Development of highly active hydrodesulfurization catalysts - Effect of the Addition of CyDTA and Boria -

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Introduction
To meet the severe regulation for reductions of SOx, NOx, and SPM contained in the exhaust gases from diesel vehicles, the improvement of catalyst performances especially for hydrodesulfurization (HDS) is one of the most important subjects. van Veen et al. reported that CoMo catalysts modified with nitric triacetic acid (NTA) show higher activities for HDS of thiophene at atmospheric pressure. We have investigated effects of other chelating reagents such as ethylenediamine-N, N, N', N'-tetra-acetic acid (EDTA) and trans-1, 2-Cyclohexanediamine-N, N, N', N'-tetraacetic acid (CyDTA) and found that CyDTA improves the activity of CoMo/Al2O3 catalyst for HDS of dibenzothiophene (DBT) at high pressure more more effectively than NTA. Besides, CyDTA is found to be effective for hydrogenation of o-xyylene and tetralin over NiW/Al2O3 catalyst. Since CyDTA forms stable complexes with Co or Ni in the impregnating solution, it is suggested that CyDTA retards the sulfidation of Ni species, leading to the effective formation of active phases, namely Co(Ni)-Mo-S or Ni-W-S phases.

On the other hand, the addition of boric acid to NiMo/Al2O3 catalyst has been reported to improve the activities for HDS of DBT6. From EXAFS analysis of NiMo/B2O3/Al2O3 catalyst, the addition of boric acid improves the sulfidation degree of Mo sulfide species. Since Decanio et al. showed that the addition of boric acid to γ-Al2O3 affects the distribution of hydroxyl groups on γ-Al2O3 surface by means of IR spectroscopy, it is suggested that boria weakens the interaction between Mo sulfide species and γ-Al2O3.

Since the additions of CyDTA and boric acid affects the structure of sulfide phases in different ways, it is expected that the simultaneous addition of both CyDTA and boric acid improves the HDS activities of hydrotreating catalysts than CyDTA and boric acid alone. Thus, in the present study, we have prepared the catalysts modified with both CyDTA and boric acid and investigated their activities for HDS of 4, 6-dimethylbienzo thiophene (4,6-DMDBT) and their surface fine structures.

Experimental
Catalyst Preparation. Catalysts were prepared by an incipient wetness method. γ-Al2O3 was impregnated with an aqueous H3BO3 solutions followed by drying and calcination. B2O3/Al2O3 thus prepared was then impregnated with an aqueous solution containing ammonium heptamolybdate (or ammonium metatungstate), cobalt nitrate (or nickel nitrate) and CyDTA followed by the drying at 393 K. MoO3 (WO3) loading of the prepared catalyst was 10 (or 14) mass% with Co(Ni)/Mo(W) molar ratio of 0.32.

Activity Measurement. The catalyst was packed in a fixed bed flow reactor and sulfided in-situ in a stream of 5% H2/S2H2 at 673 K and 1.1 MPa. After the sulfidation, the catalyst was cooled down to 573 K and the feed composed of 0.3 mass% 4, 6-DMDBT and decalin. was flown into the catalyst bed under the flow of H2 at 5.1 MPa.

Characterization. SO2 Uptake Measurement. The catalyst was pretreated in a stream of H2 673 K and 0.1 MPa. Then, SO2 was introduced into the catalyst bed by pulse method. SO2 uptake was determined with GC-TCD. NO Uptake Measurement. The catalyst was sulfided in the same manner as employed for the activity measurements, and then NO was introduced into the catalyst bed by pulse method. NO uptake was detected with GC-TCD. EXAFS Measurement. The catalyst was pressed into a self-supporting wafer and set in the high-pressure EXAFS cell. The catalyst wafer was sulfided in the same manner as employed for the activity measurements. X-ray absorption spectra near W LIII edge were measured in a transmittance mode at room temperature using EXAFS 2000 spectrometer (RIGAKU).

Results and Discussion
The effect of CyDTA and boria on HDS activities for 4,6-DMDBT. In HDS of 4,6-DMDBT, dimethylycyclohexane (DMBiCH), dimethylycyclohexylbenzene (DMCHB) and dimethylbiphenyl (DMBiPh) and their isomers were observed to be produced. We have investigated the effects of CyDTA and boria on HDS activity for 4,6-DMDBT. Here, HDS activity is defined by the sum of product yields per the loading amount of Co(Ni) and Mo(W).

![Figure 1. Effect of CyDTA and boria on HDS activities of Co(Ni)Mo/Al2O3 and NiW/Al2O3 for 4,6-DMDBT.](Image)

Figure 1 shows HDS activities of Co(Ni)Mo/Al2O3 and NiW/Al2O3. The main product is DMCHB over every catalysts. Comparing HDS activities of the catalysts without additives, the order of HDS activity is as follows: CoMo/Al2O3 < NiW/Al2O3 < NiMo/Al2O3. By the addition of CyDTA, no positive effects appears on HDS activities for 4,6-DMDBT while HDS activity of CyDTA-NiW/Al2O3 for DBT was about 1.6 times higher than NiW/Al2O3. From this result, it is suggested that the active phase which is selectively formed by CyDTA isn't efficient for HDS of 4,6-DMDBT. As with CyDTA, HDS activities were not improved by the addition of boria. Contrary to these results, catalysts modified with both CyDTA and boria shows much higher HDS activity than non-modified catalysts. In other word, we found the synergetic effect between CyDTA and boria on HDS activity of 4,6-DMDBT. The effect of both CyDTA and boria on HDS activity of NiW catalyst is more remarkable than those of Co(Ni)Mo/Al2O3. Perhaps, it is related to the fact that sulfidation of W species is more difficult than that of Mo species.

The effect of CyDTA and boria on the surface structure of NiW/Al2O3. Sulfur dioxide (SO2) is known to adsorb on the basic
OH groups on Al2O3 surface. Therefore it is expected to investigate the effect of boria on Al2O3 surface by using SO2 as probe molecules. Figure 2 shows SO2 uptake on B2O3/Al2O3. As B2O3 loading increases, SO2 uptake sharply decreases and it reaches almost zero at above 60 * 1013 B atoms/cm2-Al2O3 (10 mass% B2O3). This indicates that boria interacts with basic OH groups of Al2O3. Considering the fact that WO3 species interact with basic OH groups of Al2O3, it is expected that boria induces the change of the structure of WS2 after sulfidation.

The dispersion of WS2 is explained in terms of the number of CUS. Therefore, it is assumed that boria interacts with basic OH groups of Al2O3. Considering the fact that WO3 species interact with basic OH groups of Al2O3, it is expected that boria induces the change of the structure of WS2 after sulfidation.

Consequently, it is suggested that highly active site is selectively formed by the simultaneous addition of both CyDTA and boria, and it leads to the improvement of HDS activity for 4,6-DMDBT.

In contrast to this, W-S coordination number increases with the increase in boria loading. This result suggests that the sulfidation degree of WS2 is improved by the addition of boria. Therefore, the decrease of the number of CUS by the addition of boria is due to the increase in the crystallinity of WS2. Since there is a good correlation between HDS activity and the sulfidation degree of WS2, the improvement of HDS activity by the addition of boria to CyDTA-NiW/Al2O3 is explained in terms of the sulfidation degree of WS2. This means that boria induces the improvement of the quality of CUS. To sum up, the addition of boria causes the opposite effects on the surface structure of CyDTA-NiW/Al2O3; in other words, the improvement of the HDS activity of CUS and the decrease in the number of CUS.

**Table 1. Structural Parameter of W-S, W-W Coordination**

<table>
<thead>
<tr>
<th>Sample</th>
<th>N-S</th>
<th>R (nm)</th>
<th>N-W</th>
<th>R (nm)</th>
</tr>
</thead>
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<tr>
<td>W-S powder</td>
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<td>0.24</td>
<td>6.00</td>
<td>0.32</td>
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<td>CyDTA-NiW/Al2O3</td>
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<td>0.24</td>
<td>3.5</td>
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<td>0.24</td>
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<td>0.24</td>
<td>3.0</td>
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<tr>
<td>CyDTA-NiW/B2O3(1.0)/Al2O3</td>
<td>5.7</td>
<td>0.24</td>
<td>2.9</td>
<td>0.32</td>
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**References**