Deactivation of Hydrodesulfurization Catalysts in Two-stage Resid Desulfurization Process (Part 3)
Influence of Asphaltenic Content of Feedstock and Hydrodesulfurization Temperature at Second-stage

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Aging tests of a hydrodesulfurization (HDS) catalyst in a two-stage resid desulfurization process, which consisted of hydrodemetallization (HDM) and HDS, were carried out on a small-scale pilot plant. The purpose was to determine the influence of asphaltenic content of feedstock and that of HDM temperature in the first stage on HDS catalyst deactivation in the second stage under various reaction temperatures (HDS temperature). As feedstocks, resids of various asphaltenic content were prepared by adding propane deasphalted (PDA) asphalt to atmospheric residue of Arabian light crude. Results show that at HDS temperatures below 400°C, an increase either in asphaltenic content or in HDM temperature gradually increased the fouling rate. and at HDS temperatures above 400°C, this increase rapidly increased the fouling rate. These results suggest that, at lower HDS temperatures, coke precursor formed in the HDM reaction plays a key role in the HDS catalyst deactivation, and at higher HDS temperatures, coke precursor formed in the HDS reaction also significantly affects the HDS catalyst deactivation. The results also suggest that in the deactivation mechanism of HDS catalyst in the second stage, coke had a stronger effect on the HDS catalyst deactivation than did metal deposits.

1. Introduction

The resid desulfurization (RDS) process has widely been adopted in refineries to produce low sulfur fuel oil. In this process, fixed-bed reactors are most commonly used, where the catalyst life is determined by the performance of the catalyst system and by the feedstock properties. Recently, new guard processes involving ebullated beds, moving beds, or fixed beds have been developed to protect the downstream catalyst in a fixed bed from its deactivation by metal deposits. For the optimal utilization of the entire unit system, the effect of operating conditions of those guard systems on the deactivation of the downstream catalyst must be determined. However, few reports have discussed this effect.

The main causes of deactivation of the catalyst for RDS are coke and metal deposits. Asphaltenes are generally considered as sources of coke; for example, compared with the non-treated oil, propane deasphalted (PDA) oil produces less coke on the catalyst. Therefore, asphaltene behavior must be clarified to understand the deactivation by coke. Deactivation by metal can be explained by the plugging of the catalyst pores, namely, limitation of reactant diffusion into catalyst pores. The metal deactivation at middle of run (MOR) is a significant factor in determining the catalyst life in a conventional RDS process.

In a previous study, we investigated the effect of hydrodemetallization (HDM) conditions and crude-oil sources on the life of hydrodesulfurization (HDS) catalyst in a two-stage RDS process (HDM/HDS). We found that (a) optimum HDM temperature exists that minimizes the HDS catalyst deactivation, although this optimum varies with the source of crude oil, (b) coke formation has the dominant effect on the HDS catalyst deactivation at MOR, and (c) asphaltene quality (aromaticity) rather than quantity is the key in coke formation. These results were obtained from aging tests done under a constant product sulfur operation. In this operation mode, the influence of the HDS temperature as well as that of HDM operating conditions on the deactivation was included because the HDS temperature was changed to achieve constant sulfur content in the product.

Here, we studied the effect of HDS temperature on the HDS catalyst deactivation by doing aging tests under a constant HDS temperature operation. In addition, to analyze the mechanism of catalyst deactivation, especially coke deactivation, we studied the effect of
asphaltene content in the feedstock. This further investigation of coke deactivation is significant in understanding the HDS catalyst deactivation in a two-stage RDS process because, as mentioned above, the deactivation at MOR is due to coke, unlike general deactivation, which is due to metal deposits.

2. Experimental

2.1. Catalysts and Feedstocks

Both HDM and HDS catalysts were supplied from Japanese catalyst companies and used as received (1/22-inch trilobe extrudate). The HDM catalysts contained MoO₃ (4.2 wt%) on alumina support and their surface area (SA) was 200 m²/g, pore volume (PV) was 0.85 ml/g, and average pore size (APS) was 17 nm. The HDS catalysts contained MoO₃ (10.5 wt%), NiO (0.7 wt%), and CoO (1.2 wt%), and the SA was 211 m²/g, PV was 0.64 ml/g, and APS was 12 nm.

Three kinds of residues were prepared as feedstocks: Arabian light atmospheric residue (AL-AR), a mixture of AL-AR containing 20 wt% of AL-base PDA asphalt (flux), and a mixture of AL-AR containing 40 wt% flux. The properties of the feedstocks are listed in Table 1. By mixing the flux with AL-AR, we could control the asphaltene content in the range from 3.0 to 5.5 wt% and the metal (Ni + V) content from 45 to 77 wppm.

2.2. Feedstock Preparation (HDM treatment)

The HDM catalysts (300 ml) were loaded into a trickle-bed flow reactor and presulfided at 300°C with a mixture of light gas oil and di-t-butyl-disulfide (total S = 3.0 wt%). After the presulfiding, HDM reactions were carried out with the three feedstocks to prepare a feedstock for the subsequent HDS reaction (aging tests of HDS catalysts). HDM temperatures of 390 and 410°C were selected to obtain asphaltenes with fairly different aromaticity. The other reaction conditions were not changed: pressure of 14 MPa, liquid hourly space velocity (LHSV) of 0.5 h⁻¹, and H₂/Oil of 2000 scfb. The properties of the HDM product oils obtained are shown in Table 2.

2.3. Aging Tests

The aging tests of HDS catalysts (15 ml) were done for the six HDM product oils by using a micro flow reactor. Presulfiding was done using the same procedure used in the HDM reaction. To examine the effect of HDS temperature on the deactivation of HDS catalysts, we chose three HDS temperatures; 370, 390, and 410°C. During the aging tests, the HDS temperatures were consecutively changed from 370 to 390°C and finally to 410°C. Other HDS reaction conditions were not varied; pressure of 14 MPa, LHSV of 0.5 h⁻¹, and H₂/Oil of 5000 scfb.

2.4. Extraction and Analysis of Asphaltenes

Asphaltenes are defined as n-heptane-insoluble and toluene-soluble substances, and were prepared by the following procedure. The original feedstock or the bottom fraction (380+°C) of each of the HDM product oils (10 g) was refluxed in n-heptane (300 ml) for 24 h with a mixture of light gas oil and di-t-butyl-disulfide (total S = 3.0 wt%). After the presulfiding, HDM reactions were carried out with the three feedstocks to prepare a feedstock for the subsequent HDS reaction (aging tests of HDS catalysts). HDM temperatures of 390 and 410°C were selected to obtain asphaltenes with fairly different aromaticity. The other reaction conditions were not changed: pressure of 14 MPa, liquid hourly space velocity (LHSV) of 0.5 h⁻¹, and H₂/Oil of 2000 scfb. The properties of the HDM product oils obtained are shown in Table 2.
The residue was thoroughly washed with \( n \)-heptane in a Soxhlet extraction apparatus, then extracted with toluene. After toluene was evaporated, the extracts (asphaltenes) were dried at 110°C under vacuum overnight.

The aromaticity of the asphaltenes was determined by using \(^{13}\)C-NMR (Bruker MSL400). The measurements were done in liquid state (in CDCl\(_3\)) for 50,000 scans in a gated proton decoupled mode, where chromium trisacetylacetonate (0.02 M) was added to obtain quantitative spectra.

3. Results and Discussion

3.1. Aging Tests of HDS Catalysts

Figures 1 and 2 show the results for the aging tests of the HDS catalysts when the HDM temperature was 390 and 410°C, respectively. In these figures, the vertical axis indicates the normalized HDS temperature (\( T_n \)); \( T_n \) was calculated to adjust the product sulfur content to be 0.3 wt%, assuming that the kinetic order with respect to desulfurization and to the activation energy was 1.5 and 96 kJ/mol, respectively. For all three feedstocks, a rapid increase in the fouling occurred in the initial stage of the run (up to 100 h), possibly due to coke formation.

When the HDM temperature was 390°C (Fig. 1), the fouling curves for AL-AR+20%Flux and AL-AR+40%Flux were similar and their \( T_n \) levels were significantly higher than those for AL-AR. This result can be explained by the general tendency of sulfur in HDM product oils to condense, especially in asphaltenes and in feedstocks with Flux that have higher asphaltene content compared to that in AL-AR (see Table 2).

When the HDM temperature was 410°C (Fig. 2), the fouling curve for AL-AR remained within the lower \( T_n \) region (less than 380°C). The difference in \( T_n \) between AL-AR+20%Flux and AL-AR+40%Flux gradually increased as HDS temperature increased, although the initial rapid fouling was similar. Details on this difference will be discussed in section 3.3.

3.2. Effect of Asphaltene on HDS Catalyst Deactivation

In a previous study, we found that fouling rates of HDS catalysts obtained from aging tests under a constant sulfur operation were influenced by the combined effect of asphaltene quality and HDS temperature, regardless of asphaltene content. Therefore, systematic investigation is needed on how the asphaltene content affects the HDS catalyst deactivation under the constant HDS temperature operation. In Fig. 3, the fouling rates of the HDS catalysts are plotted against the asphaltene contents in the HDM product oil. When the HDM temperature was 410°C, the fouling rate increased with asphaltene content. The similar trend was observed for HDM temperature of 390°C, except for the HDS temperature 410°C. These observations indicate that the asphaltene content is one factor that influences the HDS catalyst deactivation under a constant HDS temperature. The insensitivity of the fouling rate to asphaltene content observed when the HDM temperature was 390°C and the HDS temperature was 410°C indicates that only a small amount of asphaltene (0.8 wt%) is sufficient to highly deactivate the HDS catalysts. This is probably because most of the asphaltene in the HDM oils have a potential to act as coke precursor and then form coke in HDS reaction. On the other hand, when both HDM and HDS temperatures were 410°C, the increase in the fouling rate to asphaltene content suggests that the HDM oils contain less amount of such asphaltene that act as coke precursor, compared to the case of HDM temperature of 390°C. This results from the higher consumption of such asphaltene at HDM temperature of 410°C.

The HDM temperature is expected to affect the HDS catalyst deactivation because it affects both the quantity and quality of asphaltene. A higher HDM temperature yields a lower asphaltene content and a higher aromaticity of the asphaltene (see Table 1). If the foul-
ing rate in Fig. 3 is approximated by a line, the slope describes the impact of asphaltene quality on the fouling rate; this slope is thus defined as an increase in the fouling rate per 1 wt% of asphaltenes. These results are summarized in Table 3. Both Table 3 and Fig. 3 clearly show the asphaltenes obtained at HDM temperature of 410°C enable to increase a fouling rate of HDS catalyst more than those of 390°C, independent of the HDS temperature. In other words, the change in asphaltene quality by HDM reaction affects the HDS catalyst deactivation. The increase in asphaltene aromaticity due to a high-temperature HDM treatment could be the main cause of HDS catalyst deactivation, similar to the effect seen in a constant product sulfur operation\(^{1,5}\).

### 3.3. Effect of HDS Temperature on HDS Catalyst Deactivation

Figure 4 shows the change in fouling rate as a function of HDS temperature for each feedstock. For AL-AR and AL-AR+20%Flux, the fouling rate slightly increased with increasing HDS temperature up to 390°C, then rapidly increased with increasing HDS temperature above 400°C. In contrast, for AL-AR+40%Flux, which had the highest asphaltene content of the three feedstocks, the fouling rate was high even at HDS temperatures lower than 400°C. Interestingly, the effect of HDM temperature was significant at HDS temperature higher than 400°C for AL-AR and AL-AR+20%Flux and at HDS temperature lower than 400°C for AL-AR+40%Flux. These observations suggest that HDS temperature, asphaltene content, and HDM temperature have a combined effect on the deactivation of HDS catalyst. However, if we assume that the HDS catalyst deactivation is determined by the balance of coke precursors formed by HDM reaction and by HDS reaction, the role of the above three factors (HDS temperature, asphaltene content, and HDM temperature) might be as follows. When the HDS temperature is lower than 400°C, the coke precursor produced by HDM reaction was the dominant factor in HDS catalyst deactivation. Thus, higher asphaltene content and higher HDM temperature enhance the formation of coke precursor. When the HDS temperature is higher than 400°C, the coke pre-
cursor produced in the second stage (HDS reaction itself) significantly contributes to yield coke precursor, and thus the higher asphaltene content and the lower HDM temperature produced higher deactivation rates because more asphaltenes still remained in the HDM product oil. The influence of metal on HDS catalyst deactivation is discussed in the next section.

3.4. Deactivation Mechanism of HDS Catalyst

Deactivation of residue hydrotreating catalysts or catalyst systems at MOR is generally governed by metal deposition\(^8\)\(^{-}10\). For a two-stage RDS process, deactivation of the catalyst in the second stage is not the case because the reaction conditions in the first stage affect the deactivation\(^4\),\(^5\). To understand the deactivation mechanism of HDS catalyst in the present study, we determined the relationship between the fouling rate and the metal deposit on the catalyst (MOC) during the aging tests (Fig. 5). In Fig. 5, data for the plot were divided into two figures, (a) and (b), in terms of HDS temperature because contribution of the coke precursor to the HDS catalyst deactivation significantly changes at the HDS temperature of 400°C; the upper figure (a) is with the data obtained at HDS temperatures of 370 and 390°C and the lower one (b) is with the data at 410°C. The MOC was calculated from the difference between the metal content (Ni + V) in the HDM product oil and that in the HDS product oil. If a linear approximation is used, the y-axis intercept indicates the fouling rate determined only by coke deactivation. For an HDM temperature of either 390 or 410°C in the upper figure (a), the fouling rate due only to coke deactivation is 0.48 and 0.51°C/day, respectively, which is more than half of the fouling rate due to both coke deactivation and metal deposits. For an HDM temperature of either 390 or 410°C in the lower figure (b), the values of the y-axis intercept are 1.1 and 0.78°C/day, respectively, which is also more than half of the fouling rate due to both coke and metal deposits. These results clearly indicate that the HDS catalyst deactivation in a two-stage RDS process is due to greater coke formation rather than to metal deposition. Furthermore, high HDM temperature enhances coke deactivation of the HDS catalyst if the HDS temperature is below 400°C, but low HDM temperature does if the HDS temperature is above 400°C. This supports our assumption in section 3.3., in which the importance of balancing the coke precursors formed by HDM reaction and by HDS reaction.

3.5. Factors Influencing HDS Catalyst Deactivation

It would be useful to summarize the relationship between factors that influence fouling rate of the HDS catalyst in two-stage RDS. The factors are feed properties such as metal content and asphaltene content, HDM temperature and HDS temperature. Concerning the coke deactivation of the HDS catalyst, quality (aromaticity) and quantity of asphaltenes in HDM oils are keys and changed by HDM temperature; the asphaltene aromaticity increases and the asphaltene content in HDM oils decreases with the increase in HDM temperature. The former has an effect to enhance the HDS catalyst deactivation (see Table 3), but the latter has the reverse effect. If the HDS temperature is constant and below 400°C, the fouling rate of HDS catalyst is determined by the balance of both effects because coke precursor formed in HDM reac-

![Fig. 5 Effect of Metal Deposition (MOC) on HDS Catalyst Deactivation; (a) HDS temperatures of 370 and 390°C, (b) HDS temperature of 410°C](image-url)

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<th>HDS temperature [°C]</th>
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a) An increase in fouling rate per 1 wt% of asphaltene content in HDM oil (unit: °C/day/ wt%).

Table 3 Effect of HDM Temperature (aromaticity of asphaltene) on Fouling Rate of HDS Catalyst

![Table 3 Effect of HDM Temperature (aromaticity of asphaltene) on Fouling Rate of HDS Catalyst](image-url)
The increase of HDS temperature increases the fouling rate if the asphaltene content in HDM oils and the HDM temperature are constant (see Fig. 4). Especially, higher HDS temperature than 400°C gives a high fouling rate because the coke precursor formed in the HDS reaction contributes to deactivate the HDS catalysts more than that formed in the HDM reaction.

The increase in asphaltene content in original feeds increases the fouling rate under any reaction conditions of HDM and HDS except when HDM and HDS temperatures are 390 and 410°C, respectively. This exception suggests that a small amount (ca. 0.8 wt%) of asphaltenes with low aromaticity is enough to highly deactivate the HDS catalyst and that a greater amount than 0.8 wt% of asphaltenes does no contribute towards the HDS catalyst deactivation.

For metal deactivation of the HDS catalyst, such factors as higher metal content in the original feed, lower HDM temperature and higher HDS temperature bring about a larger amount of metal deposits on the HDS catalyst. However, such metal deposit is less significant than coke for the deactivation of the HDS catalyst in two-stage RDS process (see Fig. 5).

4. Conclusions

The aging tests were performed with AL-base residues to study the effects of asphaltene content and of HDS temperature on the HDS catalyst deactivation. In addition, the effect of HDM temperature was also studied. The increase in asphaltene content and in HDS temperature enhanced the fouling of the HDS catalysts. The increase in HDM temperature changed both quality and quantity of asphaltenes, influencing the deactivation of HDS catalysts. At HDS temperatures below 400°C, the formation of coke precursor in HDM reaction played a key role in the HDS catalyst deactivation. On the other hand, at HDS temperatures higher than 400°C, the formation of the coke precursor in the HDS reaction itself was significant. In summary, coke had much stronger influence on HDS catalyst deactivation than did metal deposits.

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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3報）
原料油のアスファルテンおよび水素化脱硫温度の影響

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アスファルテン量の異なる3種類のアラブライド残油を用いて、二段残油水素化脱硫プロセス（HDM/HDS）の後段HDS触媒劣化に及ぼすアスファルテンおよび脱硫反応速度の影響を調べた。触媒劣化は、劣化試験より得られる劣化速度を指標とした。HDS反応温度が400℃以下の場合、アスファルテン量および前段HDM反応温度の増加とともに劣化速度は増加した。一方、HDS反応温度が400℃以上では、アスファルテン量によらず高い劣化速度を示した。これらの結果より、HDS反応温度が400℃以下では前段HDM反応におけるコーキプレーカーの生成が、400℃以上ではHDS反応時に生じるコーキプレーカーがHDS触媒劣化に大きく関与していることがわかった。また、メタル蓄積量と劣化速度との関係を調べることにより、後段HDS触媒劣化の主な原因はコーキであることが明らかとなった。

Keywords
Catalyst deactivation, Resid desulfurization, Asphaltenes, Coke formation, Metal deposition