[Regular Paper]

Oxidative Regeneration of Resid Hydrodesulfurization Catalyst —Effect of Vanadium Accumulation on Properties and Activities of Regenerated Catalyst —

Ryuichiro IWAMOTO* and Narinobu KAGAMI

Petroleum Refining Technology Center, Idemitsu Kosan Co., Ltd., 26 Anegasaki-kaigan, Ichihara, Chiba 299-0107, JAPAN

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Resid hydrodesulfurization catalyst was regenerated after commercial operation and the effect of vanadium accumulation during resid hydrotreating reaction on the following catalyst regeneration was investigated. Vanadium accumulation accelerated the aggregation of active metals such as NiMoO_4 . Moreover, vanadium accumulation lead to the formation of $\text{Al}_2(\text{SO}_4)_3$ on the catalyst during regeneration. Although sulfur-containing species such as MoS_2 and vanadium sulfide were present all over the catalyst particle before regeneration, $\text{Al}_2(\text{SO}_4)_3$ only formed around the exterior of the catalyst particle after regeneration. Since the distribution of $\text{Al}_2(\text{SO}_4)_3$ corresponded well to the vanadium distribution, vanadium species probably catalytically oxidized SO_2 into H_2SO_4 , and then transformed the alumina carrier around the vanadium to sulfate. The effect of vanadium accumulation on the resid hydrotreatment activities of the resulting regenerated catalyst was also investigated. The hydrodesulfurization, hydrodenitrogenation and hydrodemicrocarbon residue activities over the regenerated catalyst decreased with increasing amount of vanadium accumulation. Since the XRD results indicated that the formation of NiMoO_4 increased with vanadium accumulation, the deactivation of HDS activity probably resulted from the decrease in the number of active sites due to aggregation of nickel and molybdenum. On the other hand, hydrodemetallization and hydrodeasphaltene activities increased with increasing amount of vanadium accumulation. Vanadium sulfide accumulated on the catalyst may have formed new hydrodemetallation and hydrodeasphaltenization active sites.

Keywords

Oxidative regeneration, Resid hydrodesulfurization, Hydrodemetallation, Hydrodenitrogenation, Vanadium accumulation

1. Introduction

Human activity generates large amounts of various types of waste which are having an increasing and cumulative effect on the world environment. Therefore, many enterprises are trying to achieve zero emissions of waste through modification of manufacturing processes. The petroleum industries are also making great efforts to reduce emissions of wastes and to build environmentally friendly refineries. One of the most important types of waste from refineries is the hydrodesulfurization (HDS) catalyst used for the resid fraction, as large volumes of this catalyst are exchanged every year due to the high deactivation rate. Therefore, regeneration and reuse of resid HDS catalyst would greatly reduce the waste from refineries. However, the resid HDS catalyst is not generally regenerated but is sent for metal recovery, whereas the HDS catalysts

for lighter fractions such as gas oil and kerosene are commonly regenerated.

Deactivation mechanisms occurring during hydro-treatment have been extensively studied, but the regeneration mechanism and deactivation mechanism during regeneration are less well known, especially for resid HDS catalyst. Reuse of resid HDS catalyst requires understanding of the regeneration behavior. In general, regeneration of resid HDS catalyst can be classified into oxidative regeneration and rejuvenation. Oxidative regeneration is based on burning of accumulated coke, and rejuvenation is intended to reduce contamination by accumulated metals such as vanadium. Here, we will discuss the oxidative regeneration of resid HDS catalyst.

The oxidative regeneration mechanism of hydro-treatment catalyst has been studied and reviewed in detail¹⁾. Coke and contaminant metals (Ni, V and Fe) are accumulated on resid catalyst during operation. Normally, such metals are present as sulfides, as are the active metals such as MoS_2 and Co_9S_8 . For example,

* To whom correspondence should be addressed.

* E-mail: ryuichiro.iwamoto@si.idemitsu.co.jp

vanadium is considered to be accumulated as $V_3S_4^{2)}$. These metals and coke are oxidized by the regeneration process.

The oxidative regeneration reaction consists of the following reactions^{3),4)}.

where H_{org} refers to the hydrogen content of the coke, and M refers to metals on the catalyst such as Co, Ni, Mo, W, V and Fe. During oxidative regeneration, the states of coke, active metals, accumulated metals, and support change significantly^{4)~8)}. For the active metal species, the formation of β -NiMoO₄, MoO₃, Al₂(MoO₄)₃, FeMoO₄ and NiAl₂O₄ occur depending on the regeneration condition and nature of catalyst. Alumina support could also transform γ -Al₂O₃ to δ -Al₂O₃ or α -Al₂O₃ caused by the exothermal reaction due to coke combustion⁵⁾. Vanadium sulfide on catalyst transforms to V₂O₅ by oxidation⁵⁾.

Regeneration temperatures which are too high will not completely restore the activity due to sintering of active metals, even if the specific surface area recovers to the level of fresh catalyst³⁾. Vanadium accumulation may prevent restoration of activity due to blocking of the pore structure and active sites⁹⁾. Vanadium may also prevent redispersion of the active metals⁷⁾. However, regeneration under certain conditions leads to higher HDS activity compared to fresh catalyst because of greater active metal dispersion^{10),11)}. Therefore, the chemistry of HDS catalyst regeneration is not yet well understood. In particular, the effect of vanadium accumulation on the regeneration of resid HDS catalyst has been not clarified.

The present study investigated the effect of vanadium accumulation by characterization and activity tests of regenerated resid HDS catalysts with different amounts of vanadium accumulation.

2. Experimental

2.1. Catalyst Preparation

The catalyst was conventional NiO-MoO₃-P₂O₅/Al₂O₃ prepared by impregnating γ -alumina with Ni-Mo-P solution. The preparation method was already described elsewhere¹²⁾. The catalyst was loaded into a commercial atmospheric residue hydrodesulfurization unit (ARDS) and then operated to produce fuel oil with sulfur content of *ca.* 0.3 wt%. After commercial operation for 1 year, catalyst samples with different amounts of contaminant metal accumulation (vanadium and nickel) were obtained from different parts of the reactor, as the metal content depends on the loading position and operating conditions. The used catalysts obtained were dried in an oven under nitrogen

at 573 K for 3 h and then calcined in air at 723 K for 3 h for regeneration.

2.2. Catalyst Characterization

The concentrations of various metals (V, Ni, Mo) on the catalyst were determined by inductively coupled plasma analysis (ICP) using a SPS5100 (SII Nanotechnology Inc.) Coke and sulfur on the catalyst were analyzed by LECO meter using a CS-444LS (LECO Corp.). The surface area was measured by nitrogen adsorption using an Autosorb-6 (Quantachrome Instruments). The structural change of the catalyst and the dispersion of Ni-Mo precursors were investigated by X-ray diffractometer equipped with a goniometer, a monochromator, and a Cu X-ray tube using a RINT Ultima III (RIGAKU). Distributions of the catalyst components through the catalyst particles were measured by electron probe micro analysis (EPMA) using a JXA-8200 (JEOL).

2.3. Catalytic Activity Measurement

Resid hydrotreatment was carried out with a fixed bed high pressure flow micro reactor to measure the activity of regenerated catalyst. The feedstock was Middle East atmospheric residue containing 3.73 wt% sulfur, 2240 ppm nitrogen, 11.5 wt% micro carbon resid, 4.8 wt% *n*-C₇ insoluble (asphaltene), 74 ppm vanadium and 26 ppm nickel with density 0.9745 g/ml. Catalyst (50 ml) with the original shape was loaded into the reactor without dilution. The catalyst was pre-sulfided with 2.0 wt% dimethyl disulfide (DMDS) dissolved in light gas oil for 24 h. The HDS, hydrodenitrogenation (HDN), hydrodemetallization (HDM), hydrodemicrocarbon residue (HDMCR) and hydrodeasphaltenization (HDAs) activities were measured at 633 to 653 K, LHSV 0.28 h⁻¹, 13 MPa and H₂/oil = 700 N/l at time on stream of 100 to 300 h. The sulfur content of the product oil was analyzed with a sulfur meter RX-610SA (TANAKA SCIENCE). The part of the H₂S formed during the HDS reaction dissolved in the product oil was removed by stripping with nitrogen gas before the sulfur analysis. Product nitrogen, vanadium and nickel on catalyst were analyzed by ICP.

The activities were evaluated on the basis of the reaction rate as follows.

$$k = \text{LHSV}/(n-1) \times ((1/P_1)^{n-1} - (1/P_0)^{n-1}) \quad (\text{in case of } n > 1)$$

$$\text{or } k = \text{LHSV} \times \ln(P_0/P_1) \quad (\text{in case of } n = 1)$$

n: reaction order (HDS: *n* = 1.6, HDN, HDM, HDMCR and HDAs: *n* = 1)

*P*₀: feed concentration (wt% or ppm)

*P*₁: product concentration (wt% or ppm)

3. Results

3.1. Properties of Regenerated Catalyst

Properties of the regenerated catalysts are shown in **Table 1**. The sulfur on the regenerated catalyst increased with greater vanadium accumulation, which

Table 1 The Properties of Regenerated Catalyst

Catalyst	Before regeneration				After regeneration		
	Vanadium ^{a)} [wt%]	Nickel ^{a)} [wt%]	Coke [wt%]	Sulfur [wt%]	Coke [wt%]	Sulfur [wt%]	S.A. [m ² /g]
Fresh catalyst	—	—	—	—	—	—	172
Regenerated catalyst-1	0.7 ^{b)}	1.1	26.6	4.3	0.67	0.20	166
Regenerated catalyst-2	1.4	1.1	18.4	6.3	0.90	0.82	164
Regenerated catalyst-3	2.0	1.5	19.9	6.5	0.57	1.25	147

a) Vanadium and nickel accumulation calculated based on the fresh catalyst.

b) Precise quantitative analysis is >1.0 wt%.

MOC = 1.8 wt%: regenerated catalyst-1, MOC = 2.5 wt%: regenerated catalyst-2, and MOC = 3.5 wt%: regenerated catalyst-3.

Fig. 1 X-Ray Diffraction Patterns of the Fresh and Regenerated Catalysts

was not due to incomplete regeneration, because the coke on the catalyst was reduced to an adequately low level. Specific surface area also decreased with greater vanadium accumulation, especially above 2 wt%.

3. 2. Structural Change of Regenerated Catalyst

The total amount of vanadium and nickel accumulation as metal during the HDM reaction based on fresh catalyst was defined as Metal on Catalyst (MOC). **Figure 1** shows the effect of MOC on the structure of the regenerated catalyst measured by X-ray diffraction (XRD). The fresh catalyst showed only broad peaks belonging to the γ -alumina support, and no peaks for nickel or molybdenum compounds. However, the regenerated catalysts-1, 2 and 3 showed peaks assigned to NiMoO_4 , which indicates the presence of aggregated nickel and molybdenum components. Furthermore, other peaks for $\text{Al}_2(\text{SO}_4)_3$ were observed above 2.5 wt% of MOC (regenerated catalysts-2 and 3). The peak intensities of NiMoO_4 and $\text{Al}_2(\text{SO}_4)_3$ increased with increasing amount of MOC. Regenerated catalyst-1 showed two peaks assigned to Fe_2O_3 . This iron species is attributed to contamination by scale due to process corrosion. Therefore, this finding was excluded from this discussion.

Observation of the cross section of the regenerated

Fig. 2 EPMA Line Analysis of the Regenerated Catalyst (MOC = 8 wt%)

catalyst showed that the exterior of catalyst particle was yellow whereas the interior was the original light green. **Figure 2** shows the EPMA line analysis of aluminum, molybdenum, nickel, vanadium and sulfur for the regenerated catalyst (to emphasize the effect of vanadium on the distribution of the catalyst component, the sample with MOC = 8.1 wt% was used). The EPMA measurement indicated that vanadium and sulfur tended to accumulate around the exterior of the catalyst particle. The yellow exterior of catalyst particle might be due to the vanadium accumulation. **Figure 2** shows that the distribution of sulfur and vanadium was quite similar. In contrast, nickel, molybdenum and aluminum had almost uniform distributions over the catalyst particle as well as the original fresh catalyst.

3. 3. Activity of Regenerated ARDS Catalyst

Figure 3 shows the relationship between MOC and HDS activity over the fresh catalyst, regenerated catalyst-1 and regenerated catalyst-3. The HDS activity decreased gradually with increasing amount of metal accumulation. The regenerated catalysts showed the same activation energy as the fresh catalyst (*ca.* 25,000 cal/mol) which did not change significantly with MOC.

Figure 4 shows the relationship between MOC and HDN activity over the fresh catalyst, regenerated catalyst-1 and regenerated catalyst-3. The HDN activity also decreased with increasing amount of MOC. The

MOC = 1.8 wt%: regenerated catalyst-1 and MOC = 3.5 wt%: regenerated catalyst-3.

Fig. 3 HDS Activity of the Fresh and Regenerated Catalysts

MOC = 1.8 wt%: regenerated catalyst-1 and MOC = 3.5 wt%: regenerated catalyst-3.

Fig. 5 HDV Activity of the Fresh and Regenerated Catalysts

MOC = 1.8 wt%: regenerated catalyst-1 and MOC = 3.5 wt%: regenerated catalyst-3.

Fig. 4 HDN Activity of the Fresh and Regenerated Catalysts

MOC = 1.8 wt%: regenerated catalyst-1 and MOC = 3.5 wt%: regenerated catalyst-3.

Fig. 6 HDNi Activity of the Fresh and Regenerated Catalysts

activation energy of HDN was almost the same as the fresh catalyst (*ca.* 18,000 cal/mol) but the deviation was rather larger.

Figures 5 and 6 show the relationships between MOC and hydrodevanadiumation (HDV), and hydrodenickelation (HDNi) activities over the fresh catalyst, regenerated catalyst-1 and regenerated catalyst-3, respectively. In contrast to the HDS and HDN results, the HDV and HDNi activities increased with increasing amount of MOC. The activation energy of HDV may also increase with MOC from *ca.* 11,000 to 15,000 cal/mol. The activation energy of HDNi was *ca.* 12,000 cal/mol and the deviation was relatively larger.

Figure 7 shows the relationship between MOC and hydrodemicrocarbon residue activity (HDMCR) over the fresh catalyst, regenerated catalyst-1 and regenerated catalyst-3. The HDMCR activity decreased with increasing amount of MOC, like the HDS activity. The activation energy of HDMCR also decreased with

MOC from *ca.* 12,000 to 9000 cal/mol and the deviation was rather larger. Figure 8 similarly shows that the hydrodeasphaltene activity (HDAs) increased with increasing amount of MOC, like the HDM activity. The activation energy of HDAs seemed to decrease with MOC from *ca.* 19,000 to 15,000 cal/mol.

4. Discussion

The present study found that vanadium accumulation enhanced the aggregation of NiMoO₄ (Fig. 1). It is not clear whether the aggregation of active metal species occurred during the hydrotreatment reaction and/or during the regeneration procedure. However, the regeneration procedure is likely to be the main contributor to the aggregation of active metals, since the aggregation of Ni and Mo sulfide is not obvious in the used catalyst and the regeneration procedure significantly changes the support properties such as the formation of

MOC = 1.8 wt%: regenerated catalyst-1 and MOC = 3.5 wt%: regenerated catalyst-3.

Fig. 7 HDMCR Activity of the Fresh and Regenerated Catalysts

MOC = 1.8 wt%: regenerated catalyst-1 and MOC = 3.5 wt%: regenerated catalyst-3.

Fig. 8 HDAs Activity of the Fresh and Regenerated Catalysts

$\text{Al}_2(\text{SO}_4)_3$.

The amount of sulfur on the regenerated catalyst increased with increasing amount of vanadium as shown in **Table 1**. The accumulation of sulfur can be attributed to the formation of $\text{Al}_2(\text{SO}_4)_3$, based on the results of XRD and EPMA measurements in **Figs. 1** and **2**. The distributions of sulfur and vanadium were quite similar. Vanadium species are well known to accumulate around the exterior of the catalyst particle due to the relatively higher HDV reaction rate^{13,14}. One possibility is that the sulfur component of vanadium sulfide reacts with the alumina support. However, the amount of sulfur combined in molybdenum sulfide is similar all over the catalyst particle. Therefore, $\text{Al}_2(\text{SO}_4)_3$ should form anywhere over the catalyst, although the sulfur is present only on the exterior of the catalyst particle as shown by EPMA (**Fig. 2**). Another possibility is that the vanadium on the exterior of the catalyst may catalytically oxidize SO_2 to H_2SO_4 during the regeneration, and then the surrounding alumina sup-

port is transformed to sulfate, since vanadium oxide is an excellent oxidation catalyst. The reaction can be described as the following equations.

This type of $\text{Al}_2(\text{SO}_4)_3$ formation might be a unique phenomenon during the regeneration of resid HDS catalyst.

The HDS, HDN and HDMCR activities decreased with increasing amount of MOC (**Figs. 3** and **4**). Since the XRD results indicated that the formation of NiMoO_4 increases with MOC, the deactivation of HDS mainly results from the decrease in the number of active sites due to aggregation of nickel and molybdenum. The HDS mechanism may not change with the accumulation of contaminant metals, as the activation energy does not change obviously. The effect of nickel accumulation is rather difficult to elucidate. However, the nickel accumulation might act as a poison for the HDS reaction, because the nickel content of fresh HDS catalyst is already optimized and excess nickel loading on the catalyst tends to decrease HDS activity¹⁵. The decrease in HDN activity might indicate a decrease in hydrogenation activity. The HDMCR and HDS activities normally show a good correlation, as seen in this study.

On the other hand, the HDV activity and the activation energy increased with increasing amount of MOC as shown in **Fig. 5**. This result suggests that the accumulated vanadium sulfide forms new HDM active sites. The accumulated vanadium sulfide may trap other vanadium in the feed. This result well agrees with the previous result that vanadium accumulation on regenerated catalyst increases the selectivity of HDM¹⁶. Furthermore, HDAs and HDM activities showed almost the same trend. Vanadium accumulation might enhance the scission of the V-C bond in heavier molecular fractions.

Coke accumulation might also affect the regeneration behavior and resulting catalytic activity. However, the amount of coke was not the main factor in this discussion, because of the lower correlation with the activity as shown in **Fig. 9**. The effect of pore structure was also excluded, as the pore structure was not obviously changed by the regeneration procedure in this study. Therefore, the MOC may be the most important factor affecting the activity of the regenerated resid HDS catalyst.

5. Conclusion

The effect of vanadium accumulation during the resid hydrotreatment reaction on oxidative catalyst re-

(a) Relationship between MOC and HDS activity, (b) Relationship between coke and HDS activity.

Fig. 9 Relationship between the Catalyst Properties before Regeneration and HDS Activity of the Regenerated Catalysts

generation was investigated. The accumulation of vanadium species on the resid HDS catalyst led to the formation of NiMoO_4 and $\text{Al}_2(\text{SO}_4)_3$. The accumulated vanadium might oxidize SO_2 into H_2SO_4 and then transform the alumina support into $\text{Al}_2(\text{SO}_4)_3$. The vanadium accumulation decreased resid HDS, HDN and HDMCR activities due to the formation of NiMoO_4 . On the other hand, HDM and HDAs activities increased with increasing amount of metal accumulation.

Therefore, vanadium sulfide accumulated on the catalyst may form new HDM active sites.

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要 旨

**重油脱硫触媒の再生
—バナジウム蓄積が再生触媒の物性と活性に与える影響—**

岩本 隆一郎, 各務 成存

出光興産(株)石油技術センター, 299-0107 千葉県市原市姉崎海岸26番地

商業装置で1年間運転された重油脱硫触媒を再生し、バナジウムの蓄積量が再生触媒の物性および活性に与える影響について検討した。XRD 測定からバナジウムの蓄積量に比例して再生時に NiMoO_4 のような活性金属の凝集が促進されることが分かった。また、バナジウムの蓄積量に比例して再生時に硫酸アルミニウムの生成が促進されることを見出した。硫酸アルミニウムとなる硫黄源は再生前にはモリブデン硫化物やバナジウム硫化物として触媒上に十分存在しているにもかかわらず、硫酸アルミニウムの分布はバナジウムの分布とよく一致して触媒粒子の外表面近傍にしか存在しなかった。この理由として、バナ

ジウムの酸化活性が再生時に生成する SO_2 を酸化して硫酸を生成し、さらにこの硫酸が担体のアルミナの硫酸化を促進していると考えられる。さらに、バナジウムの蓄積が再生触媒の触媒活性に与える影響について検討した結果、重油脱硫活性、脱窒素活性、脱残炭活性はバナジウムの蓄積量に比例して低下した。この活性低下の原因は活性金属の凝集によると考えられる。一方、脱バナジウム活性、脱ニッケル活性、脱アスファルテン活性は、バナジウムの蓄積量に比例して向上した。これは蓄積バナジウム自身が新たな活性点となり、重質留分の反応性を促進していると考えられる。

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