1. Introduction

The demand for heavy fuel oil is estimated to decrease in the future1). Therefore, it is important to develop methods to efficiently convert heavier fractions to lighter fractions. The hydrodesulfurization process of residue (RDS) produces not only clean heavy fuel but high quality feedstocks for fluid catalytic cracking (FCC) and/or residue fluid catalytic cracking (RFCC) which yield light fractions such as gasoline2). Accordingly, treating heavier feedstock by RDS has great practical value. However, the RDS catalyst suffers higher deactivation rate and shorter life when used for the treatment of heavier feedstock3). The deactivation of RDS catalyst is mainly caused by coke and metal deposition on the catalyst surface2),4). Reduction of coke deposition on catalyst would allow treatment of much heavier feedstock at the same existing RDS unit. Coke on the catalyst is generated by adsorption, dehydrogenation and polycondensation reactions of the heavy fraction on the catalyst. A mechanism of coke formation based on the thermal hydrocracking and pyrolysis of coke precursors such as asphaltenes derived from heavy oil has been proposed6). The strength of the interaction of coke precursors with the catalyst depends on the properties of the catalyst surface and the structure of the coke precursor. Coking increases with increasing acidity of the catalyst surface11). In addition, the coke precursors in the original feed can be formed during the process if sufficient active hydrogen is not supplied6). The pore size of the catalyst may affect the deactivation rate of RDS2). RDS catalyst deactivation may be suppressed by the addition of H2O to the feed oil12). The loading order of catalyst with different pore structures also has an effect in the RDS unit13). However, RDS catalyst modified by additives, which successfully decrease the catalyst deactivation, have not been widely investigated. FeS, CoS, NiS or ZnS addition to MoS2 catalyst affects dibenzothiophene conversion14). Moreover, generation of spillover hydrogen occurs from Fe, Co, Ni, Zn on alumina support15).

The present study attempted to develop RDS catalyst with less coke deactivation based on NiMo/Al2O3 catalysts with supports modified by the addition of Fe, Co, Ni Zn and/or P. The NiMo/Al2O3 catalyst modified by Zn and P showed lower deactivation rate and excellent...
activity for hydrodesulfurization.

2. Experimental

2.1. Catalyst Preparation

Carriers were modified with Fe, Co, Ni, Zn and/or P by the kneading method. All catalysts were prepared by the wet incipient pore-volume impregnation method using an aqueous solution containing the required amounts of nickel, molybdenum and/or phosphorus on alumina support. After impregnation, this sample was air-dried followed by calcination at 500-650 °C.

2.2. Activity Test

Residues derived from Middle Eastern crude oil containing sulfur between 2.9 and 3.4 mass% were used as the feedstocks for the bench plant tests. The properties of the feed residues are shown in Table 1. Activity tests were carried out with the bench plant that contained an isothermal fixed-bed reactor operating in the down-flow mode. Prior to the activity tests, fresh catalysts were pre-sulfided in-situ with vacuum gas oil under normal hydrotreating conditions.

Hydrodesulfurization of the residual oil was carried out under the conditions shown in Table 2. The amount of sulfur in the product oil was measured by energy-dispersive X-ray fluorescence spectroscopy (RX-600SA, Mitsubishi Chemical Corp.). The reaction rate order seems to be around 2 for the sulfur concentration at the 0.3 mass% hydrodesulfurization level. In this study, the decrease in the total sulfur content of the gas oil was assumed to be on the pseudo-2 order. The following equation was used to analyze the results of the experiment

\[
k(\text{HDS}) = \frac{1}{n-1} \left( \frac{S_p}{S_i^{(1-n)}} \right) \times \text{LHSV}
\]

where \(k\) is the intrinsic rate constant (h⁻¹), \(S_p\) is the amount of sulfur in the product, \(S_i\) is the amount of sulfur in the feedstock, and \(n\) is the reaction rate order.

Commercial operations with the developed catalysts have been carried out using the commercial residue hydrotreating units at the Cosmo Oil Chiba refinery. To index the catalytic activity in commercial operation of the developed catalysts, the normalized weight average bed temperatures (WABT) were obtained by normalizing the commercial operation data under certain conditions based on our original simulation technology for catalyst performance prediction.

2.3. Analysis

2.3.1. Coke Analysis

The amount of coke on the used catalyst was determined using a Yanagimoto MT-3 CHN analyzer. The characteristics of the coke species were analyzed by the thermal gravimetry/differential thermal analysis (TG/DTA) method using a Thermo plus EVOII TG8120 (Rigaku Corp.).

2.3.2. FT-IR Measurements

The IR spectra were recorded on a Fourier transform infrared spectroscopy (FT-IR) Nicolet iN10 (Thermo Scientific). Samples were finely ground, and then thin 20 mm diameter wafers were made by pressing a 50 mg sample. The thin wafer was placed in the in-situ sample holder and was dried at 400 °C for 3 h respectively. The in-situ sample holder was set in the FT-IR spectrometer after the sample was cooled to room temperature. The FT-IR spectrum was acquired in the transmission mode at room temperature and the background spectrum of the vacant sample holder was subtracted.

3. Results and Discussion

3.1. Effect of Additives on the Catalyst Properties

Generation of spillover hydrogen from P, Fe, Co, Ni, Zn on alumina support is known to occur. Therefore, we expected these additives to suppress catalyst deactivation because spillover hydrogen should prevent dehydrogenation and polycondensation of the coke precursors. The hydrodesulfurization activity of conventional NiMo/Al₂O₃ catalyst is promoted by addition of phosphorus. Therefore, the modification effects of Fe, Co, Ni, or Zn addition to the Al₂O₃ support of P modified catalyst (NiMo/P-Al₂O₃) were examined on the deactivation rate of residue hydrodesulfurization. The physical properties of each catalyst are shown in Table 3.

The kinetic constants of the hydrodesulfurization reaction are plotted versus days on stream in Fig. 1. The catalyst modified with Zn and P (Cat. D) showed the lowest deactivation rate among the four catalysts (Cat. A-D). As a result, the hydrodesulfurization reaction rate of Cat. D became higher than the others at 10 days on stream at 390 °C. Although Ni and Co have higher spillover efficiency, Cat. B and C had lower kinetic constants during the stable period of bench plant tests. Therefore, suppression of deactivation with Zn seems to have little relationship with spillover hydrogen under this condition.
3.2. Effect of Zinc Modification

Catalysts containing a moderate amount of phosphorus are well known to have higher initial hydrosulfurization reaction rates than catalysts without phosphorus. In this study, the effect of pairing of Zn and P was examined. The properties of the catalysts are shown in Table 4.

The initial activities of the catalysts containing P (Cat. G, Cat. H) were higher than those of the catalysts without P (Cat. E, Cat. F). The initial activity of the catalyst containing Zn and P (Cat. H) was slightly lower than that of the catalyst with P (Cat. G) and the initial activity of the catalyst containing Zn (Cat. F) was slightly lower than that of the catalyst with P (Cat. G). However, the relative hydrosulfurization activity of the catalyst containing Zn and P (Cat. H) increases with operating days because of its small deactivation rate. Therefore, the effect of Zn addition on deactivation rate was much noticeable with the coexistence of P in the catalyst (Fig. 2).

Coke deposition on the used catalyst was determined by CHN analysis. NiMo/ZnP-Al2O3 catalyst (Cat. H) suffered less coke deposition than other catalysts. There are no significant differences of coke amount between the catalysts modified with Fe, Co and Ni (Fig. 3).

Surface OH groups of hydrotreating catalysts can be characterized by FT-IR.18),23),24) The intensity of the IR bands derived from the basic OH group decreased with increasing P content.18) The IR spectra of the OH stretching region were examined for Cat. E to Cat. H (Fig. 4). The IR spectra were not in perfect agreement with the reported findings, possibly because phosphorus was added to the alumina by the kneading method in this study, whereas phosphorus was added with the impregnation method in other studies. NiMo/Al2O3 and NiMo/ZnP-Al2O3 had lower intensities of IR bands derived from the relatively acidic OH group at lower wave number around 3650 cm⁻¹. Therefore, this reduced surface acidity may have resulted in the decreased coke deposition.

If the hydroxyl group is surrounded by Al³⁺, the positive electric charge of the proton in hydroxyl group increases and the acidity is increased. In contrast, if the hydroxyl group is surrounded by OH⁻ or O²⁻, the acidity is reduced.23) The order of electronegativity is O>P>Zn>Al. P and Zn have lower electronegativity than oxygen, so the acidity of the hydroxyl groups on Zn or P modified catalysts could be stronger than on unmodified catalyst. On the other hand, Zn and P might interact resulting in different effects on the acidity of the catalysts.

### Table 3 Properties of Catalysts Modified with Fe, Co, Ni or Zn

| Catalyst name | Cat. A | Cat. B | Cat. C | Cat. D |
|---------------|--------|--------|--------|--------|
| Impregnated compounds | NiMo | NiMo | NiMo | NiMo |
| Ni/Mo [mol/mol] | 0.6 | 0.6 | 0.6 | 0.6 |
| Support contents | Alumina | Alumina | Alumina | Alumina |
| Iron | Co | Ni | Zn |
| Phosphorus | Phosphorus | Phosphorus | Phosphorus |
| Metal (Fe, Co, Ni or Zn) in support/Mo [mol/mol] | 0.6 | 0.6 | 0.6 | 0.6 |
| P in support/Mo [mol/mol] | 0.2 | 0.2 | 0.2 | 0.2 |
| Surface area [m²/g] | 260 | 260 | 258 | 271 |

### Table 4 Properties of Catalysts with Different Combination of Zn and P

| Catalyst name | Cat. E | Cat. F | Cat. G | Cat. H |
|---------------|--------|--------|--------|--------|
| Impregnated compounds | NiMo | NiMo | NiMo | NiMo |
| Ni/Mo [mol/mol] | 0.6 | 0.6 | 0.6 | 0.6 |
| Support contents | Alumina | Alumina | Alumina | Alumina |
| Zinc | Phosphorus | Phosphorus | Phosphorus | Phosphorus |
| Zn in support/Mo [mol/mol] | 0 | 0.6 | 0 | 0.6 |
| P in support/Mo [mol/mol] | 0 | 0 | 0.2 | 0.2 |
| Surface area [m²/g] | 262 | 269 | 279 | 258 |
hydroxyl groups compared to single element modification.

3.3. Performance of Zinc Modified Catalysts

Generally, combinations of more than three types of catalysts are charged in the RDS unit. The performance of zinc modified catalysts was evaluated in the three catalyst combination system. In the experimental catalyst system A, conventional hydrodemetallation (HDM) catalyst was used for the first stage, and Zn and P modified catalysts for the second and third stages (Fig. 5 and Table 5).

According to the results of bench plant tests using atmospheric residue as feedstock derived from the Middle East crude, the catalyst system A which contained zinc modified catalyst showed lower deactivation rate than the conventional catalyst system B (Fig. 6).

Used catalysts from these bench plant tests were sampled and analyzed to measure the amounts of coke and metal with the CHN and inductively coupled plasma (ICP) analyzers. Coke and metal amounts on the catalysts are plotted against the vertical position in the down flow reactor in Figs. 7 and 8. Zn and P modified catalysts had less coke deposition than catalysts without Zn. On the other hand, the nickel and vanadium contents were the same in catalyst systems A and B, suggesting that the reduction of coke resulted in mild deactivation of catalyst system A.

3.4. Effect of Zn Additive Amount

Bench plant tests were carried out with four types of catalysts (Zn additive = 0, 0.05, 0.10, 0.15 mmol/g) to investigate the effects of the Zn additive amount on the hydrodesulfurization activity and initial deactivation.
rate. The properties of the tested catalysts are shown in Table 6.

The effect of Zn addition on HDS deactivation was highest for Cat. J. Table 6 also shows the kinetic constants of the starting term of run $k_{\text{HDS}}$SOR and the middle term of run $k_{\text{HDS}}$MOR. Although the kinetic constant of the initial term was almost the same for Cats. I-L, the kinetic constant for Cat. J became higher than others with time. As a result, Cat. J showed a lower deactivation rate for hydodesulfurization. Consequently, these test results were reflected in the composition of the industrial catalyst, and C-25D (2nd stage catalyst) and C-14D (3rd stage catalyst) were developed.

### 3.5. Commercial Operation

The catalysts C-25D and C-14D were charged in the commercial RDS unit in the Cosmo Oil Chiba refinery. Figure 9 shows the required WABT against days on stream at the commercial unit. Here the required WABT means the weight bed average temperature to obtain product oil containing 0.3 mass% sulfur. This temperature was calculated with the Arrhenius equation using 2-order kinetics and 150 kJ/mol as the apparent activation energy, as previously reported. We had already established the instrumental difference between our bench plant and commercial plant. Then, the prediction line of the developed catalyst system under certain process conditions in the commercial plant was calculated by the Cosmo Oil simulation technology. As shown in Fig. 9, the required temperature of the developed catalyst system was consistent with the prediction line. Therefore, improvement of the HDS deactivation rate was successfully achieved in the commercial RDS unit with developed catalyst system.
Table 6 Properties and HDS Activities of Catalysts with Different Amounts of Zn

| Catalyst name | Cat. I | Cat. J | Cat. K | Cat. L |
|---------------|--------|--------|--------|--------|
| Impregnated compounds | NiMo | NiMo | NiMo | NiMo |
| NiMo [mol/mol] | 0.6 | 0.6 | 0.6 | 0.6 |
| Support contents | Alumina | Alumina | Alumina | Alumina |
| Zinc Phosphorus [mol/mol] | 0 | 0.6 | 1.2 | 1.8 |
| P in support/Mo [mol/mol] | 0 | 0.2 | 0.2 | 0.2 |
| Surface area [m²/g] | 279 | 271 | 279 | 275 |
| (HDS)MOR/7 days | 0.67 | 0.66 | 0.64 | 0.64 |
| (HDS)MOR/28-30 days | 0.50 | 0.55 | 0.52 | 0.49 |
| (HDS)MOR/28-30 days | 0.75 | 0.83 | 0.81 | 0.77 |

4. Conclusion

The present study showed that combined Zn and P additives in NiMo/Al₂O₃ resulted in lower deactivation rate, although Zn caused little change in the promotion effect of phosphorus for residue hydroprocessing. NiMo/ZnP-Al₂O₃ catalyst had less deposition of coke based on carbon analysis of used catalyst from the bench plant test. Moreover, acidic OH groups decreased on NiMo/ZnP-Al₂O₃ catalyst, which might have resulted in less deposition of coke. This neutralization of Zn to P resulted in lower coke deposition and deactivation rate for hydrodesulfurization. Subsequent commercial operation demonstrated lower initial deactivation rate and higher hydrodesulfurization activity in the middle of run with catalysts modified with Zn and P, consistent with the data of the bench plant test. These developed catalysts can be used to treat heavier residues than conventional catalysts in commercial production.

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Fig. 9 Required WABT to Maintain 0.3 mass% Sulfur in Product Oil at Commercial Residue Hydrodesulfurization Unit with Developed Catalyst

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要  旨
残油水素化脱硫における亜鉛・リン修飾NiMo/Al₂O₃触媒の脱硫活性と安定性

中嶋 伸昌†1, 芹口 慶洋†2, 加藤 賢美†3, 吉成 幹記†4, 吉田 俊男†5, 渡辺 克哉†6
†1 コスモ石油(株)中央研究所, 〒340-0193 埼玉県幸手市栃虎堂1134-2
†2 コスモ石油(株)千葉製油所, 〒290-8558 千葉県市原市五井海岸2

重質油を付加価値の高い軽質留分に転化することは重要である。これを達成する方策の一つとして、直接脱硫装置より重質な原料油を処理し、この生成油をFCCやRFCCで処理することが挙げられる。直接脱硫装置より重質な原料油を、同一触媒、同一プロセス条件において処理した場合には、生成油の硫黄分が上昇し、これを補うために運転温度を上昇させることが必要となる。この運転温度上昇は結果として触媒寿命の短縮につながる。そのため、残油水素化脱硫触媒について多くの研究が行われており、NiMo/Al₂O₃触媒にリンを添加すると脱硫活性が向上することは良く知られている。本研究では、このリン添加NiMo/Al₂O₃触媒の調製時にアルミナ担体を亜鉛でさら

に修飾すると触媒上へのコーク堆積量が減少し、脱硫活性の初期劣化を抑制できることを明らかにした。IR分析により触媒表面のOH基を分析したところ、リン添加は触媒上の酸性OH基を増加させるが、さらに亜鉛で修飾することで酸性OH基の増加が抑制され、これが触媒のコーク劣化を抑制したものと考えられる。亜鉛・リン修飾技術を用いたNiMo/Al₂O₃残油水素化処理触媒はベンチプラントにおける長期寿命試験においても初期劣化が抑制され、結果として優れた安定期での脱硫活性を示した。本触媒を商業装置に用いて実証運転を行った結果、想定の優れた性能が発揮された。

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