content of the Top sample was lower than that of the Bottom sample. Furthermore, the carbon content for both samples increased with run time and peaked at around 30 days. It is generally accepted that the amount of coke on a catalyst is fairly constant under constant temperature if coke reaches equilibrium\(^{45-46}\). However, Inoguchi et al. reported an increase in catalyst activity in HDS during aging under constant reaction temperature (390\(^\circ\)C), and suggested that this unusual increase was caused by disruption of the dynamic balance between the rate of coke adsorption on the catalyst and that of coke desorption\(^{21}\). Our result agrees with that by Inoguchi et al., and clearly shows evidence that the amount of coke on a catalyst changes during aging under constant reaction temperature. Because the Top sample showed a higher metal content and a larger decrease in carbon content compared with the Bottom sample, the decrease in carbon content might be caused by the hydrogenation reaction with metals deposited on the catalyst. Deposited metals such as Ni and V exist in the form of sulfides\(^{8,15}\), and Ni-sulfide has a higher activity for hydrogenation than does V-sulfide\(^{22}\). Therefore, the decrease in coke after 30 days might be due to the hydrogenation reaction of coke by Ni-sulfide. In fact, the atomic ratio of hydrogen to carbon (H/C) for the Top and Bottom samples increased after 30 days of run time (Table 2). In addition, an increase in H/C and a decrease in aromaticity (fa) of coke removed from the middle sample confirm the hydrogenation of coke (Table 3). The EPMA measurements show that V was localized mainly at the edge of the catalyst pellet whereas Ni was uniformly distributed from the edge to the center of the catalyst pellet (Fig. 3). Coke was also uniformly distributed like Ni. These observations suggest that hydrogenation of coke occurs preferentially with Ni-sulfide, supporting the possibility that the decrease in coke after 30 days is due to the hydrogenation reaction of coke by Ni-sulfide. Note that the recovery of HDN activity seen in Fig. 1 is presumably

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**Table 2** Elemental Analysis and Physical Properties of Used Catalysts

<table>
<thead>
<tr>
<th>Run time [days]</th>
<th>Element analyses(^{a}) [wt%]</th>
<th>H/C</th>
<th>SA(^{a}) [m(^{2})/g]</th>
<th>PV(^{a}) [m(^{3})/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>S</td>
</tr>
<tr>
<td>Fresh</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.8</td>
</tr>
<tr>
<td>Top</td>
<td>5</td>
<td>6.7</td>
<td>1.2</td>
<td>0.3</td>
</tr>
<tr>
<td>15</td>
<td>6.9</td>
<td>1.2</td>
<td>0.3</td>
<td>5.1</td>
</tr>
<tr>
<td>30</td>
<td>8.1</td>
<td>1.3</td>
<td>0.3</td>
<td>5.9</td>
</tr>
<tr>
<td>90</td>
<td>6.7</td>
<td>1.3</td>
<td>0.3</td>
<td>5.9</td>
</tr>
<tr>
<td>180</td>
<td>5.5</td>
<td>1.3</td>
<td>0.2</td>
<td>6.7</td>
</tr>
<tr>
<td>Bottom</td>
<td>5</td>
<td>7.5</td>
<td>1.2</td>
<td>0.3</td>
</tr>
<tr>
<td>15</td>
<td>8.9</td>
<td>1.3</td>
<td>0.3</td>
<td>5.0</td>
</tr>
<tr>
<td>30</td>
<td>9.3</td>
<td>1.3</td>
<td>0.3</td>
<td>5.4</td>
</tr>
<tr>
<td>90</td>
<td>8.9</td>
<td>1.3</td>
<td>0.4</td>
<td>5.7</td>
</tr>
<tr>
<td>180</td>
<td>8.0</td>
<td>1.3</td>
<td>0.3</td>
<td>5.7</td>
</tr>
</tbody>
</table>

a) Based on fresh catalyst as reference.
due to the increase in hydrogenation activity caused by deposited Ni-sulfide.

It is important to examine how metals and coke act to deactivate the catalysts. In general, metal deposits contribute to the plugging of the catalyst pores, thus inhibiting the reactant diffusion. Figure 4 shows the pore radius distribution of fresh and used catalysts (Top sample). The fresh catalyst had a pore radius distribution ranging from 2 to 10 nm. As the run time increased up to 30 days, the pores in the 2-3 nm range and the pores at around 5 nm, which was the main peak in the distribution, significantly decreased. When the run time exceeded 30 days, a new peak appeared at 1.8 nm. This peak can be attributed to a pore of the inkbottle type and implies that pore narrowing by metal deposits occurred after 30 days of aging. The main peak at around 5 nm remained relatively constant.

Coke and metal deposits are known to make sealed space in a catalyst in which active sites do not participate in any reactions due to the pores being completely plugged even if they are still alive. The volume of sealed space can be calculated by assuming that Ni and V exist as NiS and V3S4, respectively, and assuming that the densities of coke, NiS, and V3S4 are 1.6, 5.8, and 3.6 g/ml, respectively. Figure 5 shows the relationship between metal on catalysts (MOC) and the volume of sealed space determined by using the following equation:

\[
\text{Volume of sealed space} = PV_f - (PV_u + V_c + V_m)
\]

where \(PV_f\) and \(PV_u\) are the pore volume of the fresh and used catalysts, respectively, and \(V_c\) and \(V_m\) are the volume of coke and metal sulfides, respectively. The figure shows that the volume of sealed space is small (< 0.02 ml/g) at an MOC of less than 1.5 wt% (30-day samples), and then proportionally increases with increasing MOC. The Top sample (180 days) had the highest volume, about 20% of the total volume for the fresh catalyst. In contrast, no clear relationship was observed if the volume of sealed space was plotted against coke yield. These observations indicate that the sealed space is due to the complete plugging of pores by metal deposits.

Table 3 Elemental Analysis and Aromaticity of Coke Isolated from the Middle Sample

<table>
<thead>
<tr>
<th>Run time [days]</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>H/C</th>
<th>fa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Middle</td>
<td>5</td>
<td>43.6</td>
<td>2.3</td>
<td>1.0</td>
<td>0.63</td>
</tr>
<tr>
<td>15</td>
<td>45.4</td>
<td>2.1</td>
<td>1.1</td>
<td>0.55</td>
<td>0.89</td>
</tr>
<tr>
<td>30</td>
<td>50.9</td>
<td>2.2</td>
<td>1.1</td>
<td>0.52</td>
<td>0.91</td>
</tr>
<tr>
<td>90</td>
<td>49.1</td>
<td>2.2</td>
<td>1.3</td>
<td>0.53</td>
<td>0.91</td>
</tr>
<tr>
<td>180</td>
<td>41.4</td>
<td>2.1</td>
<td>1.1</td>
<td>0.60</td>
<td>0.89</td>
</tr>
</tbody>
</table>

a) wt% based on fresh catalyst as reference.
3.3. Activities of Used Catalysts

The remaining HDS and hydrogenation activities of the used catalysts were evaluated by using model compounds. By using model compounds, the poisoning of active sites can be determined regardless of the diffusion effect because the model compounds are much smaller than the catalyst pore size. Figure 6 shows the result of thiophene pulse reaction with the used catalysts. The thiophene HDS activity of the Bottom sample up to 30 days of aging was similar or slightly higher than that of the Top sample, but was lower after 30 days of aging. The same tendency was observed for 1-MN hydrogenation activity (Fig. 7). The results of these activity tests indicate that catalyst at the bottom of the reactor is deactivated more than that at the top during the initial stage of the run, and that the deactivation mechanism changes after 30 days.

HDS activity tests of fresh and used catalysts (30 and 180 days) were done using real feed (HDM oil). Figure 8 shows the results. After 30 days of aging, both the Top and Bottom samples obtained after 30 days showed a slightly lower HDS activity than did the fresh catalyst, whereas the Top and Bottom samples showed no difference in activity. In contrast, after 180 days of aging, the Bottom sample (180 days) showed a significantly higher HDS activity than did the Top sample, agreeing well with the results from the activity tests with model compounds. This agreement suggests that when the real feed is used, the diffusion of the reactants into catalyst pore is not so limited.

3.4. Deactivation Mechanism of HDS Catalyst

Coke and metal deposits are the main cause of the deactivation of HDS catalysts. In a long-term run, the catalyst deactivation is divided into three stages: an initial rapid deactivation by coke (SOR), a gradual deactivation by metal deposits (MOR), and a final catastrophic fouling by plugging of pore mouths (EOR). In our study, the period up to 30 days corresponds to the SOR because the activities became stable after 30 days (see Fig. 1). During SOR, deactivation by coke rather than by metals would be predominant because for 30 days of aging, the Top sample, which contains less coke and more metals than the Bottom one, showed a higher activity in the tests with model compounds and with real feed. The pore size (2-3 nm), which selectively disappeared at SOR, coincides relatively well with the size of asphaltenes (coke precursor). Therefore, deactivation at SOR might be due in part to the plugging of pores by asphaltenes.

Based on the deactivation mechanism at MOR determined in the present study, metal deposits predominantly deactivate the catalyst. Our characterization of used catalysts by using elemental analyses, pore radius distribution, and activity tests support this conclusion. In particular, calculation further supported the generation of sealed space as well as the pore narrowing.

4. Conclusions

Long-term aging tests under constant temperature...
were done to investigate the deactivation mechanism of HDS catalyst in a two-stage RDS process (HDM/HDS). Our results show that coke was reduced at MOR by the hydrogenation reaction with Ni-sulfide deposited on the catalyst. This implies that coke level is not likely to reach equilibrium even at a constant temperature.

Based on elemental analyses, measurement of pore radius distribution, and activity tests of used catalysts, the following conclusions can be made about the deactivation mechanism:

1. deactivation at SOR by coke is more significant than that by metals
2. plugging of catalyst pores with a radius of 2-3 nm at SOR are presumably by asphaltenes
3. deactivation by metal deposits is predominant at MOR
4. metal deposits cause pore mouth plugging with the generation of sealed space.

Acknowledgments
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References
要 旨

二段直接脱硫プロセスにおける脱硫触媒の劣化（第4報）
長期等温試験における劣化機構の解明

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二段直接脱硫プロセスにおける後段脱硫触媒の長期等温劣化実験を試験メタル処理したアラブヘビーカール複雑油を用いて行い、その劣化機構について検討した。触媒上のコーカスは、運転初期に急激に増加したが、30日を境に減少した。この原因は、蓄積した硫黄ニッケルの水素化作用であると結論づけられた。細孔分布測定の結果、運転初期には径の小さな縄孔の消失（2nm付近）および全体的な縄孔の狭まりが観測された。前者はアスファルチンの分子サイズとほぼ一致することより、アスファルチンによる細孔の完全閉鎖と推定される。また、運転中期においては、メタル蓄積による細孔の狭まりおよび閉鎖不完全性の存在が確認された。以上の結果および使用済み触媒の残存活性評価試験から、長期等温運転における初期はコーカス劣化が、中期はメタル劣化が支配的であることが明らかとなった。


Keywords

Residue desulfurization, Deactivation mechanism, Long-term test, Pore plugging, Coke formation