1. Introduction

Removal of sulfur from petroleum fractions is one of the most important issues for the resolution of current environmental problems. Commercial hydrosulfurization (HDS) plants commonly use MoO$_3$-based hydro-treating catalysts, because of the excellent performance as well as economic advantages$^{1)}$. In a previous paper, we reported that addition of polyethylene glycol (PEG) can moderately improve HDS catalysts$^{2)}$. PEG is a viscous transparent water soluble organic compound (WSOC) with the structure of HO$\_$(CH$_2$OCH$_2$)$_n$OH. The addition of PEG to the impregnation solution improved the HDS activity of CoO-MoO$_3$/Al$_2$O$_3$ for dibenzothiophene and light gas oil (diesel). X-Ray photoelectron spectroscopy (XPS) measurement suggested that addition of PEG results in better dispersion of cobalt and molybdenum on the alumina support and improves dibenzothiophene and resid hydrosulfurization activity. The effect of PEG addition was significant for catalyst prepared from alumina with lower specific surface area and higher phosphorus content, in which the active metal precursor tends to easily aggregate. PEG might block the aggregation of active metal precursors during the drying step and may increase the number of hydrosulfurization active sites.

Keywords
Nickel molybdenum catalyst, Phosphorus, Hydrosulfurization, Polyethylene glycol, Water soluble organic compound, Catalyst preparation

2. Experimental

2.1. Catalyst Preparation

Various amounts of polyethylene glycol (PEG) as a water soluble organic compound to the impregnation solution during catalyst preparation was investigated to improve NiO-MoO$_3$/Al$_2$O$_3$ and NiO-MoO$_3$-P$_2$O$_5$/Al$_2$O$_3$ hydrosulfurization catalysts. XPS measurement suggested that PEG addition increases the dispersion of nickel and molybdenum on the alumina support and improves dibenzothiophene and resid hydrosulfurization activity. The effect of PEG addition was significant for catalyst prepared from alumina with lower specific surface area and higher phosphorus content, in which the active metal precursor tends to easily aggregate. PEG might block the aggregation of active metal precursors during the drying step and may increase the number of hydrosulfurization active sites.
SSA of 220 m²/g. The Ni impregnation solution was prepared by dissolving Ni(CH₃CO₂)₂ (Wako Pure Chemical Industries, Ltd.) in pure water at 343 K, and then various amounts of PEG were dissolved in the Ni solution at room temperature. After impregnation, the catalysts were dried at 493 K in air for 3 h and then calcined at 823 K in air for 3 h. The amount of NiO loaded on the catalyst was 3 wt%. These catalysts are denoted as Ni/Al(x), in which x represents the mass (g) of PEG added per 100 g of support.

NiO-MoO₃/Al₂O₃ catalysts were obtained by impregnating Ni-Mo solution on γ-alumina with various SSA from 160 to 315 m²/g. The Ni-Mo impregnation solution was prepared by dissolving MoO₃ (Wako Pure Chemical Industries, Ltd.) and Ni(CO₃)·nH₂O (Wako Pure Chemical Industries, Ltd.) in pure water with DL-malic acid at 343 K, and then PEG was dissolved in the Ni-Mo solution at room temperature. After impregnation, the catalysts were dried at 393 K in air for 3 h and then calcined at 823 K in air for 3 h. The amounts of NiO and MoO₃ loaded on the catalysts were 3 wt% and 14 wt%, respectively. These catalysts are denoted as Ni-Mo/Al(x) in which x represents the mass (g) of PEG added per 100 g of support.

NiO-MoO₃-P₂O₅/Al₂O₃ catalysts were prepared by impregnating the Ni-Mo-P impregnation solution on γ-alumina with SSA of 200 m²/g. The Ni-Mo-P impregnation solution was obtained by dissolving MoO₃, Ni(CO₃)·nH₂O and P₂O₅ (Wako Pure Chemical Industries, Ltd.) dissolved in the feedstock at 523 K, and then PEG was incorporated into the Ni-Mo-P solution at room temperature. After impregnation, the catalysts were dried at 393 K in air for 3 h and then calcined at 823 K in air for 3 h. The amounts of NiO, MoO₃ and P₂O₅ loaded on the catalysts were 3 wt%, 14 wt% and 2.0 wt%, respectively. These catalysts are denoted as Ni-Mo-P/Al(x) in which x represents the mass (g) of PEG added per 100 g of support.

### 2.2. Catalyst Characterization

The XPS spectra of Al(2s), Ni(2p) and Mo(3d) in oxide form were measured to obtain the intensity ratio of $I_{Al}^{2p}$ and $I_{Mo}^{2p}$ with a JPS-9000MC (JEOL Ltd.) equipped with an Al X-ray source working at 150 W. Binding energy was referenced to the Al 2p peak at 74.8 eV.

The effect of PEG on the dispersion of Ni-Mo precursors was also investigated by XRD. Ni-Mo-P impregnation solutions with and without PEG were dried at 393 K for 3 h. X-Ray diffraction patterns were measured with a RINT Ultima III (Rigaku Corp.) equipped with a goniometer, a monochromator, and a Cu X-ray tube.

### 2.3. Catalytic Activity Measurement

Hydrodesulfurization of dibenzothiophene (DBT) was carried out with a fixed bed high pressure flow microreactor. Feedstock containing 1.18 wt% sulfur was prepared by dissolving DBT in tetraline. Catalyst (2.5 ml) sieved from 0.5 to 1.0 mm was loaded in the reactor. The catalysts were sulfided with 2 wt% dimethyl disulfide (DMDS) (Wako Pure Chemical Industries, Ltd.) dissolved in the feedstock at 523 K, LHSV 4.0 h⁻¹, 5 MPa and H₂/oil = 250 Nl/l for 24 h before the HDS reaction. After sulfiding, the temperature was increased to the reaction temperature of 563 K or 573 K. The sulfur content and properties of the product oil were analyzed with a sulfur meter (Tanaka Scientific Ltd., RX-610SA). H₂S formed during the HDS reaction was dissolved in product oil, so a stream of nitrogen gas passed through the liquid.

Resid hydrotreatment was also carried out with a fixed bed high pressure flow microreactor. Feedstock was Middle East Arabian Light based atmospheric residue containing 3.18 wt% sulfur, 1840 ppm nitrogen, 9.33 wt% micro carbon resid, 2.98 wt% n-C₇ insoluble (asphaltene), 37.6 ppm vanadium and 10.8 ppm nickel with density (specific gravity) 0.9621 g/ml. Catalyst (50 ml) with the original shape was loaded into the reactor without dilution. The catalyst was presulfided with 2.0 wt% DMDS dissolved in light gas oil, and then treated with the above feedstock for 24 h. Then, HDS, hydrodenitrogenation (HDN), hydrodemetalization (HDM), hydromicrocarbon resid (HDMCR) and hydrodesphaltenate (HDAs) activities were measured at time on stream 320 h, 653 K, LHSV 0.3 h⁻¹, 13.5 MPa and H₂/oil = 860 Nl/l after nitrogen bubbling. The relative activities were evaluated with reference to the reaction rate of NiO-MoO₃-P₂O₅ catalyst as follows.

\[
k = \text{LHSV} \times (n-1) \times \left( \frac{(1/P_{1})^{n-1} - (1/P_{0})^{n-1}}{n} \right)
\]

\[n: \text{reaction order} (\text{HDS} n = 2, \text{HDM} n = 1, \text{HDN} n = 1, \text{HDMCR} n = 1, \text{HDAs} n = 1)\]

\[P_{0}: \text{Feed concentration} \text{ (%), } P_{1}: \text{Product concentration} \text{ (%)}\]

### 3. Results

#### 3.1. NiO–MoO₃/Al₂O₃

#### 3.1.1. XPS Measurement

The catalysts in oxide form were characterized by XPS to clarify the effect of PEG addition on nickel and molybdenum dispersion. Figure 1 shows the relationship between the amount of PEG addition and the ratio of $I_{Al}^{2p}/I_{Mo}^{2p}$. This relationship is shown in **Figure 1**. The relationship between the SSA of the alumina and the effect of PEG addition was also studied. Dispersion of nickel and molybdenum over Ni-Mo/Al(0) and Ni-Mo/Al(10) prepared from alumina with different
SSA was measured by XPS (Fig. 2). $I_{Ni}/I_{Al}$ and $I_{Mo}/I_{Al}$ definitely depended on the SSA of alumina and became maximum around 230 m²/g. The ratio of $I_{Ni}/I_{Al}$ and $I_{Mo}/I_{Al}$ rather decreased with further increases in SSA, as the amounts of alumina were relatively increased compared to those of the metals. The effect of PEG on the ratio of $I_{Ni}/I_{Al}$ and $I_{Mo}/I_{Al}$ also strongly depended on the SSA of alumina. The $I_{Mo}/I_{Al}$ for Ni-Mo/Al(10) was higher than that for Ni-Mo/Al(0) in the region of SSA lower than 200 m²/g, but seemed to be the same above 230 m²/g. The $I_{Ni}/I_{Al}$ for Ni-Mo/Al(10) was also much higher than that for Ni-Mo/Al(0) with SSA lower than 270 m²/g, but was almost the same above 300 m²/g. The binding energy of alumina, nickel, molybdenum and alumina hardly changed with addition of PEG as shown in Table 1.

### 3. 1. 2. Catalytic Activity

The results of DBT HDS for Ni-Mo/Al(0) and Ni-Mo/Al(10) prepared from alumina with different SSAs is shown in Fig. 3. The effect of PEG on DBT-HDS activity depended on the SSA of the alumina used. The HDS activity was improved apparently with PEG addition if the SSA was lower than 200 m²/g, but was not improved with SSA higher than 200 m²/g.

#### 3. 2. NiO-MoO₃-P₂O₅/Al₂O₃

##### 3. 2. 1. XPS Measurement

The effect of phosphorus and PEG on the dispersion

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**Table 1** XPS Binding Energy of NiO-MoO₃/Al₂O₃ Prepared with and without Polyethylene Glycol

<table>
<thead>
<tr>
<th>Preparation condition</th>
<th>XPS binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSA of alumina [m²/g]</td>
<td>Mo [eV]</td>
</tr>
<tr>
<td>270</td>
<td>0</td>
</tr>
<tr>
<td>270</td>
<td>10</td>
</tr>
<tr>
<td>314</td>
<td>0</td>
</tr>
<tr>
<td>314</td>
<td>10</td>
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Fig. 1 Relationship between Amount of Polyethylene Glycol Addition and XPS Intensity Ratio of $I_{Ni}/I_{Al}$, $I_{Mo}/I_{Al}$ for NiO/Al₂O₃ and MoO₃/Al₂O₃

Fig. 2 XPS Intensity Ratio of $I_{Ni}/I_{Al}$, $I_{Mo}/I_{Al}$ for NiO-MoO₃/Al₂O₃ Prepared from Alumina with Different Specific Surface Areas

Fig. 3 DBT-HDS Activity of NiO-MoO₃/Al₂O₃ Prepared with and without Polyethylene Glycol
of nickel and molybdenum over NiO-MoO₃-P₂O₅/Al₂O₃ was measured by XPS. The relationship between the P₂O₅ content and the ratio of \( I_{Ni}/I_{Al} \), \( I_{Mo}/I_{Al} \) are shown in Fig. 4. Phosphorus addition decreased the dispersion of molybdenum gradually, as the ratio of \( I_{Mo}/I_{Al} \) decreased with increasing phosphorus addition. On the other hand, the ratio of \( I_{Ni}/I_{Al} \) increased with phosphorus addition up to 4 wt%. However, excess addition of phosphorus above 6 wt% rather decreased the dispersion of nickel. PEG addition prevented the decrease in nickel dispersion up to 8 wt% of P₂O₅.

3.2.2. XRD

XRD patterns of dried Ni-Mo-P and Ni-Mo-P-PEG impregnation solution without supports are shown in Fig. 5. Without PEG addition, Ni-Mo-P precursor aggregated obviously and formed an apparent crystalline phase. With PEG addition, Ni-Mo-P precursor achieved good dispersion and formed no crystalline phase. Since the boiling point of PEG is higher than that of water, PEG must remain even after the removal of water. Therefore, the presence of PEG might prevent the aggregation of Ni-Mo-P precursor.

3.2.3. Catalytic Activity

Figure 6 shows the relationship between phosphorus content and DBT HDS activity for NiO-MoO₃-P₂O₅/Al₂O₃ with and without PEG. Phosphorus addition increased the conversion of DBT up to 4 wt% of P₂O₅, but further addition of phosphorus decreased conversion drastically. The selectivity for hydrogenated cyclohexylbenzene also increased with phosphorus addition up to 6 wt% of P₂O₅.

DBT conversion over the catalysts with PEG showed the same trend at lower phosphorus content up to 4 wt% of P₂O₅. However, PEG addition strongly prevented the decrease of DBT conversion above 6 wt% of P₂O₅. On the other hand, PEG addition hardly affected hydrogenated cyclohexylbenzene selectivity.

The resid hydrotreatment activity of Ni-Mo-P/Al (0 to 10) is also shown in Fig. 7. Addition of PEG improved HDS activity to a maximum at 6 wt% PEG. This positive effect of HDS was observed during operation in a commercial plant over one year. The resid hydrodenitrogenation (HDN) and hydrodemicrocarbon-resid (HDMCR) activities also increased slightly with the addition of PEG. The hydrodeasphaltene (HDAs) activity was little affected by the PEG addition. The hydrodevanadium (HDV) and hydrodenickel (HDNi) activities seemed to slightly decrease with the addition of PEG.

4. Discussion

The XPS and XRD results show that addition of PEG to NiO-MoO₃/Al₂O₃ and NiO-MoO₃-P₂O₅/Al₂O₃ is effective for improving the dispersion of nickel and molybdenum as well as CoO-MoO₃/Al₂O₃. The mechanism of positive PEG effect can be explained as follows. Since PEG does not remain on the final catalyst, PEG is not directly responsible for the positive effect. Therefore, PEG modifies the catalyst preparation. Based on the XRD results, PEG addition acts during the course of impregnation. Just after conventional impregnation, nickel and molybdenum precursors dissolve in water stably on the alumina surface. The nickel and molybdenum precursors may have fewer interactions with the alumina support and easily move on the alumina surface. When water is removed from the alumina surface gradually around 373 K, the concentration of nickel and molybdenum precursors finally exceeds the limit of solubility.
Subsequently, the precursors tend to aggregate. On the other hand, if PEG is added to the impregnation solution of nickel and molybdenum, PEG still remains on the alumina support after removal of the water, as PEG has a higher boiling point than water. Therefore, the metal precursors are still stably dissolved in the PEG even after water removal and no aggregated crystalline phase is formed. PEG may act as a blocking agent for nickel and molybdenum precursors as well as CoO-MoO$_3$/Al$_2$O$_3$. During the calcination step, PEG decomposes at around 523 K after nickel and molybdenum precursors interact with the alumina$^{6}$. PEG might increase the dispersion of nickel more effectively than that of molybdenum, as the ratio of $I_{\text{Ni}}/I_{\text{Al}}$ increased up to higher amounts of PEG than $I_{\text{Mo}}/I_{\text{Al}}$. The different trends of PEG effects on nickel and molybdenum are not clear yet and require more study.

In addition, the effect of PEG strongly depended on...
the SSA of alumina support used for the preparation as shown in Fig. 2. Mo atom disperses on alumina support at ca. 0.24 nm²/atom \( ^{6-8} \). Therefore, active metals could remain highly dispersed on a higher SSA of support and lower metal content. Therefore, the blocking effect of PEG might be not apparent under such preparation conditions. On the other hand, the PEG addition works effectively with lower SSA, as the dispersion of active metals tends to decrease.

PEG addition increased DBT-HDS activity over NiO-MoO₃/Al₂O₃. The HDS improvement can be attributed to the improvement of active metal dispersion which leads to more active sites such as Ni-Mo-S. PEG addition may only increase the number of active sites but hardly affect the structure of the active sites, based on the finding that the binding energy of XPS and the selectivity for hydrogenated cyclohexylbenzene in DBT-HDS did not change with PEG addition. This observation agrees with the finding that triethylene glycol does not interact with molybdenum precursor \(^9\).

Addition of PEG also improved DBT-HDS over NiO-MoO₃-P₂O₅/Al₂O₃. The positive effect was especially obvious at higher phosphorus content above 6 wt% P₂O₅, where the dispersion of active metals tended to decrease due to excess addition of phosphorus \(^{10}\).

Considering all the above results, PEG addition should prevent any decrease in HDS activity at the catalyst preparation stage in which the dispersion of active metals tends to decrease. Therefore, the PEG effect depends on the physicochemical properties of the catalyst such as SSA, phosphorus content and metal content.

PEG addition was also effective for improving resid HDS, although other resid hydrotreating reactions such as HDN and HDM were not strongly improved. The reason for the selective improvement of HDS activity is not clear yet. However, one explanation is that the HDS reaction proceeds through the direct HDS route, which is not related to hydrogenation \(^{10}\). On the other hand, HDN and HDM reactions mainly occur after aromatic saturation and the active site of hydrogenation reaction is different from that of the HDS reaction \(^{11-13}\). Therefore, PEG addition may preferably improve the direct HDS route and not hydrogenation activity as shown in Fig. 6(b). Excess addition of PEG rather decreased the positive effect of PEG addition. The decrease in resid HDS activity over 10% of PEG addition as shown in Fig. 7(a) might be attributed to decreased stability of Ni-Mo-P precursor, as PEG interacts strongly with water and excess PEG may dehydrate water associated with the Ni-Mo-P precursor. Therefore, there is an optimum PEG addition for improving catalyst activity.

5. Conclusions

Polyethylene glycol (PEG) as a water soluble organic compound (WSOC) was investigated as an additive to improve the HDS activity of NiO-MoO₃/Al₂O₃ and NiO-MoO₃-P₂O₅/Al₂O₃ catalysts. Addition of PEG to the impregnation solution during catalyst preparation improved dibenzothiophene HDS and resid HDS activity significantly, although hydrogenation activity was not improved. PEG addition may increase nickel and molybdenum dispersion by blocking the aggregation of nickel and molybdenum in the drying step, and consequently increases the number of HDS active sites. The effect of PEG addition was especially obvious in catalyst preparation from alumina with lower SSA and higher phosphorus content, in which the active metal precursor tends to easily aggregate. Therefore, the optimum amount of PEG depends on the target feedstock and physicochemical properties of catalyst.

Acknowledgments

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References

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NiO-MoO_3/Al_2O_3 および NiO-MoO_3-P_2O_5/Al_2O_3系水素化脱硫触媒へのポリエチレンリコールの添加効果

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ニッケル-モリブデン系脱硫触媒の脱硫性能を向上するためには, 水溶性有機高分子化合物の一種であるポリエチレンリコールの添加効果を検討した。XPS測定の結果から, ニッケル-モリブデン/アルミナ触媒およびニッケル-モリブデン-リン/アルミナ触媒の調製において, ポリエチレンリコールを含浸液に添加すると, 活性金属であるニッケルおよびモリブデンの分散性を向上できることが分かった。また, ポリエチレンリコールを添加することで, ジベンゾチオフェンおよび重油の脱硫活性が著しく向上した。特に, 活性金属が凝集しやすいと考えられる低比表面積および高リン添加量領域において効果が著しかった。沸点の高いポリエチレンリコールは, 乾燥工程において水を除去された後も残存することで, 活性金属の凝集を物理的にブロックし, 活性点を増大していると考えられる。