Deactivation of Hydrodesulfurization Catalysts in Two-stage Resid Desulfurization Process (Part 7) Influence of Reaction Conditions at the First Stage on Deactivation Mechanism

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Aging tests of hydrodesulfurization (HDS) catalysts were performed in the operation mode of constant sulfur-removal using product oils derived from hydrodemetallization (HDM) of Kuwait atmospheric residue under various reaction conditions. The used catalysts obtained were characterized to clarify the effects of HDM reaction conditions, focusing on reaction temperature, at the first-stage on the deactivation mechanism of the HDS catalysts at the second-stage. A good correlation occurred between the fouling rate of HDS catalysts and the content of hard-coke (insolubles in light gas oil) on the used HDS catalysts when the HDM and HDS temperatures were below 400°C, indicating that coke formation causes the HDS catalyst deactivation. When the HDM temperature at the first-stage was increased from 400 to 430°C, the HDS catalysts showed an increase in the fouling rate, despite a decrease in hard coke and metal deposits. This unusual phenomenon could be explained by introducing the concept of soft coke (solubles in light gas oil), which was removed during the preparation of used catalysts. Furthermore, details about the effect of HDM temperature on the deactivation mechanism of HDS catalysts were discussed.

1. Introduction

Understanding of the deactivation mechanism of catalysts for resid desulfurization (RDS) is important for the efficient operation of RDS units in refineries, for the design of catalyst systems, and for the improvement of catalyst performance. In general, metal deposits and coke formation are the main causes of RDS catalyst deactivation. Deactivation of RDS catalysts due to metal deposits is attributed to the narrowing or plugging of the catalyst pores and significantly influences the run length at middle of run (MOR). Therefore, because a catalyst spends most of its life in the MOR, the overall life of a catalyst is governed by the amount of metal deposits. On the other hand, deactivation of RDS catalysts due to coke is attributed to the coverage of active sites and to the plugging of catalyst pores. This deactivation by coke is dominant at start of run (SOR).

Two types of coke deposits on used RDS catalysts have been reported. For example, Ternan et al. classified these types of coke as reactive coke, which is subsequently converted to products, and unreactive coke, which remains to block catalytic sites. Zeuthen et al. classified these as type 1, which shows a CO2 peak around 460°C in temperature-programmed oxidation measurements, and type 2, which shows this peak around 620°C and is associated with vanadium deposits. With a solvent-separation method, Snape and coworkers separated the coke on used catalysts into soft coke, which is chloroform solubles, and hard coke, which is chloroform insolubles. Despite being inconsistent, these classifications of coke could be useful in clarifying details of catalyst deactivation by coke.

We have been studying the deactivation of hydrodesulfurization (HDS) catalysts in a two-stage RDS process, which consists of hydrodemetallization (HDM) in the first-stage and HDS in the second-stage. We found that coke formation is a primary cause of HDS catalyst deactivation at MOR. Thus, the deactivation mechanism of the HDS catalysts in two-stage RDS processes differs from that in conventional RDS processes. To further clarify the coke deactivation of HDS catalysts in two-stage RDS processes, in this study we characterized used catalysts, which we obtained in a previous study by doing aging tests to investigate the effect of HDM reaction conditions on the fouling of HDS catalysts. In this study, we used the concept of soft coke and hard coke to help clarify the deactivation mechanism of HDS catalysts in the second-stage. Here, soft coke and hard coke are defined as the solubles and the insolubes, respectively, when treated with light gas oil (LGO) at 350°C for 6 h. Using this concept, we studied the dependence of the
deactivation mechanism of HDS catalysts on HDM reaction conditions, focusing on temperature.

2. Experimental

2.1. Materials

HDM catalysts contained MoO$_3$ (4.2 wt%) and HDS catalysts contained MoO$_3$ (10.5 wt%), NiO (0.7 wt%) and CoO (1.2 wt%) on an alumina support. Both catalysts were commercially available and used as received (1/22 inch trilobe extrudate). Details on the physical properties of both catalysts are described elsewhere$^{13}$.

Kuwait atmospheric residue (KW-AR) was used as the feedstock for HDM reaction. The feedstock contained sulfur of 4.45 wt% and metals (Ni + V) of 81 ppm; other properties are listed in Table 1.

2.2. HDM Reaction (preparation of feed for HDS reaction)

The HDM reaction was carried out with 300 ml of HDM catalyst in a bench-scale unit. We did eight runs, each under different reaction conditions as shown in Table 2. Properties of the product oil (HDM oil) are also presented in Table 2.

2.3. HDS Reaction (aging test of HDS catalyst)

Before the aging tests of the HDS catalyst, the HDS catalyst was pre-aged with KW-AR to shorten the period of SOR. Namely, KW-AR was treated at 370°C for 3 days, 375°C for 3 days and 380°C for 10 days. After the treatment, the HDS catalyst was in situ washed in the reactor with LGO at 350°C for 6 h to remove KW-AR and soft coke. The catalyst taken out of the reactor was then washed with toluene and dried at 110°C in vacuum overnight, obtaining “aged catalyst.” The aged HDS catalysts were kept in vacuum until they were used for the aging tests.

With the aged HDS catalyst (15 ml) and the HDM oil as feed, aging tests were carried out for 20 days under the reaction conditions shown in Table 3: H$_2$ pressure of 8.0 MPa, liquid hourly space velocity

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Table 1 Properties of Feedstocks (KW-AR)

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<tr>
<th>Property</th>
<th>Density [g/ml @15°C]</th>
<th>Viscosity [mm²/s @50°C]</th>
<th>CCR [wt%]</th>
<th>Sulfur [wt%]</th>
<th>Nitrogen [wtppm]</th>
<th>Ni [wtppm]</th>
<th>V [wtppm]</th>
<th>Asphaltene [wt%]</th>
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Table 2 HDM Reaction Conditions and Properties of HDM Oils

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<th>Temperature [°C]</th>
<th>Pressure [MPa]</th>
<th>LHSV [h⁻¹]</th>
<th>Properties</th>
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<td>Run-4</td>
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</table>

<table>
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<td>11</td>
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<td>1.6</td>
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<td>&lt;1</td>
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Table 3 HDS Reaction Conditions and Fouling Rate of HDS Catalysts

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<tr>
<th>Reaction conditions</th>
<th>Pressure [MPa]</th>
<th>LHSV [h⁻¹]</th>
<th>H₂/Oil [Nm³/kJ]</th>
<th>IT [°C]</th>
<th>FT [°C]</th>
<th>Target S [wt%]</th>
<th>FR [°C/day]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Run-1</td>
<td>Run-2</td>
<td>Run-3</td>
<td>Run-4</td>
<td>Run-5</td>
<td>Run-6</td>
<td>Run-7</td>
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<td>IT [°C]</td>
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<td>378</td>
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<td>353</td>
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<td>380</td>
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<tr>
<td>FT [°C]</td>
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<td>412</td>
<td>401</td>
<td>419</td>
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<td>Target S [wt%]</td>
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<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
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<td>FR [°C/day]</td>
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<td>0.72</td>
<td>1.10</td>
<td>0.86</td>
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a) Initial temperature. b) Final temperature. c) Fouling rate at MOR.
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(LHSV) of 0.5 h⁻¹, H₂/Oil of 840 Nm³/kl. The re-
action temperature was raised to achieve a constant sul-
fur-content in product oil (see Table 3). The in situ
LGO-washing at 350°C was performed for 6 h after the
tests.

The fouling rate at MOR was determined as increase
in temperature/day for each run after a rapid fouling;
the initial rapid fouling for each run, which was proba-
bly due to the adsorption of soft coke, was observed for
3 days. For the Run-8, the aging test was forced to
stop at 9 days of the run time since ΔP generated.

2.4. Preparation and Characterization of Used
Catalysts
The catalyst removed from the reactor was washed
with toluene in a Soxhlet apparatus to remove LGO,
and finally, dried at 110°C under a vacuum oven
ight, obtaining used catalyst. The used catalyst contains
the hard coke, but not the soft coke.

Contents of C, H and N on the used catalysts were
measured on a CHN coder (YANAKO MT-5) and sul-
fur content was determined by using the Leco method.
The metal contents (e.g., Ni and V) were analyzed 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
Coolter Omunisorp-360. The results were summa-
rized in Table 4.

2.5. Preparation and Characterization of Asphalt-
enes and Resins
Asphaltenes were defined as n-heptane-insoluble and
toluene-soluble substances and were isolated from the
HDM oils according to the method described in our
early works²⁵,²⁶. Resins were separated from the n-
heptane solubles (maltene) by column chromatography
as final elution materials. Aromaticity (fa) of
asphaltenes and resins was determined by ¹³C-NMR
(JEOL JNM LA400), where a relaxation agent, chromi-
um trisacetylatedonate (Cr(acac)₃, 0.02 M), was added
to obtain quantitative ¹³C-NMR spectra. The mea-
surements were done for 20,000 scans in a gated proton
decoupled mode.

3. Results and Discussion

3.1. Characterization of Used HDS Catalysts
Table 4 shows the characteristics of the fresh cata-
lyst, aged catalyst, and used catalysts. Using these
data (Runs 2, 3, 5 and 8), we plotted the surface area,
porc volume, and average pore diameter of the used
catalysts against HDM temperature at the first stage in
Fig. 1. The surface area and pore volume only
slightly changed for temperatures up to 390°C, and
then increased in the higher temperature. This varia-
tion can be explained as follows; the higher the HDM
temperature, the lower the required HDS temperature at
the second stage in the operation mode of constant sul-
fur content as shown in Table 3. This low severity in
HDS operation results in high surface area and pore
volume. Note that the average pore diameter, which
we calculated assuming that the catalyst pore was
cylindrical, only slightly changed with increasing HDM
temperature, suggesting that the plugging of pores was
not significant.

Figure 2 shows the hard coke and metal deposit
contents on the used catalyst as a function of HDM
temperature. The hard coke content and metal
deposits were calculated by subtracting the contents for
the aged catalyst from those for the used catalysts,
namely, the amount accumulated during the 20 days of
aging. Both hard coke and metal deposits decreased
with increasing HDM temperature. This decrease is
understandable, because when the HDM temperature
increases, the HDM product oil has less metal, and
therefore the HDS temperature in the second stage

Table 4 Characterization of Fresh, Aged and Used HDS Catalysts (fresh catalyst basis)

<table>
<thead>
<tr>
<th>Elemental analyses</th>
<th>Fresh</th>
<th>Aged¹</th>
<th>Run-1</th>
<th>Run-2</th>
<th>Run-3</th>
<th>Run-4</th>
<th>Run-5</th>
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</table>

a) Pre-aged catalyst used for aging tests.
decreases, thus causing a decrease in the coke and metal deposits on HDS catalysts. When the HDM temperature was 430°C, accumulation of hard coke and metals was so small, as to be considered negligible.

3.2. Deactivation Mechanism of HDS Catalyst at Second Stage

Deactivation mechanism of resid hydrotreating catalyst at MOR is generally accepted to result from the plugging of the pores by metal deposits (metal deactivation)\(^3\),\(^12\). This is not always true for the deactivation of the catalysts at the second stage in two-stage RDS processes\(^3\)^{13}–\(^15\). In a previous study, we concluded that, under the reaction conditions studied here in the current study as well, the HDS catalysts at the second stage were deactivated mainly by coke\(^3\),\(^14\). This conclusion was based on our experimental results summarized as follows: (a) an increase in metal deposits determined by analyses of HDS product oil did not increase the fouling rate\(^3\), and (b) a good correlation occurred between the fouling rate and aromaticity of asphaltenes, which can be regarded as a coke precursor\(^19\). Despite that conclusion, interpreting the high fouling rate of 1.25°C/day when the HDM temperature was 430°C is difficult (see Run-8 in Table 3), because the contents of hard coke and metal deposits were negligible, as shown in Fig. 2. To confirm the coke deactivation, we plotted the fouling rate as a function of the content of hard coke and that of metal deposits (Fig. 3). Although no clear correlation occurred between the fouling rate and metal deposits, a good correlation occurred between the fouling rate and hard coke content, indicating that coke is the primary cause of the deactivation of the HDS catalyst. The result for Run-8 (HDM temperature of 430°C) deviates too far from the correlation line to be included in the correla-
tion; the point for Run-5 might also be regarded as a deviated point from the correlation line like the point for Run-8. Figures 2 and 3 clearly show that deactivation factors other than hard coke and metal deposits need to be considered when the HDM temperature is above 410°C. The used catalysts were characterized after in situ washing with LGO, and thus they did not contain soft coke. Therefore, soft coke contributes to the deactivation of the HDS catalysts at reaction state. In general, adsorption of asphaltenes and/or resins on acidic sites on the catalysts is likely to occur19). The soft coke derived from these asphaltenes and resins might cause catalyst deactivation by its adsorption on the catalyst. Compared to asphaltenes and resins treated below an HDM temperature of 400°C, those treated above 400°C have higher aromaticity (fa) as shown in Table 2. This higher fa of asphaltenes and resins could be favorable for the adsorption on HDS catalysts. Generally, the size of asphaltenes and/or resins after the HDM becomes smaller with an elevated HDM temperature, especially above 400°C25,26). This decrease in size could help asphaltenes and resins diffuse into the HDS catalyst and then increase an amount of their adsorption, resulting in the catalyst deactivation by the soft coke.

It would be useful to note about the soft coke from our another experiment; the same aging tests as those in this study were performed with HDM oils derived from Arabian light atmospheric residues (AL-AR) and the soft coke were collected from the used HDS catalysts by toluene washing and subsequent LGO washing. The LD-MS measurements suggested that, in the case of AL-AR, the soft coke consisted mainly of asphaltenes in the HDM oils since the average molecular weight (MW) and MW distribution for the soft coke were similar to those for the asphaltenes in the HDM oils.

Based on our results, the probable proportion of metal, hard coke, and soft coke to HDS catalyst deactivation as a function of HDM temperature is shown in Fig. 4. By comparing the frequency factors of the HDS catalyst before and after LGO washing, we estimated the effect of soft coke on the entire catalyst deactivation when HDM temperature was 370°C, and found that 15% of the entire deactivation was due to soft coke13). In this estimation, we assumed that the effect of hard coke and that of metals were the same, because it was difficult to accurately distinguish between them. When the HDM temperature is increased up to about 400°C, the effect of soft coke would be only slightly changed because asphaltenes and resins, which are considered to act as soft coke, do not show a significant change in either their chemical structure or molecular weight distribution20). In contrast, the effect of metal deposits gradually decreases because more metals are removed at the first stage as the HDM temperature increases. When the HDM temperature is elevated above 400°C, the effect of soft coke becomes significant, finally being responsible for the entire deactivation at 430°C. The decrease in the hard coke effect at HDM temperatures higher than 400°C, corresponding to the increase in the effect of soft coke, can be explained by considering the following reaction:

soft coke (asphaltenes and resins) $\rightarrow$ hard coke

As the HDM temperature increases, the HDS temperature at the second stage decreases in the operation mode of constant sulfur content in the products (Table 3). This HDS temperature decrease suppresses the conversion of soft coke into hard coke.

The proportionalities in catalyst deactivation shown in Fig. 4 are for constant HDM reaction conditions other than temperature. If the other reaction conditions are changed, a different view of the deactivation mechanism is expected, even for the same HDM temperature. For example, among the runs done at 410°C under different LHSV and H2/Oil conditions at the first-stage, Runs 6 and 7 showed higher hard-coke content than did Run-5, indicating a greater effect of hard coke on HDS catalyst deactivation. These different deactivation mechanisms result from the change in asphaltene quality (e.g., fa and structure), which is influenced by the reaction conditions in both HDM and HDS.

4. Conclusions

Used HDS catalysts obtained by aging tests were characterized to clarify the effect of HDM operating conditions, focusing on reaction temperature, on the deactivation mechanism of HDS catalyst at the second-stage. The results show that the HDS catalyst was deactivated by coke rather than by metal deposits. Furthermore, we introduced the concept of soft coke and hard coke to clarify the HDS catalyst deactivation by coke. With this concept, the following results
about the effect of HDM temperature on the deactivation mechanism of HDS catalysts were deduced:
(1) effect of metal deposits decreases with increasing HDM temperature.
(2) effect of hard coke relatively increases up to 400°C.
(3) effect of soft coke starts to increase around 400°C.
In addition, we proposed the conversion of soft coke to hard coke, possibly influenced by HDS temperature, to understand the effect of HDM temperature on deactivation factors.

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References