[Research Note]

Mechanism of NiMoO₄ Formation during Oxidative Regeneration of Resid HDS CatalystRyuichiro IWAMOTO^{†1)*}, Keisui MATSUI^{†2)}, and Atsushi YAMAZAKI^{†2)}^{†1)} Petroleum Refining Technology Center, Idemitsu Kosan Co., Ltd., 2-1 Anegasaki-kaigan, Ichihara, Chiba 299-0107, JAPAN^{†2)} School of Creative Science and Engineering, Dept. of Resources and Environmental Engineering, Waseda University, Ohkubo 3-4-1, Shinjuku-ku, Tokyo 169-8555, JAPAN

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Aggregation of the active metal components as NiMoO₄ during oxidative regeneration of residue hydrodesulfurization catalyst was studied by conventional and micro X-ray diffraction (XRD). The formation of NiMoO₄ was observed only on catalyst regenerated above 723 K by conventional XRD. Distribution of NiMoO₄ formation through the section of a catalyst particle was investigated by micro-XRD. The center of the catalyst particle showed higher aggregation of NiMoO₄ compared to the outside of the catalyst. These results indicate that NiMoO₄ formation is mainly caused by temperature increase inside the catalyst due to the heat accumulation from coke burning. Since the distribution of NiMoO₄ was not associated with that of vanadium, which was mainly present on the outside of the catalyst particle, vanadium did not chemically affect the active metal states.

Keywords

Oxidative regeneration, Resid hydrodesulfurization catalyst, Vanadium accumulation, Nickel molybdenum oxide, Micro X-ray diffraction, Coke burning

1. Introduction

The petroleum industry is making great efforts to reduce emissions of pollutants and to build environmentally friendly refineries. One of the most important wastes from refineries is used hydrodesulfurization (HDS) catalyst from the processing of the residue fraction, because a large volume of the catalyst must be exchanged every year due to the relatively higher deactivation rate. Therefore, the regeneration and reuse of resid HDS catalyst is an effective step in the establishment of environmentally friendly refinery. However, the resid HDS catalyst is very difficult to regenerate stably because of the insufficient recovery of activity and physicochemical properties^{1)~9)}. More effective regeneration of resid HDS catalyst requires the prevention of NiMoO₄ formation. Deactivation during resid HDS has been extensively studied, but the deactivation during oxidative regeneration is less well understood.

The present study investigated the mechanism of NiMoO₄ formation using conventional and micro X-ray diffraction (XRD). Micro-XRD is very useful to obtain precise information on local structural changes within a particular catalyst particle, whereas conventional XRD gives only the average structure of the catalyst¹⁰⁾.

Therefore, the distribution of NiMoO₄ over the catalyst particle was investigated using this technique to elucidate the mechanism of NiMoO₄ formation. In addition, the effect of regeneration temperature on the active metal dispersion was also investigated.

2. Experimental**2.1. Catalyst Preparation**

Conventional NiO–MoO₃–P₂O₅/Al₂O₃ catalyst was prepared by impregnating γ -alumina with Ni–Mo–P solution as described elsewhere¹¹⁾. The catalyst was loaded in a commercial hydrodesulfurization unit for atmospheric residue (ARDS). After presulfiding, the unit was operated to produce fuel oil with sulfur content of *ca.* 0.3 wt% for 1 year. Then, deactivated catalyst samples located near the bottom position were taken from the reactor. The used catalysts were regenerated at a target temperatures from 573 to 723 K in dry air as well as by commercial processing. The samples were heated up at 10 K/min to the target temperature and maintained for 10 h to eliminate deposited carbon, sulfur and nitrogen.

2.2. Catalyst Characterization**2.2.1. Analysis of Catalyst Composition**

The average composition of the catalyst component and the distribution of the components over the catalyst particle were determined by energy-dispersive X-ray

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spectroscopy (EDS) using a JSM-6360 (JEOL). Average composition was measured with powdered catalyst. The distribution of the catalyst component over the catalyst was measured by scanning the exposed section of catalyst particle from outside to center at 200 μm intervals to obtain three measurements. Coke, hydrogen, sulfur and nitrogen on the catalyst were also analyzed by CHN analysis using a CHN/O 2400 analyzer series II (Perkin Elmer Inc.).

2. 2. 2. Conventional XRD Measurement

The active metal dispersion on the regenerated catalyst was investigated by conventional XRD measurement using a RINT Ultima III (Rigaku Corp.) equipped with a goniometer and a monochromator, using $\text{CuK}\alpha$ radiation at 40 kV and tube current of 30 mA.

2. 2. 3. Micro-XRD Measurement

Micro-XRD was performed using a RINT-RAPID (Rigaku Corp.) with $\text{CuK}\alpha$ radiation at 40 kV and tube current of 30 mA. The diameter of the analysis area was limited to $100 \times 100 \mu\text{m}$ with a collimator size of 0.1 mm. The sample was fixed to 20 degree about the ω -axis and 0 degree about the ϕ -axis. Micro-XRD patterns were obtained by scanning the exposed section of the catalyst particle from outside to center at 150 μm intervals to obtain four measurements.

2. 2. 4. DTA Measurement

Differential thermal analysis (DTA) was performed with a EXSTAR 600 (SII Nano Technology Inc.) The used catalysts were washed with toluene and preheated at 673 K under a flow of nitrogen for 2 h. After cooling to room temperature, the catalyst was heated up to 1073 K at 5 K/min under a flow of dry air at 10 ml/min.

2. 3. Catalyst Activity Measurement

Thiophene HDS was carried out at atmospheric pressure in a flow type micro reactor. Catalyst samples (0.3 g) regenerated at different temperatures were sieved at 32 to 64 mesh and packed in the reactor without dilution, and presulfided at 673 K for 24 h with $\text{H}_2/\text{H}_2\text{S}$ (90/10 vol%) gas at 50 ml/min. After cooling to 573 K, thiophene was introduced into the reactors at constant pressure (50 Torr, 1 Torr = 133.322 Pa) with a hydrogen flow rate of 10 ml/min. The products were analyzed by gas chromatography after 3 h.

3. Results and Discussion

Figure 1 and Table 1 show the carbon, hydrogen, sulfur and nitrogen contents of the catalysts regenerated at different temperatures. These compositions changed drastically depending on the calcination temperature. These components started to decrease above 573 K and almost disappeared at 673 K. These results basically agree with the findings of continuous temperature programmed oxidation^{12)~18)}.

Figure 2 shows the conventional XRD patterns of the resid HDS catalysts regenerated at different temper-

Fig. 1 Effect of Regeneration Temperature on Carbon, Sulfur and Nitrogen Contents of the Catalyst

atures, as well as fresh and used catalysts. The fresh and used catalysts mainly showed a few broad peaks belonging to the γ -alumina support around 37, 46 and 67 degree/ 2θ . The peak for NiMoO_4 was absent in these catalysts, indicating the aggregation of the nickel and molybdenum components^{6),19),20)}. The regenerated catalysts showed no distinct differences up to 623 K. Therefore, no obvious aggregation of nickel and molybdenum components is likely to occur at this stage. However, the catalyst regenerated at 723 K showed a clear peak of NiMoO_4 around 26 degree/ 2θ . Figure 3 shows the thiophene HDS activity for the catalysts regenerated at different temperatures. The thiophene HDS activity increased with higher regenerated temperature up to 673 K due to coke elimination, and then started to decrease above 723 K. This finding corresponds well to the aggregation of active metals as shown in Fig. 2.

Figure 4 shows the micro-XRD patterns for the sec-

Table 1 Carbon, Sulfur and Nitrogen Contents of the Regenerated Catalyst

	Used catalyst	Regeneration temperature							
		573 K		623 K		673 K		723 K	
		5 h	10 h	5 h	10 h	5 h	10 h	5 h	10 h
C	36.1	36.9	32.0	21.9	6.3	0.5	0.3	0.1	0.2
H	3.8	2.9	2.6	1.7	1.5	1.4	1.0	1.3	1.2
N	0.3	0.4	0.4	0.3	0.3	0.0	0.0	0.0	0.0
S	5.8	6.1	5.3	3.1	0.9	0.4	0.3	0.2	0.2

Concentrations were calculated based on the weight of fresh catalyst as 100%.

(a) Fresh catalyst, (b) Used catalyst, (c) Catalyst regenerated at 573 K, (d) Catalyst regenerated at 623 K, (e) Catalyst regenerated at 673 K, (f) Catalyst regenerated at 723 K.

Fig. 2 X-ray Diffraction Patterns of the Fresh, Used and Regenerated Catalysts Calcined for 10 h

Fig. 3 Thiophene HDS Activity of Catalysts Regenerated at Different Temperatures

tion of a catalyst particle containing average 2.8 wt% vanadium and regenerated at 723 K. The peak of NiMoO_4 was observed at 26 degree/ 2θ over the section of the catalyst. The peaks of alumina were also obtained around 46 and 67 degree/ 2θ . A peak at 43 degree/ 2θ was assigned to the (1_1_3) plane of $\alpha\text{-Al}_2\text{O}_3$. This $\alpha\text{-Al}_2\text{O}_3$ might be very orientated, as this was not clearly observed in the conventional XRD pattern. To investigate the NiMoO_4 distribution, the amount of NiMoO_4 over the catalyst particle was plotted as the intensity ratio of NiMoO_4 peak/ Al_2O_3 peak in Fig. 5(a). The result clearly indicates that the forma-

Fig. 4 Micro X-ray Diffraction Patterns from the Outside to the Center of the Regenerated Catalyst Particle

tion of NiMoO_4 increased linearly towards the center of the catalyst particle.

No evidence for the aggregation of nickel and molybdenum components was observed in the used catalyst or the catalyst regenerated below 673 K, as shown in Fig. 2. The formation of NiMoO_4 was only observed above 723 K and tended to increase toward the center of the catalyst particle, where heat release may be worse compared with the outside of the catalyst. Therefore, the aggregation of Ni and Mo must be related to the temperature increase.

To confirm the above discussion more theoretically, the effect of coke burning on the catalyst temperature was calculated. Oxidative regeneration can be described by the following.

If the H/C molar ratio of coke on the catalyst is 0.8, as seen in Table 1, and the specific heat of alumina based catalyst is $1.1 \text{ kJ/kg} \cdot \text{K}^{21}$, 1 wt% of coke burning in adiabatic reaction can increase the temperature of the catalyst by about 40 K. Therefore, rapid coke burning and heat release restriction might cause the aggregation of nickel and molybdenum at higher regeneration temperatures.

Figure 5(b) also shows the distribution of vanadium over the section of the catalyst particle measured by

(a) $\text{NiMoO}_4/\text{Al}_2\text{O}_3$ peak intensity ratio calculated from micro-XRD, (b) Vanadium content measured by EDS. Peaks of NiMoO_4 and Al_2O_3 were assigned at 26 and 46 degree/ 2θ , respectively.

Fig. 5 Distribution of NiMoO_4 and Vanadium over the Catalyst Particle

EDS. As the vanadium is present mainly outside the catalyst, the amount of NiMoO_4 formation was not correlated with the position of the vanadium. This finding does not agree with the previous observation that NiMoO_4 formation during regeneration is correlated with the vanadium content⁹⁾. Therefore, the presence of vanadium may not directly affect the aggregation of nickel and molybdenum through chemical interaction. However, vanadium may affect NiMoO_4 formation indirectly as follows.

- 1) Vanadium acts as an oxidation catalyst to accelerate coke burning, resulting in higher temperatures inside the catalyst particle, while outside of the catalyst particle cools down.
- 2) Higher accumulation of vanadium on the catalyst is associated with less refractory coke, located at the upper part of the reactor and exposed to lower reaction temperatures^{12)~18)}. Therefore, coke burning is easier and leads to higher temperatures inside the catalyst particle.
- 3) Pore mouth plugging by vanadium prevents heat re-

lease from inside the catalyst.

In fact, the formation of NiMoO_4 is also observed on regenerated HDS catalyst for the distillation fraction, which contains no vanadium^{12),19)}. This also may suggest that vanadium is indirectly involved in NiMoO_4 formation.

5. Conclusion

Aggregation of active metal components as NiMoO_4 during oxidative resid HDS catalyst regeneration was investigated using conventional and micro-XRD.

The findings were as follows.

- (i) NiMoO_4 formation is only observed with regeneration above 723 K.
- (ii) NiMoO_4 preferentially forms inside the catalyst particle.
- (iii) Vanadium does not chemically affect the states of the active metal, but may be indirectly related with NiMoO_4 formation.
- (iv) Increased temperature inside the catalyst due to the heat released by coke burning might be the main factor causing active metal aggregation during regeneration. Therefore, aggregation of active metals might be prevented with milder regeneration conditions such as lower temperature and lower heating rate.

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要 旨

重油脱硫触媒の再生における NiMoO_4 生成機構

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重油脱硫触媒の再生における NiMoO_4 生成機構について、一般的な粉末 X 線回折測定とマイクロ X 線回折測定により解析した。一般的な粉末 X 線回折測定からは NiMoO_4 の生成は再生温度 723 K 以上でのみ観測された。さらに、触媒粒子断面内の NiMoO_4 の生成分布をマイクロ X 線回折により測定した結果、粒子中心部の方が外周部よりも NiMoO_4 生成が多かった。これ

らの結果は NiMoO_4 の生成が触媒内部におけるコーク燃焼熱蓄積による温度上昇が主原因であることを示唆している。また、重油脱硫触媒では主にバナジウムは外周部に存在しており、 NiMoO_4 の分布とは一致していないことから、バナジウムの化学的作用は NiMoO_4 の凝集の主原因ではないと考えられる。