CATALYST DESIGN FOR THE SELECTIVE DESULFURIZATION OF 4,6-DIMETHYLDIBENZOTHIOPHENE

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https://doi.org/10.11501/3117279
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THE SELECTIVE DESULFURIZATION
OF 4,6-DIMETHYLDIBENZOTHIOPHENE

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1996
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Chapter 1

Introduction

1 Necessity for the Deep Desulfurization of Gas Oil

Thirty to 40 millions Kl of both gasoline and gas oil are consumed annually in Japan [1]. The growth of their consumptions is 3% and 8 - 10%, respectively. Such a huge amount of their consumption has brought about serious air pollution in the urban areas. (Figure 1-1) [1]. The air pollution from gasoline cars was much improved in Japan in 1970' by unleaded gasoline and three way catalyst for removal of NOx, CO, and hydrocarbon gases. However, exhaust gas from diesel cars is still basically untreated. However, high concentration SO2 and SO3 brought about corrosion problem as well as pollution. The exhaust gas recovery (EGR) was reported to enhance the combustion of particulates [2]. However, the sulfur in the gas oil was also reported to prevent from equipment of EGR system. Thus, Japanese Central Council for Control of Environment Pollution proposed two-steps method to reduce the sulfur level of the gas oil to 0.2 wt% in 1993 and 0.05 wt% by 1997, respectively [3].
Figure 1-1  Concentration\(^1\) of NO\(_x\) in the air.

Figure 1-2  GC-FPD profile of the gas oil\(^4\)
1. The first group consists of most of the alkyl BTs, except C3-BT-4, C4-BT-7, and C7-BT-1 with the substituents probably at the 2- or/and 7-positions:

\[ k > 0.10 \text{ min}^{-1} \]

![Alkyl BT Structure](image1)

2. The second group consists of C3-BT-4, C4-BT-7, C7-BT-1, DBT, and alkylated DBT homologes without substituents at the 4- and 6-positions:

\[ k = 0.034 - 0.100 \text{ min}^{-1} \]

![Alkyl DBT Structure](image2)

3. The third group consists of alkyl DBTs with one of the alkyl groups at either the 4- or 6-position:

\[ k = 0.013 - 0.034 \text{ min}^{-1} \]

![Alkyl DBT Structure](image3)

4. The fourth group consists of alkyl DBTs with two of the alkyl groups at the 4- and 6-positions

\[ k = 0.005 - 0.013 \text{ min}^{-1} \]

![Alkyl DBT Structure](image4)

Figure 1-3  The rate constants of the hydrodesulfurization of sulfur species in the gas oil.\(^5\)
Based on the above background, the present study aimed to design the new catalysis and catalyst for deep desulfurization of gas oil. This chapter reviews the hydrodesulfurization (HDS) reaction of sulfur species, and structure and catalytic activity of the HDS catalysts, to define the aim and outline of the present thesis.

2 HDS Reaction of the Sulfur Compounds

2-1 Sulfur Compounds in the Gas Oil and their HDS Reactivities

Figure 1-2 illustrates the GC-FPD profile of the sulfur species in the gas oil [4]. Forty two and 29 kinds of alkylbenzothiophenenes and -dibenzothiophenenes are found in the gas oil from an Arabian crude. Such sulfur species were classified into some groups according to their reactivities for the HDS as reported previously [5]. Figure 1-3 summarizes the rate constants of the representative sulfur species in the gas oil which form four groups of different reactivities. The first group consists of the alkylbenzothiophenenes (alkyl-BTs), except for C3-BT-4, C4-BT-7, and C7-BT-1 with the subsitients at 2- or / and 7-positions. The second group consists of C3-BT-4, C4-BT-7, dibenzothiophene (DBT), and alkylated DBT homologes without subsitents at 4- or 6-positions. The third group consists of alkyl-DBTs with one of the alkyl groups at either 4- or 6- position. The fourth group consists of alkyl-DBTs with two of the alkyl groups at 4- and 6- positions. Thus, 4-methyl- and 4,6-dimethyl dibenzothiophene have been recognized as the typical refractory sulfur species of the third and fourth groups, respectively [4].

2-2 Reaction Networks

Figures 1-4 to -7 illustrate the desulfurization reaction pathway of thiophene [6], benzo thiophene [7], dibenzo thiophene [8], and benzonaphtothiophene [9], respectively. There are evidently two parallel paths for the desulfurization of aromatic sulfur compounds: one is the desulfurization through the hydrogenation of one phenyl ring at least and successive cleavage of the C-S bond, and the other is direct desulfurization.
Figure 1-4  Hydrodesulfurization reaction pathway of thiophene.  

Figure 1-5  Reaction network for benzothiophene.  

Figure 1-6  Reaction network for dibenzothiophene.  

Figure 1-7  Reaction network for benzonaphthothiophene.
without apparent hydrogenation of phenyl rings. Desulfurization reactivities of the sulfur species are discussed in the respective reaction pathways. The desulfurization rate constants of the reactive sulfur species are summarized in Table 1-1 [10]. HDS reactivities decrease with increasing numbers of the phenyl rings neighbouring to thiophene ring, being in the order of thiophene, benzothiophene, and dibenzothiophene.

It is inferred that the difficulty of the sulfur atom in the substrate to approach the active site on the catalyst, influence the reactivity by reflecting the steric hindrance of the phenyl groups neighbouring to the sulfur atom.

The rate constants of dimethyldibenzothiophene isomers are summarized in Table 1-2 [11]. Their desulfurization reactivities are strongly influenced by the location of substituted methyl groups to neighboring the sulfur atom, probably through their steric hindrance.

3 HDS Catalysts

3-1 Roles of Co and Ni in the Activities of Mo Sulfide Based Catalyst

The binary sulfides supported on Al₂O₃ have been widely used as conventional catalysts for the hydrotreating where Ni or Co is the promotor for the Mo or W sulfide based the catalysts [12]. Their catalytic activity appeared after the sulfiding by H₂ with H₂S gas treatment [12].

Figure 1-8 illustrates the relationships between the position of each transition metal sulfides in the periodic table and desulfurization activity of dibenzothiophene [13]. The second row transition metal sulfides are superior to the first ones for the HDS reactivities. Particular Ru, Rh, Os, and Ir sulfide catalysts exhibit higher activity for the desulfurization reaction than other sulfides. It should be noted that Mo, Co, and Ni sulfide catalysts alone are inferior to the former sulfides, whereas combination of Mo and Co or Ni increases markedly the catalytic activity which is much higher than those of nobel metals.
Table 1-1  Desulfurization Rate Constants of Sulfur Species.\textsuperscript{10}

<table>
<thead>
<tr>
<th>reactant</th>
<th>structure</th>
<th>pseudo-first order rate const, (g of catalyst•s)</th>
</tr>
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<tbody>
<tr>
<td>thiophene</td>
<td>![Thiophene Structure]</td>
<td>$1.38 \times 10^{-3}$</td>
</tr>
<tr>
<td>dibenzothiophene</td>
<td>![Dibenzothiophene Structure]</td>
<td>$6.11 \times 10^{-5}$</td>
</tr>
<tr>
<td>7,8,9,10-tetrahydro-benzo[1]naphto-[2,3-d]thiophene</td>
<td>![7,8,9,10-tetrahydro-benzo[1]naphto-[2,3-d]thiophene Structure]</td>
<td>$7.78 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: batch reactor using n-hexadecane solvent (0.25 mol % reactant concentration), 300 °C, 71 atm, Co-Mo/Al\textsubscript{2}O\textsubscript{3} catalyst. Each reactant reacted individually.

Table 1-2  Desulfurization Rate Constants of Dimethyl dibenzothiophenes.\textsuperscript{11}

<table>
<thead>
<tr>
<th>reactant</th>
<th>structure</th>
<th>pseudo-first order rate const, L/(g of catalyst•s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dibenzothiophene</td>
<td>![Dibenzothiophene Structure]</td>
<td>$7.38 \times 10^{-5}$</td>
</tr>
<tr>
<td>2,8-dimethyl dibenzothiophene</td>
<td>![2,8-dimethyl dibenzothiophene Structure]</td>
<td>$6.72 \times 10^{-5}$</td>
</tr>
<tr>
<td>3,7-dimethyl dibenzothiophene</td>
<td>![3,7-dimethyl dibenzothiophene Structure]</td>
<td>$3.53 \times 10^{-5}$</td>
</tr>
<tr>
<td>4,6-dimethyl dibenzothiophene</td>
<td>![4,6-dimethyl dibenzothiophene Structure]</td>
<td>$4.92 \times 10^{-6}$</td>
</tr>
<tr>
<td>4-methyl dibenzothiophene</td>
<td>![4-methyl dibenzothiophene Structure]</td>
<td>$6.64 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: flow reactor, n-hexadecane carrier oil, each reactant allowed to react individually at 300 °C, at 102 atm in the presence of a Co-Mo/Al\textsubscript{2}O\textsubscript{3} catalyst.
Figure 1-8  Periodic trends for hydrodesulfurization of transition metal sulfide catalysts.\textsuperscript{13)} Unsupported catalysts tested for desulfurization of dibenzothiophene.

Figure 1-9  Effect of the co-catalyst for the desulfurization activity of Mo sulfide.\textsuperscript{14)}

Figure 1-10  Orientation of tiny MoS\textsubscript{2} crystallites on the surface of Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{15)}
Figure 1-9 illustrates the roles of the co-catalyst to increase the HDS activity of Mo sulfide [14]. The ratios of Co / Mo = 0.8 and Ni / Mo = 0.3 were reported to provide the highest activities while more or less Ni or Co contents reduced the activities.

3-2 Structures of the Active Sites

There have been reported that the tiny MoS$_2$-like crystals (15Å) were formed on Al$_2$O$_3$ support after sulfiding, where the Mo species were fixed by the Mo-O-Al bond as shown in Figure 1-10 where Co$_9$S$_8$ crystals were distributed in the neighbours of MoS$_2$ crystals while other forms of Co were bound to Al$_2$O$_3$ [15]. The active site was reported to be ascribed to the sulfur vacancy at the corner and edge of the MoS$_2$ planer crystals [15].

MoS$_2$ in Mo / Al$_2$O$_3$ is reported [16] to consist of a few layers sitting along the support surface, whereas the large and thick crystals, short and 5 - 6 layers of crystal are present in CoMo / Al$_2$O$_3$ and NiMo / Al$_2$O$_3$, respectively, using by high resolution transmission electron microscopy. The role of Ni atoms is to connect each MoS$_2$ slabs, because of its six coordination sites, whereas Co atoms form the end of the MoS$_2$ layers, because of its four coordination sites, respectively. NiMo catalyst is well known to have higher activity for the hydrogenation reaction than CoMo catalyst, whereas the latter catalyst exhibits higher HDS activity than the former. The difference structures of MoS$_2$ layers may provide the different catalytic activities.

Recently, the finer structure of the highly dispersed catalyst is solved by a technique of extended X-ray absorption fine structure (EXAFS). Topsøe has proposed the models for active site of CoMo / Al$_2$O$_3$ catalyst [17], based on IR, Mossbauer spectroscopy (MES), EXAFS, and X-ray photoelectron spectroscopy. Figure 1-11 illustrates the MES spectroscopy of CoMo / Al$_2$O$_3$ of variable Co contents. There were found three kinds of Co species such as Co-Mo-S, Co$_9$S$_8$, and Co aluminate at Co / Mo atomic ratios less than 0.53. A linear correlation is found as shown in Figure 1-12 between HDS activity of thiophene and the amount of Co-Mo-S phase on the CoMo / Al$_2$O$_3$ catalyst [17].
Figure 1-11 In situ Mössbauer spectra obtained at 300K of sulfided catalysts with different Co/Mo ratios.\textsuperscript{17}

Figure 1-12 Activity parameter plotted as a function of the amount of Co in the Co-Mo-S phase.\textsuperscript{17}

Figure 1-13 IR spectra of NO adsorbed on sulfided catalysts: (a) 8\% Mo/Al\textsubscript{2}O\textsubscript{3}, (b) 2\% Co/Al\textsubscript{2}O\textsubscript{3}, and (c) Co-Mo/Al\textsubscript{2}O\textsubscript{3} (Co/Mo=0.44). Spectrum (d) is the theoretical sum spectrum of (a) and (b). Arrows show the band positions of the corresponding calcined Co-Mo/Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{19}

Figure 1-14 Fine structure of Co-Mo-S phase analysis by EXAFS.\textsuperscript{20}
Formation of the particular phases is reported to depend on the amount of additive Co, calcination temperature, and its preparation procedure [18].

NO molecule is reported to be adsorbed on the vacancy site of the sulfide catalyst where the covalent bond is formed [19]. The information for the vacancy site of the catalysts is obtained by IR spectra of adsorbed NO species. Figure 1-13 illustrates the IR spectra of adsorbed NO species on CoMo / Al₂O₃ catalysts [11]. Adsorbed NO forms dinitrosyl on the anion vacancy sites of Mo and Co sulfide, providing the adsorption bands at 1785 and 1690 cm⁻¹ over the former sulfide, 1850 and 1785 cm⁻¹ over the latter sulfide, respectively. CoMo / Al₂O₃ and the blend of Co and Mo provide three sharp peaks of NO adsorbed, of which sum absorbance coincides to the total content of Co and Mo. It should be noted that the absorbance at 1690 cm⁻¹ over CoMo / Al₂O₃ catalyst was smaller than that of the blend, suggesting that Co atom occupies the vacancy of the Mo sulfide in the Co-Mo-S phase to reduce the vacancy.

Figure 1-14 illustrates the fine structure of Co-Mo-S phase analyzed by high resolution EXAFS [20]. It should be pointed out that one Co atom is located at the edge of the MoS₂ plane, where another Co atom is bonded to four S atoms, which coordinate to the Mo atoms.

3-3 Mechanism of HDS Reaction

In the initial stages of the HDS reaction, cyclic sulfur compounds must adsorb to the catalyst through its sulfur atom, on the vacant sulfur sites of the sulfide catalyst surface. It is so-called one-point end-on mechanism establishment of metal (d orbital) - sulfur (p orbital) bonds as was widely believed [21].

Figure 1-15 illustrates the electronic structure of thiophene and its electronic orbitals [21]. Thiophene is a planar molecule with point group symmetry C₂ᵥ. Its electronic structure is very similar to that of benzene. Aspects two highest occupied molecular orbitals (HOMO) lie below the LUMO (the energy gap is approximately 4 eV), yet all above the next occupied orbital (by about 3 eV). Both orbitals of carbon atoms are combinations of 3p atomic orbitals from the various ring atoms, perpendicular to the
Figure 1-15 The electronic structure of thiophene. Solid lines indicate positive phase, dotted lines negative phase. A schematic representation of this orbital is included.\(^{21}\)

Figure 1-16 Schematic representation of HDS reaction mechanism\(^{21}\). The catalyst structures in both A and B are top of the geometry of Figure 1-14, with and without atom SE. Metal atoms are not included. In (A), thiophene binds to catalyst through ST-SE bonding, resulting in the formation of butadiene, H_2S and a vacancy on the surface of the catalyst. This is the sulfur-sulfur mechanism. In (B), the well-known one-point end-on mechanism is included.
plane of the molecule. No contribution from the sulfur atom is observed to the HOMO of neighbouring carbon atom. The orbitals bind the sulfur atom and carbon atoms in the ring and referred to as sulfur "lone pair".

Recently, Smit has reported that ππ interactions between the sulfur atom in the thiophene molecule and sulfur atom in the catalyst are responsible for the weak thiophene-catalyst binding during the adsorption on the basis of a series of scattered-wave density-functional calculations, assuming the simple catalyst-thiophene complexes [21, 22]. Once a thiophene-catalyst adsorption complex has been formed, subsequent desulfurization must involve cleavage of the C-S bonds in thiophene. It is clear that the sulfur atom of thiophene (S₇) can form a bond with the apical sulfur atom (Sₑ) located on the edge of the Ni atom, where an electrostatic attraction between Ni and the two sulfur atoms on the edge is also expected, in addition to their direct orbital interactions. This is consistent with experimental findings and supported by full-potential density-functional calculations. The sulfur - sulfur unit is unstable most likely in the H₂ / H₂S environment where the HDS process takes place. Attack by two hydrogen atom will result in the formation of H₂S regenerating the original edge structure (with five-fold coordination), as shown in Figure 1-16 (A). In the sulfur-sulfur bonding mechanism, a sulfur vacancy is not required for the adsorption of thiophene onto the catalyst. The mechanism is not inconsistent with elemental sulfur and other sulfur species present on the surface of the transition metal sulfide catalyst. This issue is now open to strong debate.

Figure 1-16 (B) is the standard end-on mechanism on the vacant sulfur sites. In this model, vacancies are supposed to have been created through the prior formation of hydrogen sulfur. The validity of this process have not established yet, but two mechanisms of (A) and (B) may operate simultaneously.

4 Problems of the Deep desulfurization of Gas Oil

Much more attention has been focused on the deep desulfurization of gas oil to meet global environmental requirement. However, several problems should be solved to reach the final goal of 0.05 wt% or more in the HDS of gas oil. Conventional desulfurization
operated at moderate temperatures (340 - 360°C) and hydrogen pressures (3 - 5 MPa), usually over CoMo / Al₂O₃ catalyst is unable to achieve the goal [3], because sufficient HDS of refractory sulfur species such as 4,6-dimethyldibenzothiophene is not achieved. Thus, it is necessary to understand the HDS mechanism of refractory sulfur species in the gas oil as the bases for the enhancement of the reactivity. More active catalysts are wanted to achieve such an extensive desulfurization. Some major problems associated with deep desulfurization are summarized as follows:

1) First of all, desulfurization schemes of refractory sulfur species should be clarified.

2) In a practical HDS of gas oil, both aromatic species existing in the feed and various types of sulfur species compete to the active sites on the catalyst surface. H₂S can be an inhibitor for the HDS of the less reactive sulfur species. The effects of inhibition should be clarified in a series of reaction conditions and feeds.

3) In order to meet the demand for low sulfur level oil, proposal and design of more efficiential deep desulfurization catalyst are urgently required while the cost to the refinery should be kept minimum. The development catalyst should be designed to achieve the HDS of refractory species.

4) The catalysts for selective deep desulfurization of refractory species should be designed.

5 Approach and Outline of the Present Study

The present thesis has clarified the inhibition mechanism in the desulfurization of refractory sulfur species and designed a new deep desulfurization catalysts to achieve the sulfur level of gas oil less than 0.05 wt% under the conventional conditions. First of all, the refractory sulfur species found in the gas oil such as 4-methyl- and 4,6-dimethyldibenzothiophene were synthesized, and their HDS reactivities in decalin and its mixture with aromatic hydrocarbons and other sulfur species were examined, using the conventional NiMo and CoMo / Al₂O₃ catalysts. Severe inhibition by such coexisting
compounds was quantified in the respective pathways and steps of 4,6-dimethyldibenzothiophene HDS.

Secondary, desulfurization of 4,6-dimethyldibenzothiophene was studied over the Ru added CoMo/Al₂O₃ catalyst and a blend of Ru/Al₂O₃ and CoMo/Al₂O₃ to find the selective hydrogenation of the sulfur species in the dominant presence of aromatic hydrocarbons. Structure of Ru-CoMo/Al₂O₃ was also studied, using by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and high resolution transmission electron microscopy (HREM). The specific objectives and approaches of the respective catalysts in this thesis are summarized as follows:

Chapter 1. The back ground, problems, and approaches of deep desulfurization of gas oil were reviewed.

In Chapter 2, the HDS reactivities of 4-methyl- and 4,6-dimethyldibenzothiophene (0.3 wt%) were examined over the conventional of NiMo and CoMo/Al₂O₃ catalyst (10 wt%) in decalin at 270 - 340 °C under 2.5 - 4.1 MPa H₂ pressures to clarify, the characteristics of their desulfurization in comparison with that of dibenzothiophene.

In chapter 3, the HDS reactivities and routes of dibenzothiophene and 4,6-dimethyldibenzothiophene (0.3 wt%) were studied over the conventional NiMo/Al₂O₃ catalyst (10 wt%) in decalin containing naphthalene or tetralin (0 - 30 wt%) at 270 - 340 °C under 2.5 - 4.1 MPa H₂ pressures, to qualify the extents of their inhibitions in the respective routes of desulfurization.

In chapter 4, inhibition by coexisting benzothiophene and dibenzothiophene (0.05 wt%) in the desulfurization of 4,6-dimethyldibenzothiophene (0.05 wt%) was studied in decalin under the fixed conditions, using conventional NiMo/Al₂O₃ catalyst (10 wt%). Inhibition by the by-products from benzothiophene such as H₂S and styrene (2.6 x 10⁻³ mol) in the desulfurization of 4,6-dimethyldibenzothiophen (2.6 x 10⁻³ mol) was also examined, to clarify the inhibition in the latter stage of the deep desulfurization.

Chapter 5 showed the selective HDS for the 4,6-dimethyldibenzothiophene (0.1 wt%) in the presence of naphtalene (0 - 10 wt%), using the Ru added the CoMo/Al₂O₃ catalyst.
catalyst, at 300°C under 2.5 MPa H₂ pressure. The surface structure of the catalyst was characterized by XPS, XRD, and HREM.

In chapter 6, selective HDS of 4,6-dimethyldibenzothiophene in the dominant presence of naphthalene was studied over the blend of Ru / Al₂O₃ (0 - 20 wt%) and CoMo / Al₂O₃ (15 wt%) catalysts under the conventional conditions to find another route for selective HDS of the refractory sulfur species.

Chapter 7 summarized the conclusions of this thesis.

6 Literature Cited


Chapter 2

HDS Reactivities of Alkyldibenzothiophenes in Decalin

1 Introduction

Reduction of the sulfur level in the gas oil to less than 0.05 wt% will be regulated by 1997 in Japan, to protect the environment of the urban area. Three stages desulfurization method of gas oil was reported [1] that consist of the desulfurization in the first and second stages over CoMo / Al₂O₃ and NiMo / Al₂O₃ respectively both at 360°C, and the color removal in the third stage over NiMo / Al₂O₃ or Pd at 220°C, respectively. Such a procedure achieved the sulfur level of 0.04 wt% in the product oil without fluorescent color.

Less hydrogen consumption is an advantage in this process, because most of the sulfur species are desulfurized over CoMo / Al₂O₃ catalyst in the first stage. The desulfurization of 4-methyl- and 4,6-dimethyldibenzothiophene at the second stage is the key issue to achieve such an extensive desulfurization in the gas oil. Kilanowski [2] has reported the HDS of alkyldibenzothiophenes over CoMo / Al₂O₃ under atmospheric pressure. The major reaction pathway was the desulfurization without apparent hydrogenation of their
phenyl ring; i.e.; direct desulfurization. However, these experimental conditions were far from conditions for the deep desulfurization in the refinery. Houalla et al. [3,4] and Girdil et al. [5] have reported the kinetics of alkyldibenzothiophenes in the HDS reaction. However, their reaction networks are not established.

In the present study, the desulfurization reactivities of 4-methyl- and 4,6-dimethyl-dibenzothiophenes which were the most refractory sulfur species in the gas oil were studied in decalin over the conventional NiMo and CoMo / Al₂O₃ catalysts under the conditions of 270 - 340°C and 2.5 - 4.1 MPa H₂ pressure which are similar to those in the refinery. Desulfurization reactivities of dibenzothiophene were also included for comparison under such conditions. Such results are expected to provide basic understandings for design of the catalysts for the deep desulfurization of the gas oil.

2 Experimental Section

2-1 Chemicals

Commercially available dibenzothiophene (DBT) and decalin were used. 4,6-dimethyldibenzothiophene (4,6-DMDBT) and 4-methyldibenzothiophene (4-MDBT) were synthesized according to the reference [6]. They were used after purifying, by column chromatography and recrystallization.

2-2 Catalysts

Commercially available NiMo / Al₂O₃ and CoMo / Al₂O₃ (KF-842 and 742 by Nippon Ketjen Co.) were used as catalyst. Chemical compositions of the catalysts disclosed are summarized in Table 2-1. Catalysts were sulfided at 360°C for 6h by flowing H₂S (5 vol%) in H₂ under atomospheric pressure just before its use.

2-3 Reaction and Analysis

HDS reaction was performed in a 50 ml batch-autoclave at 270 - 340°C under 2.5 - 4.1 MPa H₂ pressure for 0 - 180 min, using 1.0 g catalyst and 10g substrate including the
### Table 2-1 Chemical Compositions of Catalysts

<table>
<thead>
<tr>
<th>Name</th>
<th>Support</th>
<th>Metal load [Wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KF-742</td>
<td>alumina</td>
<td>CoO: 4 MoO₃: 15</td>
</tr>
<tr>
<td>KF-842</td>
<td>alumina</td>
<td>NiO: 3 MoO₃: 15</td>
</tr>
</tbody>
</table>

### Table 2-2 Hydrodesulfurization Selectivity of 4-Methyldibenzothiophene and 4,6-Dimethyldibenzothiophene under various Reaction Conditions

<table>
<thead>
<tr>
<th>Reaction selectivity (%)</th>
<th>4-methyldibenzothiophene</th>
<th>4,6-dimethyldibenzothiophene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ba1 +2</td>
<td>Ba3</td>
</tr>
<tr>
<td>320°C-2.5MPa-5min.</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>320°C-2.5MPa-0.5h</td>
<td>35</td>
<td>36</td>
</tr>
<tr>
<td>320°C-2.5MPa-1h</td>
<td>34</td>
<td>39</td>
</tr>
<tr>
<td>250°C-2.5MPa-1h</td>
<td>27</td>
<td>39</td>
</tr>
</tbody>
</table>

### Table 2-3 Ratio of Direct- / Hydrodesulfurized Compound (320°C-2.5MPa-1h)

<table>
<thead>
<tr>
<th>Substrates</th>
<th>NiMo</th>
<th>CoMo</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBT</td>
<td>0.94</td>
<td>3.17</td>
</tr>
<tr>
<td>4-MDBT</td>
<td>0.37</td>
<td>0.93</td>
</tr>
<tr>
<td>4,6-DMDBT</td>
<td>0.12</td>
<td>0.37</td>
</tr>
</tbody>
</table>
solvent. The concentration of the substrate was 0.3 wt%. The heating up in the reactor took 40 min to reach 320°C. It took 30 min to reach 190°C by 30 min, 190°C by 30 min, and 254°C to 320°C by 5 min, respectively. It confirmed that no reaction was observable below 250°C. The conversions of these substrates were about 10% at 250°C for 1 h, and 6% at 320°C under 2.5 MPa H₂ pressure when the temperature in the reactor just reached at 320°C. Hence, the reaction during the heating up can be negligible to count their reactivity at the reaction temperature.

After the reaction, products were qualitatively and quantitatively analyzed by GC-MS, GC-FID, GC-FPD (Yanaco G-3800) equipped with a silicone capillary column (OV-101: 0.25 mm x 50 m).

Desulfurized product through the hydrogenation of one or both phenyl rings, desulfurized product without apparent hydrogenation, and hydrogenated 4,6-DMDBT are abbreviated to B₄₆, A₄₆, C₄₆, and H, respectively. These structures are illustrated in Figure 2-3.

3 Results

3-1 HDS Products

Figure 2-1 (A) illustrates the GC-FID profiles of the desulfurized products from 4,6-DMDBT in decalin and their molecular weight analyzed by GC-MS, respectively. Three kinds of products were obtained, of which molecular weights (M.W.) were 182, 188, and 194, respectively. The peak at M.W. = 188 was doublet. One sharp peak at M.W. = 182 was ascribed to 3,3'-dimethylbiphenyl (C₄₆), which was desulfurized without apparent hydrogenation of the phenyl ring. Two peaks at the M.W. = 188 and 194 were assigned to hydrogenated dimethylbiphenyls at their one or two phenyl rings which suggests the desulfurization after hydrogenation of one or both phenyl rings. Figures 2-1 (B) and (C) illustrate the GC-FID profiles of hydrogenation products from 3,3'- and 3,4'-dimethylbiphenyls under the present conditions, respectively. The retention times of hydrogenation products from the former substrate coincided with those of the
(A) Desulfurized products of 4,6-dimethyldibenzothiophene
(B) Hydrogenated products of 3,3'-dimethylbiphenyl
(C) Hydrogenated products of 3,4'-dimethylbiphenyl

Figure 2-1  Desulfurized products for 4,6-dimethyldibenzothiophene. (NiMo, 320°C-2.5MPa-1h)
(D) Desulfurized products of 4-methyldibenzothiophene
(E) Hydrogenated products of 3-methylbiphenyl
(F) Hydrogenated products of 4-methylbiphenyl

Figure 2-2  Desulfurized products for 4-methyldibenzothiophene.
( NiMo, 320°C -2.5MPa-1h)
desulfuration products from 4,6-DMDBT, whereas the products from the latter exhibited much longer retention times. Pd / carbon catalyst, of which support was not acidic also provided the same hydrogenation products from 3,3'-dimethylbiphenyl. It suggested that the doublet GC peaks in Figure 2-1 (A) were ascribed to the hydrodesulfuration products of the stereoisomers from 4,6-DMDBT. Hence, the product of $M.W. = 188$ and 194 were identified to be 3,3’-dimethylcyclohexyltoluene ($A_{4,6}$), and 3,3’-dimethylbicyclohexyl ($A_{4,6}$), respectively.

Figure 2-2 also illustrates the GC-FID profiles of the desulfurized products from 4-MDBT in decalin by the same procedure. Three kinds of products were identified: 5-methylcyclohexylbenzene ($B_{4,3}$), 5'-methylcyclohexylbenzene ($B_{4,1}, B_{4,2}$), and 3-methylbiphenyl ($B_4$). The former two were produced through the hydrogenation of one phenyl ring, while the last was the direct desulfurization product without apparent hydrogenation.

### 3-2 HDS Profiles

Figure 2-3 illustrates the HDS conversions and product yields of DBT, 4-MDBT, and 4,6-DMDBT in decalin vs. reaction time, respectively, over NiMo / Al$_2$O$_3$ catalyst at 320°C under 2.5 MPa. DBT exhibited the highest reactivity among the substrates examined, providing its conversion of 50% by 0 min, 90% by 30 min, and 100% by 60 min, respectively. There were two desulfurization reaction pathways of DBT, direct desulfurization and hydrodesulfurization route [7]. The major desulfurization product from DBT was biphenyl (DPH). Yield of DPH increased with increasing the reaction time, whereas its yield sharply decreased beyond 30 min. The second major was cyclohexylbenzene (CHB), of which yield increased linearly with reaction time, suggesting the hydrogenation of DPH to CHB.

4-MDBT was desulfurized during heating up, its conversion being 30% for 0 min. 100% conversion of 4-MDBT was obtained for 120 min, however it required 2 times longer reaction time than that of DBT. 4-MDBT produced rather selectivity the methylcyclohexylbenzenes ($B_{4,1}, B_{4,2}$, and $B_{4,3}$) of 75% regardless of reaction time. Their
Figure 2-3  Product distributions in the desulfurization of dibenzothiophene, 4-methyl dibenzothiophene, and 4,6-dimethyldibenzothiophene. (NiMo, 2.5MPa-320°C, solvent: decalin)
yields increased with depending the reaction time, whereas that of methylbiphenyl \((C_4)\) was slightly reduced beyond 60 min. The hydrodesulfurization pathway appears preferential to the direct desulfurization one in the reaction of 4-MDBT.

No definite product from 4,6-DMDBT was found at 320°C for 0 min. Significantly lower reactivities of 4,6-DMDBT was noted than those of former two substrates, its conversion being 50\% by 30 min and 70\% by 60 min, respectively. One hundred and eighty minutes required for providing its 100 \% conversion. Eighty to 90\% of the products were those through the hydrogenation regardless of the reaction time, whereas the yield of direct desulfurization product (dimethylbiphenyl; \(C_{4,6}\)) was below 10\%.

The yields of the desulfurization products from 4-MDBT and 4,6-DMDBT are summarized in Table 2-2. The selectivities among the products of 4-MDBT stayed constant regardless of its conversion, providing the selectivity for \(B_43\) of 36\%, \(B_41\) and \(B_42\) of 32\%, and \(C_4\) of 27\%, respectively. 4,6-DMDBT showed a similar trend, giving the selectivity for dimethylcyclohexylbenzene \((B_{4,6})\) of 62\%, dimethylbicyclohexyl \((A_{4,6})\) of 10\%, and dimethylbiphenyl \((C_{4,6})\) of 16\%, respectively. The significant yield of hydrogenated 4,6-DMDBT \((H)\) was noted at 320°C under 2.5 MPa \(H_2\) pressure by 5 min. The yield of \(H\) decreased with longer reaction time. Selectivity of \(B_{4,6}\) at the latter stage of the reaction may reflect the successive desulfurization by \(H\). The selectivity of \(C_{4,6}\) stayed constant regardless of the reaction conditions.

The ratios of direct desulfurization to hydrodesulfurization products from the three substrates under the standard conditions are summarized in Table 2-3. The ratio decreased in the order of DBT at 0.94, 4-MDBT at 0.37, and 4,6-DMDBT at 0.12, over NiMo / \(Al_2O_3\). The hydrodesulfurization route appears preferential to the direct desulfurization route with increasing numbers of substituted methyl groups at the neighbouring positions of the sulfur atom in the dibenzothiophene skeleton.
3.3 Dependency of the HDS Reactivities on the Reaction Temperatures and Pressures

Figure 2-4 illustrates the HDS reactivities of alkyldibenzothiophenes as a function of reaction temperatures over NiMo / Al₂O₃ catalyst under 2.5 MPa H₂ pressure for 1h. Their desulfurization reactivities vs. reaction pressures at 320°C for 1h are shown in Figure 2-5. HDS reactivities of alkyldibenzothiophenes markedly increased with higher reaction temperatures and pressures. The difference of their reactivity was larger at lower temperature and pressure. Conversions and the ratios of direct- / hydrodesulfurization products at 270 and 320°C are summarized in Table 2-4. DBT exhibited the highest desulfurization reactivity, its conversion being 75% at 270°C, whereas 4,6-DMDBT exhibited the lowest desulfurization reactivity among the substrates examined, providing its conversion of 31% at 270°C. The ratios of 1.88 and 0.08 were obtained from the former and the latter substrates, respectively, suggesting the main reaction pathway was hydrodesulfurization scheme in the reaction of the latter substrate, although the direct desulfurization was the major reaction pathway in the reaction of the former substrate. Their desulfurization reactivities were enhanced at higher reaction temperatures, the conversion being 82% for 4-MDBT and 70% for 4,6-DMDBT, respectively, at 320°C, whereas their direct- / hydrodesulfurization ratio exhibited 0.37 for the former and 0.12 for the latter substrate. It should be noted that their hydrodesulfurization reaction takes place preferentially over the direct desulfurization route regardless of the reaction conditions.

3.4 Comparison of NiMo and CoMo in the HDS of Alkyldibenzothiophenes

Figure 2-6 illustrates the reactivities of alkyldibenzothiophene over CoMo / Al₂O₃ catalyst at 320°C by 1h. DBT exhibited the highest desulfurization reactivity regardless of the catalysts. Especially, its direct desulfurization reactivity was enhanced over the CoMo / Al₂O₃ catalyst, comparing the results of Figure 2-5. NiMo / Al₂O₃ was superior to the CoMo / Al₂O₃ for the desulfurization of 4,6-DMDBT by 1.3 -1.6 times than the latter catalyst. Higher activity reflected higher yield of B₄,6 over NiMo / Al₂O₃. The
Figure 2-4 Conversion and products of desulfurization at various temperatures. (NiMo, 2.5MPa-1h, solvent: decalin)
Figure 2-5  Conversion and products of desulfurization under various H\textsubscript{2} pressures. (NiMo, 320\textdegree{}C-1h, solvent: decalin)

Figure 2-6  Conversion and products of desulfurization under various H\textsubscript{2} pressures. (CoMo, 320\textdegree{}C-1h, solvent: decalin)
ratios of direct- / hydodesulfurization over NiMo and CoMo / Al₂O₃ catalysts are compared in Table 2-3. The ratios of 4- and 4,6-DMDBT were always lower than that of DBT on both catalysts, indicating that the steric hindrance was significant on both catalysts, however the ratios were much higher over the NiMo / Al₂O₃, suggesting that the higher hydrogenation activity.

4 Discussion

4-1 HDS Products and Its Stereochemistry

Possibility of the methyl migration in 4,6-DMDBT has been reported based on the heat of formation of their isomers by MM2 calculation procedure [8]. However, there was no migration of the substituted methyl groups in alkyl dibenzothiophenes over conventional NiMo / Al₂O₃ and CoMo / Al₂O₃ catalysts under the present conditions.

There are two kinds of hydodesulfurization products from 4,6-DMDBT, indicating their stereoisomers. Figure 2-7 illustrates the structures of stereoisomers of HDS products from 4,6-DMDBT. Two kinds of isomerism are present; one is cis- and trans-isomerism in terms of the location of two methyl groups, and the other is cis- and trans-isomerism in term of two hydrogen atoms at the positions of 1'- and 2'- on the phenyl ring, respectively.

4-2 Reaction Pathway and Kinetics Analysis of Alkyl dibenzothiophenes

Figures 2-8 to -10 illustrate the desulfurization reaction pathways of DBT, 4-MDBT, and 4,6-DMDBT, respectively. Major reaction pathway of 4,6-DMDBT was reported the successive hydrogenation of dimethylbiphenyl after the direct desulfurization [4]. However the present study confirmed two points, (1) hydrogenated alkyl dibenzothiophenes were observed on the desulfurization reaction pathway and (2) alkylcyclohexylbenzenes were hardly hydrogenated at the latter stage of the reaction. These two results strongly indicate the hydodesulfurization reaction pathway of
Figure 2-7 Structures of hydrodesulfurized products for 4,6-dimethyldibenzothiophene.

Table 2-4 Ratio of Direct- / Hydrodesulfurized Compound. (NiMo, 2.5MPa-1h)

<table>
<thead>
<tr>
<th>Substrates</th>
<th>270 °C (Total conversion)</th>
<th>320 °C (Total conversion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBT</td>
<td>1.88 (75%)</td>
<td>0.94 (98%)</td>
</tr>
<tr>
<td>4-MDBT</td>
<td>0.45 (47%)</td>
<td>0.37 (82%)</td>
</tr>
<tr>
<td>4,6-DMDBT</td>
<td>0.08 (31%)</td>
<td>0.12 (70%)</td>
</tr>
</tbody>
</table>
Figure 2-8  Reaction pathway of 4,6-dimethyldibenzothiophene.
(NiMo, 320°C-2.5MPa-1h, solvent: decalin)

Figure 2-9  Reaction pathway of 4-methyldibenzothiophene.
(NiMo, 320°C-2.5MPa-1h, solvent: decalin)

Figure 2-10  Reaction pathway of dibenzothiophene.
(NiMo, 320°C-2.5MPa-1h, solvent: decalin)
alkyldibenzothiophenes, where the hydrogenation of phenyl ring proceeds before the removal of sulfur atom.

Pseudo first-order rates [9] of each reaction pathways in alkyldibenzothiophenes are also shown in Figures 2-8 to -10, respectively. In the present study, the kinetic analysis was performed based on the two points. (1) no reaction of alkyldibenzothiophenes was occurred during heating-up and (2) the selectivities for the products did not change regardless of the reaction time. Figure 2-11 plots the logarithmic concentration of the remaining of 4-MDBT vs. reaction time. The concentration of the direct- and hydrodesulfurization products from 4-MDBT were also plotted. First order kinetics was observable to calculate the respective rate constants. The HDS step of alkyldibenzothiophenes is prior to that of the direct desulfurization step through the rate determining step at the hydrogenation of their phenyl rings. The rate constant of the direct desulfurization step of DBT is larger by 3 - 9 times than that of alkyldibenzothiophenes, it being 2.02 x 10^{-5} of k_2 at 4,6-DMDBT and 6.9 x 10^{-5} of k_{10} at 4-MDBT, respectively, whereas the k_{13} of DBT was 1.82 x 10^{-4}. However, desulfurization step of hydrogenated 4-MDBT and 4,6-DMDBT exhibit larger by 30 - 35 and 110 times than that of their direct desulfurization step, respectively. It indicates that desulfurization reactivities of alkyldibenzothiophenes are markedly reduced by the substituted methyl groups.

The hydrogenation activity of 4-MDBT was slightly higher than that of 4,6-DMDBT, although the similar rate constant for the desulfurization step of their hydrogenated intermediates as found regardless of the substrates. The HDS product where was hydrogenated at both phenyl rings was observed in 4,6-DMDBT, while 4-MDBT did not provide such a product. It may reflect the former kinetic results. The steric hindrance of the substituted methyl groups affects not only for the direct desulfurization but their hydrogenation step.

The activation energies [9] for each desulfurization steps of 4- and 4,6-DMDBT, based on their kinetics data under 2.5 MPa H_2 pressure, are summarized in Table 2-6. Preceding results are supported by their activation energies.
Figure 2-11  Concentrations of 4-methyl dibenzothiophene vs. reaction time. (NiMo, 320°C-2.5MPa, solvent : decalin)

Table 2-5  Rate Constant for the Hydrogenation of 4,6-Dimethyldibenzothiophene under various Reaction Conditions.

<table>
<thead>
<tr>
<th>reaction condition</th>
<th>rate constant : $k_3$ a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo / 270°C-2.5MPa-1h</td>
<td>$9.51 \times 10^{-5}$</td>
</tr>
<tr>
<td>NiMo / 300°C-2.5MPa-1h</td>
<td>$1.87 \times 10^{-4}$</td>
</tr>
<tr>
<td>NiMo / 320°C-2.5MPa-1h</td>
<td>$2.76 \times 10^{-4}$</td>
</tr>
<tr>
<td>NiMo / 320°C-4.1MPa-1h</td>
<td>$5.09 \times 10^{-4}$</td>
</tr>
<tr>
<td>CoMo / 320°C-2.5MPa-1h</td>
<td>$8.4 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

a) $k_3$: rate constant of 4,6-DMDBT to 4,6-HDMDBT

Table 2-6  Activate energy of desulfurized steps of 4-methyl- and 4,6-dimethyldibenzothiophene. (NiMo, 320°C-2.5MPa-1h, solvent : decalin)

<table>
<thead>
<tr>
<th>Reaction pathway</th>
<th>4-MDBT</th>
<th>4,6-DMDBT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct desulfurization</td>
<td>$E_{10} = 26.7$</td>
<td>$E_2 = 68.5$</td>
</tr>
<tr>
<td>Hydrogenation of phenyl ring</td>
<td>$E_7 = 22.2$</td>
<td>$E_3 = 57.1$</td>
</tr>
<tr>
<td>Desulfurization of hydrogenated substrate (a)</td>
<td>$E_8 = 19.1$</td>
<td>$E_4 = 21.7$</td>
</tr>
<tr>
<td>Desulfurization of hydrogenated substrate (b)</td>
<td>$E_9 = 29.3$</td>
<td>$E_5 = 54.2$</td>
</tr>
</tbody>
</table>
Based on the above results, lower reactivities of alkyldibenzothiophenes originates as follows: (1) steric hindrance of methyl groups against direct desulfurization and (2) rate determining step of hydrogenation pathway, respectively.

4.3 The Promotors for the HDS Reactivites

Rate constants for the hydrogenation of 4,6-DMDBT under various reaction conditions are summarized in Table 2-5. It is reasonable that the NiMo / Al₂O₃ was superior to the CoMo / Al₂O₃ catalyst for the HDS of 4,6-DMDBT. It is important to note that hydrogenation of phenyl ring in alkyldibenzothiophenes is necessary to enhance their desulfurization reactivities. Hence, the advantage for the two stages desulfurization process of the gas oil [1] is concluded due to enhance the desulfurization reactivity of alkyldibenzothiophenes over NiMo / Al₂O₃ catalyst at the second stage.

4.4 The Other Factors for Lower Reactivity of 4,6-Dimethyldibenzothiophene

It has been reported that significant amount of aromatic hydrocarbons such as alkynaphthalenes and -tetralins are included in the gas oil, of which concentrations are 18 - 30 wt% [10]. More than 60 kinds of sulfur species were also reported to exist in the gas oil, such as thiol, alkylbenzothiophenes, and alkyldibenzothiophenes which carried alkyl groups with carbon numbers of 1 - 3, respectively [11]. In addition, the sulfur species are expected to provide significant amount of their desulfurization products such as alkylbenzenes, -cyclohexenes, -biphenyls, and H₂S gas.

Desulfurization reactivities of alkyldibenzothiophenes in decalin are higher than that in the feed, because the latter contains more aromatic and sulfur compounds than the former. It will be necessary to clarify the effect of coexisting compounds for the desulfurization of 4,6-DMDBT.
5 Literature Cited


Chapter 3

Inhibition in the Desulfurization of 4,6-Dimethyldibenzothiophene by Aromatic Compounds

1 Introduction

The preceding chapter indicated that HDS reactivity of alkyldibenzothiophenes in decalin was much higher than that in the feed. Practical desulfurization reactivity of 4,6-DMDBT in the gas oil must be severely hindered by the coexisting aromatic hydrocarbons and sulfur species. Since there have been many reported that the inhibition by the naphthalene [1,2] and phenanthrene [3] for the desulfurization of benzothiophene and DBT. The oxygen compounds such as cresol [4], benzo furan [3], dibenzofuran [3], phenol [5], and H2O [6], and nitrogen compounds such as quinoline [7], pyridine [8], acridine [3], and carbazole [3] are also found as the inhibitors. However, the inhibition mechanism for the desulfurization of refractory sulfur species has been never clarified, where the main desulfurization takes place after the hydrogenation of their phenyl rings. There have been reported that the yield of biphenyl from DBT suffered less inhibition by the presence of phenanthrene over sulfide Mo / Al2O3 catalyst at 300°C under 10 MPa H2 pressure, using flow reactor, although the yield of cyclohexylbenzene was markedly
reduced [3]. Benzothiophene and DBT are expected to suffer less inhibition by coexisting aromatic partners than alkyldibenzothiophenes, because of their main reaction pathway of direct desulfurization.

In this chapter, desulfurization reactivity of 4,6-DMDBT and its reaction pathway were studied over the conventional NiMo / Al₂O₃ catalyst in decalin mixed with tetralin or naphthalene, to clarify their inhibition mechanism and to propose the new catalysts for its efficient desulfurization.

2 Experimental Section

2-1 Chemicals

Commercially available naphthalene and tetralin were used as aromatic partners, because these substrates were typically contained in the gas oil, and their GC peaks did not overlap that of the HDS products from 4,6-DMDBT each other. Commercially available DBT and decalin were also used. 4,6-DMDBT was synthesized according to the reference [9].

These substrates were dissolve in decalin solvent, which carried 0 - 30 wt% of aromatic hydrocarbons and 0.3 wt% of sulfur species, respectively.

2-2 Catalysts

Commercially available NiMo / Al₂O₃ (KF-842 by Nippon Ketjen Co.) was used in the present study. Compositions of the catalyst were described in chapter 2. (Table 2-1) The catalyst was sulfided at 360°C for 6h by flowing H₂S (5 vol%) in H₂ under atmospheric pressure just before its use.

2-3 Reaction and Analysis

Desulfurization reaction was performed in a 50 ml batch-autoclave at 270 - 340°C under 2.5 - 4.1 MPa H₂ pressure for 0 - 3h, using 1.0 g catalyst and 10g substrate including the solvent. The details about heating up in the reactor were described in
chapter 2. Reactor was cooled down and H₂ gas was replaced for 2h reaction of 4,6-DMDBT at naphthalene of 10 wt%.

After the reaction, products were qualitatively and quantitatively analyzed by GC-MS, GC-FID, GC-FPD (Yanaco G-3800) equipped with a silicone capillary column (OV-101: 0.25 mm x 50 m).

3 Results

3-1 Desulfurization Reactivity of 4,6-Dimethyl dibenzothiophene in the Presence of Naphthalene

Figure 3-1 (a) illustrates the conversions of 4,6-DMDBT in decalin or decalin with 10 wt% naphthalene as a function of reaction time over NiMo / Al₂O₃ at 320°C under 2.5 MPa H₂ pressure for 1h. The conversion of 4,6-DMDBT in decalin increased with increasing reaction time, to reach 85% by 2h, whereas the conversion was severely hindered by the presence of 10 wt% naphthalene, its conversions being 10% for 0.5h, 20% for 1h, and 50% for 2h, respectively. Naphthalene was hydrogenated into tetralin under the present conditions, its conversions being 50% for 0.5h, 70% for 1h, and 80% for 2h, respectively.

Figure 3-1 (b) illustrates the yields of major products. Their selectivities were confirmed not to change by the reaction time, the products being 60% of B₄,₆, 20% of A₄,₆, and 20% of C₄,₆. The yield of major products, B₄,₆ and A₄,₆, are severely hindered by naphthalene, being 11% and 2%, respectively, by 1h.

Figure 3-1 (c) illustrates the yields of minor products from 4,6-DMDBT. The constant yield of C₄,₆ was found regardless of naphthalene content and reaction time, it yield being 15%.

3-2 Effect of Coexisting Naphthalene Contents

Figure 3-2 illustrates the conversions of (a) DBT, (b) 4,6-DMDBT, and their products yield vs. naphthalene concentrations, respectively, at 320°C under 2.5 MPa H₂
Figure 3-1 Dependency on reaction time. (NiMo, 2.5MPa-320°C)
Figure 3-2  Inhibition with naphthalene of hydrodesulfurization (HDS) reaction. (NiMo, 320°C-2.5MPa-1h)

Figure 3-3  Dependency on H₂ pressure. (NiMo, 320°C-1h, solvent: decalin with 10wt% naphthalene)
pressure for 1h. Conversion of DBT moderately decreased with increasing naphthalene concentration, being 90 and 65% at 10 and 30 wt% of naphthalene, respectively, while its 100% conversion was achieved in decalin. Conversion of 4,6-DMDBT was markedly reduced by the addition of naphthalene, being 25 and 5% at 10 and 30 wt% of naphthalene, respectively, whereas the conversion in decalin was 70%.

The major products form DBT was biphenyl (DPH) and cyclohexylbenzene (CHB), their yields being both 50% in decalin, respectively. The yield of CHB was markedly reduced by naphthalene, its yield being 10 and 5% at 10 and 30 wt% of naphthalene. In contrast, the yield of DPH increased.

The major desulfurization product from 4,6-DMDBT, B_{4,6}, was obtained at 50% yield in decalin, however the yield was severely reduced with increasing naphthalene concentrations, being 25 and 10% at 5 and 10 wt% of naphthalene, respectively. It should be noted that no B_{4,6} was found at 30 wt% of naphthalene concentration. The yield of second major, A_{4,6}, was completely suppressed by addition of 5 wt% naphthalene.

Degrees of inhibition against each product in DBT and 4,6-DMDBT are summarized in Table 3-1. These values were calculated according to the following equation.

\[
\text{The degree of inhibition for desulfurization (\%) = } \left( \frac{\text{desulfurization conversion, or products yield in the presence of naphthalene}}{\text{desulfurization conversion, or products yield in decalin}} \right)
\]

DBT suffered less inhibition from the additive naphthalene, whereas its hydrodesulfurization route was severely retarded. Hydrodesulfurization route of 4,6-DMDBT suffered severely such an inhibition.

3-3 Reaction Pressure

Figure 3-3 (a) illustrates the conversions of 4,6-DMDBT vs. H\textsubscript{2} pressure at 320°C for 1h. The reactivities increased with increasing H\textsubscript{2} pressure in decalin, providing 70
Table 3-1  Degree of Inhibition (%) for Hydrodesulfurization Reaction by Naphthalene

<table>
<thead>
<tr>
<th>Concentration of naphthalene (wt%)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBT (Total conversion)</td>
<td>0</td>
<td>5</td>
<td>11</td>
<td>35</td>
</tr>
<tr>
<td>4,6-DMDBT (n)</td>
<td>0</td>
<td>51</td>
<td>67</td>
<td>91</td>
</tr>
<tr>
<td>DBT to CHB&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0</td>
<td>67</td>
<td>80</td>
<td>88</td>
</tr>
<tr>
<td>4,6-DMDBT to DMCHB&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0</td>
<td>63</td>
<td>78</td>
<td>97</td>
</tr>
<tr>
<td>DBT to BP&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0</td>
<td>---</td>
<td>---</td>
<td>0</td>
</tr>
<tr>
<td>4,6-DMDBT to DMBP&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0</td>
<td>---</td>
<td>14</td>
<td>---</td>
</tr>
</tbody>
</table>

<sup>a</sup> CHB; cyclohexylbenzene  <sup>b</sup> DMCHB; dimethylcyclohexylbenzene  
<sup>c</sup> BP; biphenyl  <sup>d</sup> DMBP; dimethylbiphenyl

Table 3-2  Ratio of Reaction Rate Constant of 4,6-Dimethyldibenzothiophene in various Solvents (k'/k)

<table>
<thead>
<tr>
<th>Reaction Pathway</th>
<th>k' / k&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 → 2</td>
<td>k2' / k2 = 0.851</td>
</tr>
<tr>
<td>1 → 3</td>
<td>k3' / k3 = 0.188</td>
</tr>
<tr>
<td>3 → 4</td>
<td>k4' / k4 = 0.400</td>
</tr>
<tr>
<td>3 → 5</td>
<td>k5' / k5 = 0.290</td>
</tr>
</tbody>
</table>

<sup>a</sup> k : rate constant k in decalin  
k' : rate constant k in decalin with 10 wt% naphthalene
and 87% conversion under 2.5 and 4.1 MPa, respectively, while the conversions stayed at 23 and 40%, respectively, under 2.5 and 4.1 MPa in 10 wt% naphthalene. Hydrogenation conversions of naphthalene were 70 and 85% under 2.5 and 4.1 MPa, respectively.

Yields of major products from 4,6-DMDBT are shown in Figure 3-3 (b). Especially, the yield of A4,6 increased in decalin with increasing H2 pressure, whereas no A4,6 was found in the presence of naphthalene. Reduction of inhibition by aromatic partner against the HDS of 4,6-DMDBT was difficult, because the hydrogenation reactivity of naphthalene was much superior to that of 4,6-DMDBT.

3.4 Reaction Temperature

Figure 3-4 (a) illustrates the conversion of 4,6-DMDBT as a function of the reaction temperature, at 270 - 340°C under 2.5 MPa H2 for 1h. The conversion was markedly reduced by the presence of naphthalene, being 7 and 39% at 270 and 340°C, respectively, while the conversion in decalin reached to 82% at 340°C. Such reduction in the conversion was due to the decreased yield of B4,6 and A4,6. However, its direct desulfurization reactivity was noted to increase at high temperature. Yield of C4,6 increased with increasing reaction temperature, being 3% at 300°C, 6% at 320°C, and 15 - 25% at 340°C, respectively, regardless of the presence of naphthalene.

Hydrogenation of naphthalene exhibited its conversions of 60 and 70% at 270 and 340°C, respectively.

3.5 Inhibition Extent of Aromatic Species

Figures 3-5 (A)-(a) and (B)-(a) illustrate the conversions of DBT and 4,6-DMDBT in decalin with 10 wt% of tetralin or naphthalene, respectively, at 320°C under 2.5 MPa H2 pressure for 1h. Desulfurization of DBT was moderately retarded by aromatic partners, respectively, its conversion being 100% in decalin, 97 and 93% at 10 wt% of tetralin and naphthalene, respectively. Inhibition extents were 3 and 7% by the former and the latter aromatics, respectively. Desulfurization conversion of 4,6-DMDBT decreased to 70% in decalin, 53% by tetralin, and 23% by naphthalene of 10 wt%,
Figure 3-4  Dependency on reaction temperature. (NiMo, 2.5MPa-1h, solvent: decalin or decalin with 10 wt% naphthalene)
Figure 3-5  Inhibition with aromatic compounds of hydrodesulfurization reaction. (NiMo, 320°C-2.5MPa-1h, solvent: Dec(decalin), Tet(tetralin 10wt%), Nap(naphthalene 10wt%))
respectively. Inhibition extents are as large as 24 and 67% by tetralin and naphthalene, respectively.

Their product yields are also shown in Figures 3-5 (A)-(b) and (B)-(b), respectively. Yield of CHB from DBT was markedly reduced by the aromatic partner, being 45% at tetralin and 5% at naphthalene, respectively, whereas its yield was 50% in decalin. In contrast, the yield of DPH increased from 50% in decalin to 55 and 80% at tetralin and naphthalene, respectively.

The HDS route of 4,6-DMDBT suffered more increasing aromaticity of the additive solvent, the product yield of decreasing to 18 and 6% by tetralin and naphthalene, respectively, from 25% in decalin. Yields of C₄₆ were 4% regardless of the presence of aromatic partners.

4 Discussion

4-1 Inhibition in the desulfurization Reaction and Its Kinetic Analysis

Figure 3-6 illustrates the desulfurization paths of 4,6-DMDBT and their rate constants of first order in the presence of 10 wt% naphthalene. In this present study, the rate constant was calculated by assuming two points; (1) distribution of the products from 4,6-DMDBT was not changed by additive naphthalene concentration (2) inhibition by-products can be neglected in such analysis, because the concentration of 4,6-DMDBT and its conversion were 0.3 wt% and 50% in the presence of naphthalene for 1h, suggesting the low concentration of by-products. Figure 3-7 illustrates the logarithmic conversion of mole concentration of 4,6-DMDBT vs. reaction time. Straight lines to suggest the first-order reaction were found regardless of the presence of naphthalene.

The ratios of rate constants of 4,6-DMDBT in decalin with naphthalene to that of decalin are summarized in Table 3-2. Although the all rate constants of each steps were generally reduced in the presence of naphthalene, the ratio at hydrogenation step of one phenyl ring (1 to 2; 0.188) was much smaller than that of the direct desulfurization step (1 to 2; 0.851). The latter step effects much less inhibition from the naphthalene, while
Figure 3-6  Rate constant of each reaction pathway. 
(NiMo, 320°C-2.5MPa-1h)

Figure 3-7  Logarithms conversions of concentration of 4,6-dimethyldibenzothiophene. (NiMo, 320°C-2.5MPa, solvent: decalin or decalin with 10wt% naphthalene)
desulfurization step of hydrogenated 4,6-DMDBT to give dimethylbicyclohexyl (3 to 5; 0.29) appeared to suffer severe inhibition from the aromatic partners.

The desulfurization of gas oil was certainly enhanced by higher reaction temperatures and H₂ pressures, whereas 4,6-DMDBT still suffer the inhibition by aromatic partners [10]. The aromatic partners may occupy the active site preferentially at elevated temperatures.

4-2 Active Sites on the NiMo Catalyst

The present study revealed three points; (1) DBT was affected less inhibition from the presence of aromatic partners where its main reaction pathway is direct desulfurization, (2) hydrogenation of phenyl rings in 4,6-DMDBT decreased with increases of aromatic content and aromatic ring size, and (3) its hydrogenation conversion of 4,6-DMDBT increased with decreasing amount of aromatic partners, suggesting that two kinds of active sites exist on the surface of the catalysts such as desulfurization and hydrogenation active sites. There are many reports that the evidence of two kinds of active site [11, 12]. Vrinat [11] has suggested that butenes were produced through the desulfurization of thiophene on the desulfurization active site, and such products were hydrogenated to butane on the hydrogenation active site on the same catalyst.

Based on the above discussion, it will be worthwhile to estimate the mechanism at the molecular level. 4,6-DMDBT is hydrogenated at the hydrogenation active site on the catalyst through the adsorption of its phenyl ring below 250°C, and its hydrogenated intermediate is desulfurized at the desulfurization active site in decalin. DBT may prefer adsorption on the desulfurization active site to that on the hydrogenation active site, its higher reactivity reflecting the higher selectivity of its direct desulfurization product. 4,6-DMDBT and aromatic partners must compete to the same hydrogenation active site on the catalyst and the former hydrogenation step was severely hindered. Large difference for the hydrogenation reactivities were reported from naphthalene to tetralin or from tetralin to decalin [13]. The loss of resonance energy at the latter reaction was larger than that of the former, as estimated to be 105 and 151 KJ/mol at the latter and
former steps, respectively. Thus the retardation of naphthalene for the desulfurization of 4,6-DMDBT was larger than that of tetralin, because of stronger adsorption of the former inhibitor to the hydrogenation active site on the catalyst [14].

Desulfurization reactivity of 4,6-DMDBT increases with decreasing aromatic partners through its hydrogenation, because the occupation of latter substrate on the hydrogenation active site decreased.

5 Literature Cited

(1) Lo,H., Ph.D.Disseration, University of Delaware, Newark, 1981.
(7) Bhinde,M.V., Ph.D.Disseration, University of Delaware, Newark, 1979.
Chapter 4

Coexisting Sulfur Compounds and By-product $\text{H}_2\text{S}$ Gas as Inhibitors in Desulfurization Reaction of 4,6-Dimethyl dibenzothiophene

1 Introduction

More than 60 kinds of sulfur species were found existing in the gas oil such as benzothiophene, dibenzothiophene, and their alkyl derivatives as reported previously [1, 2]. There have been reported inhibition roles of $\text{H}_2\text{S}$ for the desulfurization of thiophene [3], benzothiophene [4], and dibenzothiophene [5]. However, inhibition for the desulfurization of refractory sulfur species has not been studied. Stronger retardation on their desulfurization reaction is expected to interfere the achievement of lower sulfur level in the gas oil.

In the present study, desulfurization reactivity of 4,6-DMDBT in decalin with benzothiophene, DBT, and $\text{H}_2\text{S}$ were examined over the conventional NiMo / Al$_2$O$_3$ catalyst, to clarify the inhibition mechanism against the particular refractory sulfur species.
2 Experimental Section

2.1 Chemicals

Commercially available benzothiophene and dibenzothiophene were used as typical sulfur species in the gas oil and their GC peaks did not overlap that of the HDS products from 4,6-DMDBT. 4,6-DMDBT was synthesized according to the reference [6]. These substrates were dissolved in decalin solvent, their concentrations being 0.2 - 1.0 wt% for coexisting sulfur species and 0.3 wt% for 4,6-DMDBT, respectively.

2.2 Catalyst

Commercially available NiMo / Al₂O₃ (KF-842 by Nippon Ketjen Co.) was used as the catalyst. Their chemical compositions were described in chapter 2 (Table 2-1). It was sulfided at 360°C for 6h by flowing H₂S (5 vol%) in H₂ under atomospheric pressure just before its use.

2.3 Reaction and Analysis

HDS reaction was performed in a 50 ml batch-autoclave at 300°C under 2.5 MPa H₂ pressure for 0 - 2h, using 0.04 - 1.0 g catalyst and 10g substrate including the solvent. Partial pressures of H₂S gas added was 0.132 MPa which was similar concentration of H₂S gas producing from coexisting sulfur species.

After the reaction, products were qualitatively and quantitatively analyzed by GC-MS, GC-FID, GC-FPD (Yanaco G-3800) equipped with a silicone capillary column (OV-101: 0.25 mm x 50 m).
3 Results

3·1 Dependency of the HDS Reactivities on the Reaction Time in the Presence of Sulfur Species

Figure 4-1 illustrates the remaining amounts of 4,6-DMDBT and (A) benzo thiophene and (B) DBT vs. reaction time in decalin at 300°C under 2.5 MPa H₂ pressure. The initial concentrations were 0.05g of 4,6-DMDBT and 0.05g of benzo thiophene or DBT, respectively. Remaining amount of 4,6-DMDBT in decalin was markedly reduced by longer reaction time, being 53% for 1h and 16% for 2h, respectively. Large retardation in the desulfurization of 4,6-DMDBT was found in the presence of benzo thiophene and DBT, which left the amount of unreacted 4,6-DMDBT at 66 and 65%, respectively, and 55 and 35% by 1 and 2h, respectively.

In contrast, benzo thiophene of 57% was desulfurized during the heating-up, and its 100% conversion was observed for 0.5h. The reactivity of DBT was slightly lower than benzo thiophene, giving its conversions of 82 and 100% for 1 and 2h, respectively.

Figure 4-2 illustrates the product distributions from 4,6-DMDBT in decalin with benzo thiophene or DBT, respectively. Large retardation against the major desulfurization product, B₄,₆, was found in the presence of benzo thiophene, providing the yields of 21% for 1h and 30% for 2h, respectively, while the yields being 32 and 56% for 1 and 2h, respectively, in decalin. Yield of B₄,₆ was also reduced by DBT, being 21 and 45% for 1 and 2h, respectively. Similar trend was found for the yield of second major product, A₄,₆, its yield being 11 and 6% in the presence of DBT and benzo thiophene, respectively, for 2h, although 21% yield was observed in decalin. The hydrogenation of both phenyl rings in 4,6-DMDBT was significantly retarded by benzo thiophene. The yield of C₄,₆ from 4,6-DMDBT was unchanged regardless of sulfur species, being 4% for 2h.

It should be noted that yield of hydrogenated 4,6-DMDBT, H, was found around 6 - 7% in the presence of benzo thiophene through the reaction, whereas the desulfurization in
Figure 4-1  Proceeding of hydrodesulfurization.

(4,6-DMDBT : BT or DBT = 0.05 : 0.05g, NiMo catalyst : 1.0g, 300°C-2.5MPa, solvent : decalin)

a) BT : benzothiophene
b) DBT : dibenzothiophene
c) 4,6-DMDBT : 4,6-dimethyldibenzothiophene
Figure 4-2  Products from 4,6-dimethyldibenzothiophene.
(4,6-DMDBT : BT or DBT= 0.05 : 0.05g, NiMo catalyst : 1.0g, 300°C-2.5MPa, solvent : decalin)
decalin provided its yields of 5% for 1h and 2% for 2h, respectively, suggesting the inhibition by benzothiophene against the desulfurization of the hydrogenated intermediate.

Figures 4-3 (E) and (F) illustrate the yield of products from coexisting benzothiophene and DBT vs. reaction time, respectively. Figures 4-3 (G) and (H) also illustrate the concentration of by-product H₂S gas calculated from conversion of sulfur species. The major desulfurization product from benzothiophene was ethylbenzene, the yield being 55 and 100% for 0 and 0.5h, respectively. No styrene was found in the products as reported by Miki [11].

High concentration of H₂S gas from coexisting benzothiophene was present already at the initial stage of the HDS reaction of 4,6-DMDBT, its concentration being 2.09 x 10⁻⁴ mol for 0h and 4.27 x 10⁻⁴ mol for 0.5h, respectively.

No definite product from coexisting DBT was found by 0h. The yield of DPH increased with longer reaction time to 33 and 53% for 0.5 and 1h, respectively, while the yield of CHB were 12 and 29% by 0.5 and 1h, respectively. H₂S gas from DBT increased its concentration to 1.60 x 10⁻⁴ and 3.01 x 10⁻⁴ mol for 0.5 and 1h, respectively.

### 3.2 Competitive Reaction between 4,6-Dimethyldibenzothiophene and Other Sulfur Species

Figure 4-4 illustrates remaining amount of 4,6-DMDBT and coexisting (A) benzothiophene or (B) DBT as a function of catalyst content, respectively, at 300°C under 2.5 MPa H₂ pressure for 0.5h. The concentrations of both substrates were 0.05g in 10 g decalin. 4,6-DMDBT exhibited less desulfurization reactivity in the presence of sulfur species regardless of the catalyst content, its conversion being 4%, 6%, and 15% for 0.04, 2, and 10 wt% of the catalyst content, respectively. The conversion of benzothiophene was higher and increased more rapidly with more catalyst content, being 57 and 100% at 2 and 10 wt% of catalyst content, respectively. Conversion of DBT was slightly lower than that of benzothiophene, being 22 and 45% at 2 and 10 wt% of catalyst content, respectively. The mole ratios of reacted sulfur species are summarized in Table 4-1. The ratio of benzothiophene to 4,6-DMDBT was 3 and 6 at 0.4 and 2 wt% of the catalyst.
Figure 4-3 Products from benzothiophene or dibenzothiophene. 
(4,6-DMDBT : BT or DBT = 0.05 : 0.05g, NiMo catalyst : 1.0g, 300°C-2.5MPa, solvent : decalin)

a) Desulfurized products from coexisting BT  
b) Desulfurized products from coexisting DBT  
c) Desulfurized products from 4,6-DMDBT and coexisting BT  
d) Desulfurized products from 4,6-DMDBT and coexisting DBT
Figure 4-4 Competitive reaction of 4,6-dimethyldibenzothiophene and benzothiophene or dibenzothiophene over various catalyst content. (4,6-DMDBT : DBT or BT = 0.05 : 0.05g, NiMo catalyst, 300°C-2.5MPa-0.5h, solvent : 10g decalin)
content, respectively, while that of DBT to 4,6-DMDBT was 1 at 0.4 wt% and 2.5 at 2 wt% of the catalyst content, respectively.

Figure 4-5 illustrates the HDS conversions of 4,6-DMDBT and (A) benzothiophene or (B) DBT vs. changing ratio of reactants, respectively, at 300°C under 2.5MPa H₂ pressure for 0.5h. The conversions of 4,6-DMDBT and DBT were constant at 25 and 50%, respectively, regardless of their contents. Enough numbers of active sites on the catalyst appear available for all substrates, when the substrate to catalyst (g) ratio was 1/10.

Benzothiophene exhibited 100% conversion for the desulfurization regardless of the content of 4,6-DMDBT, whereas the conversion of 4,6-DMDBT markedly reduced with increasing content of benzothiophene, giving the conversion of 23, 18, 15, and 12% at 0, 0.02, 0.05, and 0.08 g of benzothiophene, respectively.

Figures 4-5 (C) and (D) also illustrate the yields of their desulfurization products, respectively. 4,6-DMDBT provided constant yields of products regardless of DBT content, giving B1 of 15%, H of 6%, and C₄,₆ of 2%, respectively. Similar trend was found in the product distributions from DBT, DPH of 35% and CHB of 17% being obtained regardless of 4,6-DMDBT content.

In contrast, yield of B1 (total yield of B₄,₆ and A₄,₆) from 4,6-DMDBT decreased with increasing content of benzothiophene, being 15% in decalin, 9% at 0.05g and 6% at 0.08g of benzothiophene content. No C₄,₆ was found in the presence of benzothiophene. It should be noted that the yield of H was 7% regardless of the content of benzothiophene. It suggests that increasing yield of hydrogenated 4,6-DMDBT reflects the inhibition at its desulfurization step.

3.3 Secondary Inhibition by Produced H₂S

After 4,6-DMDBT with benzothiophene was desulfurized by 1h, 0.03g of unreacted 4,6-DMDBT, 0.05g (5 x 10⁻⁴ mol) of ethylbenzene from benzothiophene, and 4 x 10⁻⁴ mol of H₂S gas were found as shown in Figure 4-1 (A). Figure 4-6 (A) illustrates desulfurization conversion of 4,6-DMDBT in the presence of ethylbenzene or H₂S vs.
Figure 4-5  Competitive reaction of 4,6-dimethyldibenzothiophene and benzothiophene or dibenzothiophene, when changing ratio of reactants. (4,6-DMDBT+BT or DBT = 0.1g, NiMo catalyst: 1.0g, 300°C-2.5MPa-0.5h, solvent: decalin)

a) EB, b) CHB, c) H, d) C_{46}, e) DPH, f) B1
Figure 4-6 Inhibition of H₂S or ethylbenzene against hydrosulfurization reaction of 4,6-dimethyl dibenzothiophene after 1h. (NiMo catalyst : 1.0g, 300°C-2.5MPa-1h, solvent : decalin)

a) H₂S partial pressure : 0.132MPa  b) ethylbenzene added: 2.624 x 10⁻³ mol
reaction time. Large retardation in the desulfurization of 4,6-DMDBT was found by H₂S, giving a conversion of 24% for 1h, whereas the conversion stayed at 53% regardless of the presence of ethylbenzene. Figures 4-6 (B) and (C) illustrate product distributions from 4,6-DMDBT. Yield of B1 was reduced markedly by H₂S, being 14%, but 42% in decalin and 39% in the presence of ethylbenzene, respectively. No C₄,₆ was found in the presence of H₂S. It should be noted that the yield of H increased by addition of H₂S, giving the yield of 8%, whereas its yield was 3% in decalin regardless of the additive ethylbenzene. A product ethylbenzene from benzothiophene was not an inhibitor when the content was low, whereas produced H₂S severely inhibited for the hydrogenation of the phenyl rings in 4,6-DMDBT.

Figure 4-7 illustrates the hydrogenation conversion of naphthalene over NiMo / Al₂O₃ catalyst in decalin under 2.5 MPa H₂ or H₂ with 0.132 MPa H₂S, respectively, at 300°C for 1h. Naphthalene provided tetralin, its conversion being 93% under H₂, whereas 75% in the presence of H₂S, respectively. Hence, H₂S is also an inhibitor for the hydrogenation activity of the Mo sulfide based catalysts, while no retardation for the hydrogenation route of DBT was reported at 300°C under 18 MPa at H₂S partial pressures of 0 - 0.06 kg mole / m³ when its direct desulfurization reactivity was markedly reduced to less than 1 / 20 [3]. The sulfide compositions in the catalysts may be changed under H₂S atmosphere, because their compositions were governed by the concentration of H₂S in the gas phase as reported previously [8, 9].

4 Discussion

4-1 Inhibition Mechanism for the Desulfurization Reaction

Degree of inhibition on the desulfurization pathways of 4,6-DMDBT is summarized in Table 4-2. These values are calculated from the following equation.

Degree of inhibition for desulfurization (%) =

( desulfurization conversion, or reduction amount of each products yield in the presence of sulfur species ) / ( desulfurization conversion, or products yield in decalin)
Hydrogenation reaction of naphthalene in decane

Hydrogenation reaction of naphthalene in decane with H₂S

Figure 4-7  Inhibition of H₂S in hydrogenation reaction of naphthalene. (NiMo catalyst : 1.0g, naphthalene:1.0g, solvent: decane 9.0g, 300°C-2.5MPa-1h)

a) partial pressure: 0.132MPa

Table 4-1  Relationships between Reaction Mole Ratio of Each Sulfur Species and Catalyst Content.

<table>
<thead>
<tr>
<th>Catalyst content (wt%)</th>
<th>0.4</th>
<th>2</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction mole of BT / reaction mole of 4,6-DMDBT</td>
<td>3</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Reaction mole of DBT / reaction mole of 4,6-DMDBT</td>
<td>1</td>
<td>2.5</td>
<td>2.3</td>
</tr>
</tbody>
</table>

a) Reaction conditions: 4,6-DMDBT+BT or DBT = 0.05 : 0.05g, 300°C-2.5MPa-0.5h, solvent : Decalin
Table 4-2  Inhibition Effect of Each Sulfur Species in HDS of 4,6-Dimethyldibenzothiophene. (NiMo catalyst: 1.0g, 300°C-2.5MPa, solvent: Decalin)

<table>
<thead>
<tr>
<th>Reaction pathway of 4,6-DMDBT</th>
<th>Inhibition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coexisting sulfur species</td>
</tr>
<tr>
<td></td>
<td>DBT&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>Total conversion</td>
<td>23</td>
</tr>
<tr>
<td>B&lt;sub&gt;4,6&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</td>
<td>20</td>
</tr>
<tr>
<td>A&lt;sub&gt;4,6&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>48</td>
</tr>
<tr>
<td>H&lt;sup&gt;c&lt;/sup&gt;</td>
<td>(+50)</td>
</tr>
<tr>
<td>C&lt;sub&gt;4,6&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>---</td>
</tr>
</tbody>
</table>

a) B<sub>4,6</sub> : 3-(3'-methylcyclohexyl)toluene  
b) A<sub>4,6</sub> : 3,3'-dimethylbicyclohexyl  
c) C<sub>4,6</sub> : 3,3'-dimethylbiphenyl  
d) H : 1,2,3,4,10,11-hexahydro-4,6-dimethyldibenzothiophene  
e) content: 0.5wt%, reaction time: 2h  
f) partial pressure: 0.132MPa, reaction time: 1h

Figure 4-8  Schematic models of hydrodesulfurization reactions inhibited by sulfur species.
Produced \( \text{H}_2\text{S} \) is the major inhibitor for the desulfurization of 4,6-DMDBT at the latter stage of the reaction, because of 100% conversions of benzothiophene and DBT by 2h reaction. No inhibition by ethylbenzene is found when the content is low. Inhibition on the desulfurization step after the hydrogenation of one phenyl ring of 4,6-DMDBT \((B_{4,6})\) increased in the order of DBT \((20\%)\) < benzothiophene \((41\%)\) < \( \text{H}_2\text{S} \) \((67\%)\), respectively. The desulfurization through the hydrogenation of both phenyl rings \((A_{4,6})\) provided the conversions of 71, 67, and 48% in the presence of benzothiophene, DBT, and \( \text{H}_2\text{S} \), respectively, by 2h. It should be pointed out that lower reactivity of 4,6-DMDBT is ascribed to the inhibition by \( \text{H}_2\text{S} \) as indicated that the hydrogenated 4,6-DMDBT stays undesulfurized.

Figure 4-8 illustrates of HDS schemes inhibited by sulfur species. Ma [2] has reported that HDS of 4,6-DMDBT in the gas oil was completely stopped at the latter stage of the reaction, as correlated to the concentrations of \( \text{H}_2\text{S} \) in the gas phase. The present scheme accounts such an inhibition. Elimination of the produced \( \text{H}_2\text{S} \) at the latter stage of the reaction is expected to enhance the deep desulfurization.

4.2 Inhibitors in the Gas Oil for the HDS Reaction

It is of value to compare the inhibitions for the desulfurization of 4,6-DMDBT by the components and products proven in the gas oil to develop a novel deep desulfurization. Table 4-3 summarizes the relative rate constants of respective reaction paths in decalin inhibited by 0 - 30 wt% aromatic hydrocarbons, and 0 - 3 w% of sulfur species. Relative rate constants for the total conversions of 4,6-DMDBT are markedly reduced to 0.63 by 10 wt% tetralin, 0.35 - 0.05 by 5 - 30 wt% naphthalene, and 0.4 - 0.63 by 0 - 3 wt% sulfur species, respectively. The hydrogenation route is severely retarded by the naphthalene, giving constants of 0.29 - 0.04. Their inhibition should be concerned, since the gas oil from middle east crude contained 70 - 82 wt% of paraffin (carbon numbers \( \text{C}_9 - \text{C}_{25} \)) and 18 - 30 wt% of aromatic hydrocarbons,

Thus the lower reactivity of 4,5-DMDBT in the gas oil is ascribed to three reasons; (1) steric hindrance of substituted methyl groups neighbouring the sulfur atom, (2) large
Table 4-3  Relative Rate Constant of 4,6-Dimethyldibenzothiophene with Coexisting Aromatic Hydrocarbons or Sulfur Species. (NiMo catalyst, 2.5MPa-1h, solvent :Decalin)

<table>
<thead>
<tr>
<th>Coexisting species in reactant solvent</th>
<th>Relative rate constant of 4,6-DMDBT</th>
<th>Total conv.</th>
<th>Hydrogenation route</th>
<th>Direct-HDS route</th>
</tr>
</thead>
<tbody>
<tr>
<td>None^a)</td>
<td>1</td>
<td>1 (90%)^d)</td>
<td>1(10%)^d)</td>
<td></td>
</tr>
<tr>
<td>Naphthalene 5wt% ^b)</td>
<td>0.35</td>
<td>0.29</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Naphthalene 10wt% ^a)</td>
<td>0.22</td>
<td>0.19</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>Naphthalene 30wt% ^c)</td>
<td>0.05</td>
<td>0.04</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Tetralin 10wt% ^d)</td>
<td>0.63</td>
<td>0.62</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>None^b), c)</td>
<td>1</td>
<td>1 (94%)^d)</td>
<td>1(6%)^d)</td>
<td></td>
</tr>
<tr>
<td>DBT 0.5wt% ^b)</td>
<td>0.63</td>
<td>0.64</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>BT 0.5wt% ^b)</td>
<td>0.65</td>
<td>0.63</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>H2S ^c)</td>
<td>0.40</td>
<td>0.39</td>
<td>0.66</td>
<td></td>
</tr>
</tbody>
</table>

a) Reaction conditions : 320°C-2.5MPa-1h, solvent : decalin, NiMo catalyst : 1.0g, 4,6-DMDBT : 0.3 wt %, naphthalene or tetralin : 0~30 wt % in sample 10g.

b) Reaction conditions : 320°C-2.5MPa-1h, solvent : decalin, NiMo catalyst : 1.0g, 4,6-DMDBT : 0.5 wt %, DBT or BT : 0.5 wt % in sample 10g.

c) Reaction conditions : 320°C-2.5MPa-1h, solvent : decalin, NiMo catalyst : 1.0g, 4,6-DMDBT : 0.3 wt % in sample 10g, H2S partial pressure : 0.132MPa

d) ( ) : selectivity
retardation in its hydrogenation step by aromatic partners, and (3) reduction in the hydrogenation activity and inhibition of the desulfurization by produced H₂S gas from reactive sulfur species.

Based on the above discussion, basic approaches can be proposed to design the new catalysts (1) increasing numbers of hydrogenation active sites on the surface of the catalyst and (2) improvement of the selectivity for the hydrogenation of sulfur species. Hence, it will be worthwhile to study the selectivity in the hydrogenation of aromatic hydrocarbons and thiophenes.

Identification and enhancement of active sites on the surface of the catalyst certainly lead to the development of better catalyst. As another side of aspects, desulfurization reactivity of 4,6-DMDBT must increase unless the methyl groups located at the 4- or 6-positions in the substrate. Thus it is worthwhile to design the desulfurization catalysts with acidity to enhance the migration or demethylation of the substituted methyl groups. The mild acidity on the catalysts will be the key to achieve such isomerization and / or cracking reactions with least coke formation.

5 Literature Cited
Chapter 5

Selective HDS of 4,6-Dimethyldibenzothiophene in the Dominant Presence of Naphthalene over Ternary Sulfides Catalyst

1 Introduction

4,6-DMDBT have been proved to be hydrodesulfurized through the hydrogenation of one or both phenyl rings in the substrate to moderate the steric hindrance of methyl groups located in the neighbours of the sulfur atom [1-3]. The neighboring phenyl rings should compete with the aromatic partners to the hydrogenation active site on catalyst.

In the present study, the catalytic activities of sulfided Ru-CoMo / Al₂O₃ were examined for the desulfurization of 4,6-DMDBT in decane and decane with naphthalene. The key step is assumed to be the hydrogenation step of 4,6-DMDBT in the competition with naphthalene. Ruthenium was the selected as the third component of metal promoters which was added to CoMo / Al₂O₃, since sulfur atom in 4,6-DMDBT can be a preferable anchor to the nobel metal sulfide [4]. Ru-CoMo / Al₂O₃ catalyst was characterized using XPS, XRD, and HREM.
Experimental Section

2-1 Chemicals and Catalysts

4,6-DMDBT was synthesized according to the reference [5]. Commercially available (NH₄)₂MoO₄, Co(NO₃)₂6H₂O, and RuCl₃3H₂O were used as catalyst precursor salts. Al₂O₃ as the catalyst support was commercially available.

The precursor salts were impregnated onto Al₂O₃ according to an incipient wetness impregnation procedure. Additives such as HCl, H₃PO₄, malic acid, and citric acid were dissolved in the impregnation solution. Metal contents of catalysts are summarized in Table 5-1.

The catalyst was dried, calcined, and sulfided by flowing H₂S (5 vol%) in H₂ just before its use.

2-2 Reaction

HDS reaction was performed in a 50 ml batch-autoclave at 300°C under 2.5MPa H₂ pressure for 0.5 - 2.5h, using 1.5g catalyst and 10g substrate including the solvent. The concentrations of 4,6-DMDBT and naphthalene were 0.1 and 0 - 10 wt%, respectively.

The details of analytical procedures were reported in chapter 2. The structure and abbreviations of the products also referred to chapter 2.

2-3 XPS

X-ray photoelectron spectra (XPS) was taken on a ESCA 1000 (Shimazu co.) with Mg Kα radiation energy of 1253.6 eV. The binding energies were referred to the Al 2p of the catalyst support, Al₂O₃ (Al 2p, 74.0 eV) as an internal standard. Further peaks were identified according to the references [6-9].
### Table 5-1  Metal Contents and Abbreviations of Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Weight (%) of metal oxide on alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RuO₂</td>
</tr>
<tr>
<td>Ru-CoMo-1</td>
<td>0.75</td>
</tr>
<tr>
<td>Ru-CoMo-2</td>
<td>0.75</td>
</tr>
<tr>
<td>Ru-NiMo</td>
<td>0.75</td>
</tr>
<tr>
<td>NiMo/Al₂O₃</td>
<td>---</td>
</tr>
<tr>
<td>CoMo/Al₂O₃</td>
<td>---</td>
</tr>
</tbody>
</table>

### Table 5-2  Hydrodesulfurization of 4,6-Dimethyldibenzothiophene and Hydrogenation of Coexisting Naphthalene over Ru-CoMo-1/Al₂O₃ Prepared with Additives.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Conversion of 4,6-DMDBT (%)</th>
<th>Conversion of Naphthalene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5h</td>
<td>2h</td>
</tr>
<tr>
<td>Additive free</td>
<td>21</td>
<td>77</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>21</td>
<td>83</td>
</tr>
<tr>
<td>HCl</td>
<td>20</td>
<td>72</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>Malic acid</td>
<td>18</td>
<td>55</td>
</tr>
</tbody>
</table>

a) 300°C-2.5MPa, 4,6-dimethyldibenzothiophene 0.1wt% + naphthalene 10wt% in decane, catalyst content 15 wt%
2.4 XRD

X-ray diffraction (XRD) was taken on a X-ray diffractor meter (Rigaku co.) with Cu target electrode at 40 KV voltage. X-ray diffraction was performed according to the procedure described by International Center for Diffraction Data [10].

2.5 HREM

High resolution electron micrographs (HREM) of catalysts were observed on JEM-2000 EX (Jeol Co.) at 200 KV acceleration voltage with magnification of 200,000 to 500,000.

3. Results

3-1 HDS Reactivities over Ru-CoMo / Al₂O₃

Figure 5-1 (A) illustrates HDS activity of 4,6-DMDBT over Ru-CoMo-1 / Al₂O₃ in decane with 10 wt% naphthalene at 300°C under 2.5MPa H₂ pressure. Addition of Ru to CoMo catalyst exhibited better for HDS activity of 4,6-DMDBT, giving the conversions of 25% by 0.5h and 80% by 2h, respectively. CoMo / Al₂O₃ was inferior to Ru-CoMo-1 / Al₂O₃ for the HDS activities, providing 50% conversion by 1h and 70% by 2h, respectively. Significant retardation was observed by additive naphthalene for the HDS activities over NiMo / Al₂O₃, providing 20% conversion by 1h and 50% by 2h, respectively.

Figure 5-1 (B) illustrates hydrogenation activities of naphthalene. CoMo and Ru-CoMo-1 / Al₂O₃ exhibited similar activities for the hydrogenation, its conversion being 80% by 2h. No decalin was found over both CoMo and Ru-CoMo-1 / Al₂O₃. Addition of Ru to CoMo / Al₂O₃ appeared basically to accelerate the HDS of 4,6-DMDBT without enhancing the hydrogenation of naphthalene. In contrast, NiMo / Al₂O₃ allowed 95% conversion for 1h. Decalin of 10 and 20% yields was found for 1 and 2h, respectively.
Figure 5-1 Conversions of 4,6-dimethyldibenzothiophene and naphthalene over Ru-CoMo-1, CoMo, and NiMo / Al₂O₃. (300°C-2.5MPa, 4,6-dimethyldibenzothiophene 0.1wt% + naphthalene 10wt% in decane, catalyst content; 15 wt% )

a) conversion of tetralin to decalin
3-2 Products from 4,6-Dimethyldibenzothiophene

Figure 5-2 illustrates the yields of major HDS products from 4,6-DMDBT over Ru-CoMo-1/Al₂O₃ at 300°C under 2.5 MPa H₂ pressure. Yield of B₄,₆ increased very sharply by addition of Ru to CoMo/Al₂O₃, giving its yields of 15% for 0.5h and 50% for 2h, respectively, as shown in Figure 5-2 (A). CoMo/Al₂O₃ exhibited slightly inferior to Ru-CoMo-1/Al₂O₃ for the yield of B₄,₆, its yields being 25% for 1h and 40% for 2h, respectively. NiMo/Al₂O₃ was much inferior, providing 10% for 1h and 25% for 2h, respectively.

CoMo and Ru-CoMo-1/Al₂O₃ gave A₄,₆ yield of 27 and 30% for 2h, respectively. NiMo/Al₂O₃ gave its yield of only 10% for 2h. Retardation of naphthalene was indicated over any catalysts of the present study, although the differences in their activities were observed. The yield decreased beyond 2h over the former catalysts. Hydrocracking of A₄,₆ may take place since the saturation of the phenyl rings enhances the cracking reactivity [11], although the detection of the product was not attempted in the present study.

Yields of H and C₄,₆ were both around 0 - 5% over Ru-CoMo-1/Al₂O₃. It should be noted that the desulfurization of hydrogenated 4,6-DMDBT was very rapid over CoMo containing catalysts.

3-3 Inhibition with Naphthalene for the HDS of 4,6-Dimethyldibenzothiophene

Figure 5-3 (A) illustrates the HDS conversions of 4,6-DMDBT in decane at various naphthalene concentrations over Ru-CoMo-1/Al₂O₃ at 300°C under 2.5 MPa for 2h. A particular Ru-CoMo-1/Al₂O₃ slightly suffered the retardation in the HDS reaction from additive naphthalene, providing 100, 87, and 83% conversions at 0, 5, and 10 wt% of naphthalene, respectively. CoMo/Al₂O₃ gave conversions of 95, 93, and 75% at 0, 5, and 10 wt% of naphthalene, respectively. HDS activities of NiMo/Al₂O₃ sharply decreased from 95% conversion in absence of naphthalene with increasing naphthalene to 60% conversion at 5 wt% naphthalene and 45% at 10 wt%, respectively.
Figure 5-2  Major hydrodesulfurization products from 4,6-dimethyldibenzothiophene over Ru-CoMo-1, CoMo, and NiMo / Al2O3. (300°C-2.5 MPa, 4,6-dimethyldibenzothiophene 0.1wt% + naphthalene 10wt% in decane, catalyst content ; 15 wt% )
Figure 5-3 Conversion and product yields of 4,6-dimethyldibenzothiophene in decane with various concentration of naphthalene after 2h reaction over Ru-CoMo-1, CoMo, and NiMo / Al2O3. (300°C-2.5MPa-2h, 4,6-dimethyldibenzothiophene 0.1 wt% + naphthalene 10 wt% in decane, catalyst content; 15 wt%)
Figure 5-3 (B) illustrates the yield of major HDS product \( B_{4,6} \). Its yield slightly decreased with increasing naphthalene concentration over Co containing catalysts, whereas its yield decreased very sharply over NiMo / Al\(_2\)O\(_3\).

3-4 Influence of Co and Ni Contents in Ru-CoMo and Ru-NiMo Catalysts

Figure 5-4 illustrates HDS conversions of 4,6-DMDBT in decane or decane with 10 wt% naphthalene over Ru-CoMo-1, -2 / Al\(_2\)O\(_3\) (Co; 0.25 and 3 wt%), and Ru-NiMo / Al\(_2\)O\(_3\) (Ni; 5 wt%) at 300°C under 2.5MPa H\(_2\) pressure for 2h. 95 - 100% conversions were obtained in decane over all catalysts examined. Addition of 10 wt% naphthalene decreased the conversion to 78% over Ru-CoMo-1, 70% over Ru-CoMo-2 / Al\(_2\)O\(_3\), and 61% over Ru-NiMo / Al\(_2\)O\(_3\), respectively. Ru-NiMo / Al\(_2\)O\(_3\) allowed the highest activity for the hydrogenation of naphthalene, providing 100% conversion and decalin of 15% yield, respectively. Ru-CoMo catalysts were less active for the hydrogenation of naphthalene. Ru-CoMo-1 / Al\(_2\)O\(_3\) gave 87% of tetralin and 5% of decalin yield. The catalyst of less Co content appeared to exhibit better selectivity for the hydrogenation of the sulfur species.

3-5 Activities of Ru-CoMo-1 / Al\(_2\)O\(_3\) Prepared with Some Additives

HDS and hydrogenation conversions of 4,6-DMDBT and naphthalene over Ru-CoMo-1 / Al\(_2\)O\(_3\) prepared with additives are summarized in Table 5-2. H\(_3\)PO\(_4\) appeared to increase desulfurization of Ru-CoMo-1 / Al\(_2\)O\(_3\), while other additives reduced the activity. HCl improved slightly the selectivity of HDS towards hydrogenation of naphthalene. Inhibiting effects of citric acid was very definite.

3-6 Characterization of the Catalysts

Figure 5-5 illustrates XPS profiles of Mo 3d in Ru(0.75 wt%)-Co(0.25 wt%)-Mo(15 wt%) / Al\(_2\)O\(_3\) [Ru-CoMo-1] before and after presulfiding. Mo(15 wt%) / Al\(_2\)O\(_3\), Co(1 wt%)-Mo(15 wt%) / Al\(_2\)O\(_3\), and Ru(1 wt%)-Mo(15 wt%) / Al\(_2\)O\(_3\) are also included for comparison. Before sulfiding, Mo 3d \( 3/2 \) and 3d \( 5/2 \) peaks were found at 235 and 232
Figure 5-4 Inhibition with naphthalene for the hydrodesulfurization reaction of 4,6-dimethyldibenzothiophene over Ru-CoMo -1, -2, and Ru-NiMo / Al2O3. (300°C-2.5 MPa-2h, 4,6-dimethyldibenzothiophene 0.1wt% + naphthalene 10wt% in decane, catalyst content: 15 wt% )
of binding energies in all catalysts, ascribed to MoO3 species regardless of their compositions [5-8]. Sulfiding shifted the peaks to 225 and 222 eV, respectively in Mo / Al2O3 and CoMo / Al2O3, which are ascribed to Mo(II) species [6-9]. Ru-CoMo-1 and Ru-Mo / Al2O3 exhibited two peaks at 222 and 218 eV with a very small shoulder at 225 eV, indicating major presence of Mo 3d_3/2 and Mo 3d_5/2 of Mo(0) at 222 and 218 eV after the sulfiding. Two kinds of Mo species such as MoS2 and metallic Mo may exist on the Ru-Mo based catalysts.

Figure 5-6 illustrates XRD profiles of the catalysts before presulfiding. There were two large peaks ascribed to alumina at 45.7° and 66.5°, respectively. Three sharp peaks at 23.4°, 25.6° and 27.3° were ascribed to MoO3. The intensity of these three peaks increased with increasing content of Ru on Ru-CoMo / Al2O3, indicating enlargement of MoO3 crystal in the presence of Ru. The peaks at 33.7° and 53.9° were identified to RuO2, while no peak was ascribed to CoO. The sulfiding removed sharp peaks except for those from Al2O3.

Figure 5-7 shows HREM micrographs of sulfided Ru(0.75 wt%)-Co (0.25 wt%)-Mo(15 wt%) / Al2O3 [Ru-CoMo-1]. Figure 5-7 (a) and (b) shows MoS2 layers and RuS2 crystals as dotted spots, respectively, under 200K magnification which were typically observed on Ru-CoMo-1 / Al2O3. Large magnification under 500K revealed larger length and thickness of MoS2 layers in Figure 5-7 (c).

4 Discussion

4-1 The Roles of Ru for the HDS Selectivity

Addition of Ru to mixed sulfides of Co and Mo enhanced HDS activity and suffured the smallest retardation from naphthalene when the mixed contents of Co and Ru were 0.25 and 0.75 wt%, respectively, by the fixed content of 15 wt% Mo. The high HDS activity over the ternary sulfide catalyst is ascribed to the selective hydrogenation of 4,6-DMDBT on Ru governing site and desulfurization of the hydrogenated 4,6-DMDBT on
Figure 5-5  XPS spectra of MoS$_2$ based on catalysts before and after presulfiding
Figure 5-6  XRD spectra of MoS$_2$ based on catalysts before presulfiding
Figure 5-7  HREM micrograph of sulfided Ru-CoMo-1 / Al₂O₃. (a)(b) magnification under x 200K, (c) x 500K
the Co-Mo-S governing site. S atom in 4,6-DMDBT may be an anchor for the selective hydrogenation to the noble metal sulfide governing site of the ternary catalyst.

Addition of Ru to NiMo / Al₂O₃ failed to improve the selective hydrogenation of 4,6-DMDBT. NiMo / Al₂O₃ itself exhibited high hydrogenation activity against naphthalene. Ru may not find a place to show the selectivity.

4.2 Characterization of Ru-CoMo Catalyst

It has been proposed that HDS active site of sulfided CoMo and NiMo catalysts was the anion vacancy at the edge plane of MoS₂ [12]. Voorhoeve and Stuiver proposed "Intercalation model" where Ni and Co are located at the edge plane of MoS₂ [13]. Delmon proposed "Contact synergy model" where the high activity originates from the contact between tiny Co₈S₉ and MoS₂ crystal [14]. Topsøe proposed the high activity of "Co-Mo-S phase" which is located at the edge plane of MoS₂ [15].

The present study pointed out several structural characteristics of the ternary catalyst according to XPS and HREM, (1) MoS₂ is easily reduced in the presence of Ru on the same support, (2) Mo and Ru existed separately on the support in forms of respective sulfides, and (3) Mo sulfide increases its crystal size in the presence of Ru.

RuS₂ on Al₂O₃ is the site for the selective hydrogenation of 4,6-DMDBT, of which hydrogenated product is transferred intermediately to the Co-Mo-S active site to be desulfurized because of moderated steric hindrance and enhanced reactivity of S atom as discussed in previous papers [1-3]. Increased crystal size of Mo sulfide may lose some activity.

Higher dispersion and activation of RuS₂ appear keys to prepare the more active and selective catalyst for HDS of 4,6-DMDBT in the major presence of aromatic inhibitors. Growth of MoS₂ crystal should be avoided when Ru is added. The activated carbon or carbon fiber may be suitable supports to achieve the better performance.
5. Literature Cited

Chapter 6

Selective HDS of 4,6-Dimethyldibenzothiophene in Major Presence of Naphthalene over CoMo / Al₂O₃ and Ru / Al₂O₃ Blend Catalysts

1 Introduction

The catalyst for the selective hydrogenation of 4,6-DMDBT in the dominant aromatic partners is most paid attention to achieve its extensive desulfurization. Preceding chapter showed the effective of additive Ru to CoMo / Al₂O₃ for the desulfurization of 4,6-DMDBT. In the present study, selective HDS for 4,6-DMDBT in decane containing a significant amount of naphthalene was examined over blends of CoMo / Al₂O₃ and Ru / Al₂O₃ to design the more selective hydrogenation and successive desulfurization of the sulfur species in the major presence of aromatic partners. In comparison to the ternary Ru-CoMo sulfides catalyst, the blend catalyst is expect to maximize the selective hydrogenation for sulfur species much less growth of MoS₂ crystal, because no interaction between MoS₂ and Ru sulfide on the separate support. Their activities were compared to those of CoMo, NiMo, and Ru / Al₂O₃ in their single use.
2. Experimental Section

2-1 Chemicals and Catalysts

4,6-DMDBT was synthesized according to the reference [1]. Commercially available catalyst precursor salts and Al₂O₃ were used in the present study as described in a preceding chapter 5. The precursor salts were impregnated onto Al₂O₃ according to an incipient wetness impregnation procedure. Contents of metal oxides supported on Al₂O₃ were as follows: Co(0.25, 3 wt%)-Mo(15 wt%) / Al₂O₃, Ni(1, 5 wt%)-Mo(15 wt%) / Al₂O₃, and Ru(6 wt%) / Al₂O₃, respectively. Composition and usage of the catalysts are summarized in Table 6-1, where four varieties of blends are included.

After the impregnation, the catalyst was dried at 160°C, calcined at 420°C under air flow, and sulfided at 360°C for 2h by flowing H₂S (5 vol %) in H₂ under atmospheric pressure just before its use.

2-2 Reaction

HDS of 4,6-DMDBT in decane with naphthalene was performed in a 50 ml batch-autoclave at 300°C under 2.5MPa H₂ pressure for 1.0 - 2.5h, using typically 1.5 - 3.5g catalyst and 10g substrate including the solvent. The concentrations of 4,6-DMDBT and naphthalene were 0.1 and 0 - 10 wt%, respectively.

2-3 Analysis

After the reaction, products were qualitatively and quantitatively analyzed by GC-MS, GC-FID (Yanaco G-3800), and GC-FPD equipped with a silicone capillary column (OV-101; 0.25 mm x 50 m). The details about the analysis were ascribed in chapter 2. Desulfurized products through hydrogenation of one or both phenyl rings, desulfurized product without apparent hydrogenation, and hydrogenated 4,6-DMDBT are abbreviated as B₄₆, A₄₆, C₄₆, and H, respectively.
Table 6-1 Compositions and Usages of Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Weight (%) of metal oxide on alumina</th>
<th>Usage (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{RuO}_2 )</td>
<td>( \text{NiO} )</td>
</tr>
<tr>
<td>Ble-1</td>
<td>6</td>
<td>0.25</td>
</tr>
<tr>
<td>Ble-2</td>
<td>6</td>
<td>0.25</td>
</tr>
<tr>
<td>Ble-3</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Ble-4</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>NiMo</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>CoMo</td>
<td>6</td>
<td>0.25</td>
</tr>
<tr>
<td>Ru/Al(_2)O(_3)</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

Table 6-2 Product Distribution of 4,6-Dimethyldibenzothiophene over NiMo, CoMo, Ru/Al\(_2\)O\(_3\), Blends-1 and -2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (^a) of 4,6-DMDBT to A(_{4,6}) (%)</th>
<th>Conversion (^a) of 4,6-DMDBT to C(_{4,6}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoMo</td>
<td>29</td>
<td>1</td>
</tr>
<tr>
<td>NiMo</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>Ru/Al(_2)O(_3)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ble-1</td>
<td>43</td>
<td>0</td>
</tr>
<tr>
<td>Ble-2</td>
<td>18</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) reaction condition: 300°C-2.5MPa-2h, 4,6-dimethyldibenzothiophene 0.1wt% and naphthalene 10wt%
2.4 MO Computation

The Computer Aided Chemistry (CAChe) worksystem provided by CAChe Scientific Inc. was used to calculate the molecular orbitals of DBT and fluorene skeletons, using the Molecular Orbital Package (MOPAC, Version 6.10). The PM3 (Modified Neglect of Diatomic Overlap, Parametric Method 3, semiempirical Hamiltonian) was employed to calculate the optimum geometry and electronic properties of both compounds, using the standard parameters [2].

3 Results

3.1 HDS Activity of the Blends

Figures 6-1 (A) and (B) illustrate the conversions of 4,6-DMDBT and naphthalene vs. reaction time over CoMo, NiMo, Ru / Al₂O₃, blends-1 and -2, respectively, at 300°C. CoMo / Al₂O₃ exhibited an excellent activity for HDS of 4,6-DMDBT, giving conversions of 46% by 1h and 74% by 2h as shown in Figure 6-1 (A). The particular NiMo / Al₂O₃ was inferior to CoMo / Al₂O₃ in the presence of 10 wt% naphthalene, giving conversions of 24% by 1h and 47% by 2h. Ru / Al₂O₃ was very inactive for HDS, giving conversions of 6% by 1h and 8% by 2h. The blend-2 showed the highest activity for HDS of 4,6-DMDBT among the catalysts examined, giving conversions of 71% by 1h, 87% by 2h, and 95% by 2.5h, when 2.0 g of Ru / Al₂O₃ and 1.5 g of CoMo / Al₂O₃ were used. Blend-1 was slightly less active than blend-2.

NiMo / Al₂O₃ showed the highest activity for the hydrogenation of naphthalene, giving a conversion of 90% for 1h. Tetralin and decalin were the hydrogenation products, the yields of the latter product being 6% by 1h and 18% by 2h, respectively. CoMo / Al₂O₃ and blend-2 exhibited similar activities, being much inferior to NiMo / Al₂O₃, to give conversions of 61 and 77% by 1h, respectively. Decalin of 8% was produced by 1h over CoMo / Al₂O₃, 5% by 1h over the blend-2. Ru / Al₂O₃ was very inactive, giving a conversion of 10% by 1h and 23% by 2h for the hydrogenation of naphthalene.
Figure 6-1 Conversions of 4,6-dimethyldibenzothiophene and naphthalene over NiMo, CoMo, Ru/Al₂O₃, Blends-1 and -2. (300°C-2.5MPa, 4,6-dimethyldibenzothiophene 0.1wt% + naphthalene 10wt% in decane)

a) Conversion of produced tetralin: ■ NiMo □ Ble-1
□ CoMo ■ Ble-2
to decalin
3-2 Products from 4,6-Dimethyldibenzothiophene

Figure 6-2 illustrates the yields of B\textsubscript{4,6} and H from 4,6-DMDBT over CoMo, NiMo, Ru / Al\textsubscript{2}O\textsubscript{3}, blends-1 and -2, respectively, at 300°C. Yields of A\textsubscript{4,6} and C\textsubscript{4,6} were summarized in Table 6-2. CoMo / Al\textsubscript{2}O\textsubscript{3} and the blend-2 provided B\textsubscript{4,6} by the yields of 24 and 35%, respectively, for 1h, 43 and 60%, respectively, for 2h, while its yields of 8% for 1h and 25% for 2h, respectively, over NiMo / Al\textsubscript{2}O\textsubscript{3}. The yield of H decreased beyond 1h over NiMo, CoMo / Al\textsubscript{2}O\textsubscript{3}, and the blend-2, indicating its consecutive reaction pathway. Large yield, 43%, of A\textsubscript{4,6} over the blend-1 was noted for 2h, while conversions were 29% and 11% for 2h over CoMo and NiMo / Al\textsubscript{2}O\textsubscript{3}, respectively. Yields of C\textsubscript{4,6} were 0 to 5% over these catalysts, indicating very minor contribution of direct elimination of sulfur from 4,6-DMDBT.

The particular Ru / Al\textsubscript{2}O\textsubscript{3} was much inferior in the desulfurization to other catalysts examined, however it produced more H, giving its yield of 6% for 1h and 9% for 2.5h. Longer reaction time beyond 1h further increased the yield, although no definite product of desulfurization was found.

3-3 HDS Selectivities of 4,6-Dimethyldibenzothiophene

Figure 6-3 illustrates the HDS conversions of 4,6-DMDBT in decane with various concentrations of naphthalene vs. reaction time over CoMo, NiMo, and blend-2 of Ru / Al\textsubscript{2}O\textsubscript{3} with Co(0.25)Mo / Al\textsubscript{2}O\textsubscript{3}, respectively, at 300°C under 2.5 MPa H\textsubscript{2} pressure. The blend-2 provided 100% conversions for HDS of 4,6-DMDBT in decane for 1h, whereas the conversions were 80% over NiMo / Al\textsubscript{2}O\textsubscript{3} and 75% over CoMo / Al\textsubscript{2}O\textsubscript{3}, respectively. HDS activity of 4,6-DMDBT was severely hindered by the addition of naphthalene over NiMo / Al\textsubscript{2}O\textsubscript{3}, giving the conversions of 50% by 1h and 55% by 2h, respectively, at 5 wt% of naphthalene, 24% for 1h and 47% for 2h, respectively, at 10 wt% naphthalene. CoMo / Al\textsubscript{2}O\textsubscript{3} suffered less inhibition by the aromatic partner, the conversion of 4,6-DMDBT being 85% at 5 wt% and 70% at 10 wt% of naphthalene, respectively, for 2h. The blend-2 exhibited excellent activities for the HDS of 4,6-DMDBT regardless of naphthalene concentrations, its conversions being 70 - 85% for 1h and 80 - 95% for 2h,
Figure 6-2  Products from 4,6-dimethyldibenzothiophene over NiMo, CoMo, Ru / Al2O3, Blends -1 and -2. (300°C -2.5MPa, 4,6-dimethyldibenzothiophene 0.1wt%+ naphthalene 10wt% in decane)
respectively. The blend-3 with Co(3)Mo / Al₂O₃ catalyst provided slightly less conversions, while a particular blend-4 with Ni(5)Mo / Al₂O₃ catalyst was inferior to the other blends for the HDS of 4,6-DMDBT in the presence of 10wt% naphthalene, giving conversions of 50% by 1h and 75% by 2h, respectively.

Figure 6-4 illustrates the yield of major HDS products B₄,₆ from 4,6-DMDBT in decane with various concentration of naphthalene. The yield over NiMo / Al₂O₃ was markedly reduced by the presence of naphthalene, being 10% for 1h and 25% for 2h, respectively, at 10 wt% of naphthalene, whereas its yields being 55% for 1h and 60% for 2h, respectively, in decane. CoMo / Al₂O₃ suffered significant inhibition by naphthalene of 5 - 10 wt%. It should be noted that the blends-2 and -3 suffered less inhibition for the major HDS route of 4,6-DMDBT by the presence of 5 wt% of naphthalene, giving 70 - 75% yield of B₄,₆ for 1h, whereas naphthalene of 10 wt% reduced the yield markedly to 30% for 1h. In contrast, the blend-4 suffered significant reduction by 5wt% of naphthalene. Longer reaction time increased the yield of B₄,₆ regardless of naphthalene concentration. NiMo / Al₂O₃ was exceptional.

The hydrogenation conversions of coexisting naphthalene to tetralin and decalin are summarized in Table 6-3. NiMo / Al₂O₃ and blend-4 provided high hydrogenation activities of naphthalene, giving 95% yield of tetralin and 6 - 8% of decalin, respectively, for 1h, indicating preferential hydrogenation of naphthalene to 4,6-DMDBT over NiMo catalyst even in the blend. CoMo / Al₂O₃ and its blends with Ru / Al₂O₃ exhibited less conversions of naphthalene. CoMo / Al₂O₃ of less Co content appeared a better partner since lower conversion of naphthalene was obtained for 1h.

4 Discussion

4-1 Blend Effect of Two Catalysts

4,6-DMDBT must compete to the hydrogenation active site with aromatic partners of dominant presence in the gas oil as observed in previous [3,4] and the present studies. Hence, the selective hydrogenation of 4,6-DMDBT is very essential to accelerate its
Figure 6-3 Inhibition with naphthalene for the hydrodesulfurization reaction of 4,6-dimethyl-dibenzothiophene.
(300°C-2.5MPa, 4,6-dimethyldibenzothiophene ; 0.1 wt%, solvent ; decane)
(A) NiMo (B) CoMo (C) Ble-2 (D) Ble-4
Content of naphthalene ; 0 wt% — , 5 wt% — , 10 wt% —
Figure 6-4 Yield of B_{4,6} from 4,6-dimethyl dibenzothiophene in decane with naphthalene. (300°C-2.5MPa, 4,6-dimethyl dibenzothiophene; 0.1 wt%)  
(A) NiMo (B) CoMo (C) Ble-2 (D) Ble-4  
Content of naphthalene; 0 wt% — , 5 wt% — , 10 wt% —
Table 6-3  Yields of Tetralin and Decalin from Coexisting Naphthalene

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Tetralin (Yield, %)</th>
<th>Decalin (Yield, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1h</td>
<td>2h</td>
</tr>
<tr>
<td>NiMo</td>
<td>95</td>
<td>96</td>
</tr>
<tr>
<td>CoMo</td>
<td>61</td>
<td>95</td>
</tr>
<tr>
<td>Ble-2</td>
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<tr>
<td>Ble-4</td>
<td>95</td>
<td>97</td>
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</table>

a) 300°C-2.5MPa, 4,6-Dimethyldibenzothiophene; 0.1 wt%, Naphthalene; 10 wt% in Decane)
Figure 6-5  HOMO distribution on the dibenzothiophene and fluorene skeletons.
desulfurization. NiMo / Al₂O₃ exhibited preferential hydrogenation of naphthalene on the conversion-base to that of 4,6-DMDBT in the dominant presence of the former substrate. The blend of CoMo / Al₂O₃ and Ru / Al₂O₃ did significant selectivity to 4,6-DMDBT, especially when Co content was low. The catalyst promoted the largest desulfurization of 4,6-DMDBT with the smallest hydrogenation of naphthalene probably due to the respective roles of the component catalysts. It will be problem for the practical application that the cost of fairly large amount of Ru / Al₂O₃ should be expensive. Better Ru catalyst should be searched.

The products from 4,6-DMDBT are classified into three categories according to the routes, direct-desulfurization, hydrogenation, and desulfurization through the hydrogenation. Ru / Al₂O₃ produces more hydrogenated 4,6-DMDBT (H) without its desulfurization than CoMo / Al₂O₃ and its blend catalysts, while the blend catalysts gave the larger yields of major product B₄₆ and second major A₄₆.

Based on the above discussion, the blend catalyst performed the selective desulfurization of 4,6-DMDBT in the dominant presence of naphthalene through the selective hydrogenation of the substrate over Ru / Al₂O₃ and the consecutive desulfurization of hydrogenated product over CoMo / Al₂O₃. High activity of NiMo / Al₂O₃ for the non-selective hydrogenation rules out the efficiency of its blend with Ru / Al₂O₃.

4-2 The Roles of Ru

Figure 6-5 illustrates the HOMO distribution on the DBT and fluorene skeletons. Their HOMO distributions are certainly different, especially large electron density is found on the sulfur atom of the former substrate. The origin of selectivity for 4,6-DMDBT may be worthwhile for speculation based on HOMO distribution, although no sufficient evidence is available at moment. The π orbital localized on the sulfur atom in 4,6-DMDBT may interact preferably to the d orbital of the sulfide catalyst than that of the naphthalene ring, being free from the steric hindrance of its methyl groups. Such a Sπ - Md interaction [5,6] may be expected more strong with Ru than Ni, Co, or Mo,
because of the higher polarizibility of Ru, allowing the higher selectivity of Ru / Al₂O₃ towards 4,6-DMDBT than naphthalene. Such an interaction is not expected with the fluorene as shown in Figure 6-5.

It has been reported that Ru sulfide exhibited excellent activities for the hydrodenitrogenation for quinoline [7], HDS for the DBT [8] and thiophene [9]. Especially, Ru sulfide was most active for HDS of DBT among the single transition metal sulfides [10], indicating its affinity to S atom, although the binary Ni or Co and Mo sulfides catalysts have been reported more active for the conventional HDS reaction.

The structures of Ru sulfide is very unique. Molecular orbital calculation showed that the bond of Ru - S was very week when hydrogen atom is adsorbed on the S atom of Ru - S bond, to eliminate the S easily as H₂S [11,12]. Such a vacant site may interact preferentially with the S atom of the DBT skeleton.

5 Literature Cited

This thesis summaries inhibitions against the HDS reaction of refractory sulfur species over sulfide catalysts and designs of its selective desulfurization catalysts. The HDS reaction of 4,6-dimethyldibenzothiophene (4,6-DMDBT) is inhibited by aromatic hydrocarbons, sulfur species, and by-product H$_2$S to variable extent, depending on the catalytic conditions including catalytic species. Selective hydrogenation of refractory sulfur species in dominant aromatic partners is emphasized prior to the desulfurization for deep desulfurization. The catalyst for such selective hydrogenation is a target of further research. The major conclusions in the present thesis are summarized as follows in this chapter.

1. **HDS Reactivities of Alkyldibenzothiophenes and their Reaction Pathway**

1) Alkyl-DBTs were found desulfurized through sulfide catalyst interactions with or without prior hydrogenation of aromatic rings. The former and latter pathways are defined as hydrodesulfurization and direct desulfurization, respectively. Their desulfurization reactivities decreased in the order of DBT, 4-MDBT, and 4,6-DMDBT.

2) The ratio of direct- / hydrodesulfurization products was 1.88 with DBT, suggesting preference of direct desulfurization, while 0.08 with 4,6-DMDBT suggests predominance of hydrodesulfurization reaction.
3) NiMo / Al₂O₃ was superior to the CoMo / Al₂O₃ catalyst by 1.3 - 1.6 times for the desulfurization of 4,6-DMDBT in decalin. Higher yield of methylcyclohexyltoluene (B₄,₆) reflects prior hydrogenation of the substrate in which the steric hindrance by substituted methyl groups is removed.

2 Inhibition Mechanism for the HDS Reaction of 4,6-Dimethyl dibenzo-thiophene

1) Conversion of 4,6-DMDBT was markedly reduced by the addition of naphthalene by reducing severely the yield of B₄,₆ and dimethylbicyclohexyl (A₄,₆). Competition to the hydrogenation active sites with dominant aromatic partner prohibits the hydrogenation before the desulfurization of the substrate.

2) DBT suffered less inhibition by aromatic partners since its main reaction pathway is direct desulfurization, whereas the partners retarded the hydrogenation of its phenyl ring to inhibit the minor pathway.

3) The desulfurization of 4,6-DMDBT were retarded by DBT and benzo thiophene, to reduce the yields of B₄,₆ and A₄,₆, while benzo thiophene was completely desulfurized at the early stage of the reaction within 0.5h.

4) H₂S in considerable concentration produced from coexisting sulfur species retarded hydrogenation of substrate and desulfurization of the hydrogenated substrate. In contrast, no inhibition by ethylbenzene of the other hydrocarbon product was observed in the desulfurization.
Selective HDS of 4,6-Dimethyl dibenzothiophene in the Dominant Presence of Naphthalene

1) Addition of Ru to CoMo catalyst increased HDS activity of 4,6-DMDBT in the presence of naphthalene through the increased yield of B_{4,6} by reducing the inhibition of the aromatic partners.

2) The blend of CoMo / Al_{2}O_{3} and Ru / Al_{2}O_{3} also provided a better activity for HDS of 4,6-DMDBT through the same mechanism above described. The desulfurization of hydrogenated intermediate over CoMo / Al_{2}O_{3} takes place consecutively after the selective hydrogenation over Ru / Al_{2}O_{3}.

3) Addition or blend of Ru to CoMo of less Co content appeared to enhance selectivity for the hydrogenation of the sulfur species. No enhancement of naphthalene hydrogenation indicates improved selectivity for the hydrogenation of 4,6-DMDBT. The π orbital localized on the sulfur atom in 4,6-DMDBT may interact more preferably to the 5d orbital of the novel metal sulfide than that of the naphthalene ring. No steric hindrance of its methyl groups is expected to such an interaction.

Surface Structures of Ru-CoMo / Al_{2}O_{3} Catalyst

MoS_{2} is easily reduced in the presence of Ru on the same support. Mo and Ru existed separately on the support in forms of respective sulfides, and Mo sulfide increases its crystal size in the presence of Ru. Such information provides better preparation procedure of the catalysts with higher activity and selectivity.
Acknowledgements

I would like to express my hearty thanks to Professor Isao Mochida for his guidance and advice throughout this study in Institute of Advanced Material Study of Kyushu University.

I would like to express my hearty thanks to Professor Yukio Nisimura in Institute of Advanced Material Study of Kyushu University and Professor Katuhiko Wakabayashi in Faculty of Engineering of Kyushu University for their advice and assist throughout production of this thesis.

To Dr. Xiaoliang Ma (The Pennsylvania State University), Associate Professor Yozo Korai, Professor Toshiaki Kabe, Associate Professor Masatoshi Nagai, Dr. Atushi Ishihara (Tokyo University of Agriculture & Technology), Dr. Teruo Suzuka (Orient catalyst Co., Ltd.), Dr. Sigeaki Fujieda, Mr. Masatomi Amemiya, Mr. Mituaki Wakita (Japan Energy Co., Ltd.), Mr. Teturo Kamo, Satoshi Abe (Nippon Ketjen Co., Ltd.), Mr. Toshiki Saruta (Mitubishi Oil Co., Ltd.), and Dr. Akio Nishijima (National Institute of Materials and Chemical Research) for their advice and fruitful discussion.

To Dr. Shizuo Kawano for his kindness and helpness.

I wish to express my special thanks to Mr. Shinich Nagao and all the members of Mochida Laboratory for their kind and cooperation to accomplish this study.

I am indebted to my parents, family, and my wife for their understanding and assisting this study, especially to my wife Miki whom I owe too much to express by words.

Takaaki Isoda

April 4, 1996