Selective Catalytic Cracked Gasoline Hydrodesulfurization
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Abstract
Hydrodesulfurization (HDS) reaction of catalytic cracked gasoline (CCG) on Co-Mo/γ-Al₂O₃ was investigated in detail to make clear the important factors for deep HDS of CCG. CCG containing 229ppm sulfur and 30.4vol% olefins was examined. Eleven alkylthiophenes and 2 alkylbenzothiophenes, 3 alkylthiacyclopentanes, and 2 disulfides were identified by GC-AED analyses. In the reaction at 220 °C, 1.6MPa using a conventional flow reactor of bench pilot scale, these sulfur compounds were hydrodesulfurized, whereas thiols were produced from H₂S and olefins.

The reactions of thiophene HDS, isoolesin and n-olefin hydrogenation were studied to clarify the active sites on the catalyst. First, the effect of H₂S on the reaction was examined. The hydrogenation of n-olefin as well as thiophene HDS was inhibited by H₂S, while the hydrogenation of isoolesin was promoted. The effects of Co on these three reactions were also examined over different Co/(Co+Mo) ratio catalyst. Thiophene HDS was promoted by Co, isoolesin hydrogenation was little affected and n-olefin hydrogenation was largely retarded. From these examinations, three types of active sites for thiophene HDS, isoolesin hydrogenation and n-olefin hydrogenation were proposed.

Oligomers of isoolesin were found in the isoolesin hydrotreated product. The possibility of improving the HDS selectivity by carbonaceous deposit was investigated for HDS reactions of CCG and model compounds. The coking pretreatment was carried out on the catalyst and each reaction was examined. HDS selectivity (higher activity for HDS and lower activity for olefin HG) on CCGHDS was improved. Relative deactivation was in the following order, isoolesin hydrogenation> thiophene HDS> n-olefin hydrogenation.

Pyridine modification (i.e. pyridine injection at 150 °C and partial pyridine desorption at 300 °C) was investigated on thiophene and olefins reaction. Thiophene HDS was little affected. Olefin hydrogenation and thiol production reaction were strongly inhibited. Improvement of HDS selectivity was observed in the reactions of CCG after pyridine modification. Improvement of HDS selectivity by pyridine modification was considered to result from the selective deactivation of the active sites for olefin reactions (hydrogenation and thiol production).
1. Introduction

CCG is produced from heavy gas oil or atmospheric residue by Fluid Catalytic Cracking Units in refineries, and is one of the major components of motor gasoline. CCG containing high levels of sulfur requires hydrodesulfurization (HDS) to reduce the effect on the environment. CCG contains 20 – 40 vol % olefins, so the present naphtha HDS process would reduce the octane value due to the hydrogenation HG of olefins. Therefore, a selective CCG HDS process providing higher HDS activity and lower olefin HG must be developed.

Control of the HDS selectivity of the catalyst requires that the HDS active site be different from the olefin HG active site. Mo catalysts modified by various treatments show differences in the two active sites, including phosphate modification of the Mo/carbon catalyst, high temperature regeneration at 700 °C with steam of the Co-Mo/γ-Al₂O₃ catalyst, and control of degree of sulfidation of the Mo/Al₂O₃ catalyst. HDS selectivity is decreased by such modifications, so the HDS active site is different from the olefin HG active site. However, the HDS selectivity ($r_{\text{HDS}}/r_{\text{HG}}$) is decreased by these modifications, and thus contradicts the object of selective CCG HDS.

We have tried to improve the HDS selectivity by investigating the relationship between HDS activity and olefin hydrogenation activity.

2. Experimental Section
2.1. Feedstocks
2.1.1. Model Compounds

Commercial grade thiophene (2.83 x 10⁻⁴ mol/mol) and/or olefin (diisobutylene or 1-octene 0.25 mol/mol) were dissolved in toluene. Commercial grade diisobutylene and 1-octene were used without further purification. The composition of diisobutylene was 2,4,4-trimethyl-1-pentene (74.9 mol %), 2,4,4-trimethyl-2-pentene (20.6 mol %) and others (4.5 mol %). Feedstocks with added pyridine (0.01 mol/mol) were also used.

2.1.2. CCG

CCG was produced from low sulfur atmospheric residue. Properties are summarized in Table 1.
2.2. Analyses

Feedstocks and HDS products were analyzed by the following methods. The contents of total sulfur and thiol-type sulfur were measured by oxidative microcoulometry (ASTM-D3120) and potentiometric methods (ASTM-D3227), respectively. Sulfur compounds were quantitatively analyzed by GC-AED (Hewlett Packard 5921A) using a 50 m PONA column. Identification of sulfur compounds was performed by a GC-MS. GC and PIONA-GC (Analytical Controls Inc.) were used for the measurement of HG reactivity of the olefins.

2.3. Catalyst and Catalyst Pretreatments

Co-Mo/γ-Al₂O₃ catalyst was prepared by a conventional pore-filling method. CoO and MoO₃ contents are 4.6 and 15.0 wt %, respectively. A total of 60mL of the catalyst was packed in a bench pilot reactor, and 4 mL of aliquot of the catalyst crushed to 0.6–1.0 mm particles was packed in a micro reactor. After the catalyst was presulfided and aged for 2 days at 300 ºC, the feedstocks were passed into the reactor with hydrogen.

2.4. Definitions of HDS

Since thiols and sulfides are produced by the HDS reaction and some successive reactions in the presence of olefins, two different HDS (%) are defined in the present paper by the following equations. Olefin hydrogenation (HG) (%) is also defined as follows.

2.4.1. Model Compound HDS

- Total HDS (%): (1 – product sulfur / feed sulfur) □ 100
- Thiophene HDS (%): {1 – (thiophene and tetrahydrothiophene sulfur in product) / thiophene sulfur in feedstock} □ 100
- Olefin HG (%): (C₈ paraffin content in product / olefin content in feed) □ 100

2.4.2. CCG HDS

- Total HDS (%): (1 – product sulfur / feed sulfur) □ 100
- Conversion of S compounds (%): {1– (product sulfur-thiol sulfur)/feed sulfur} □ 100
- Olefin HG (%): (1 – olefin content in product / olefin content in feed) □ 100

3. Results and Discussion

3.1. Hydrodesulfurization of CCG

The GC-AED analysis of CCG is shown in Figure 1. Eleven alkylthiophenes and 2 alkylbenzothiophenes, 3 alkylthiacyclopentanes, and 2 disulfides are observed. The compositions of these sulfur compounds are shown in Table 2. The total amount of alkylthiophenes is about half of alkylbenzothiophenes. As shown in Table 1, CCG contains olefins, saturates and aromatics. Internal and branched olefins are dominant in the olefins of CCG.

The HDS conditions were as follows: 210-220 ºC, 1.6MPa, LHSV 3.5/h, H₂/feed ratio 338NL/L. The compositions of sulfur compounds in the HDS products of CCG reacted
in a bench pilot plant are shown in Table 2. After HDS the total sulfur content clearly decreased, whereas thiols are produced. It is noted that alkylbenzothiophenes are more reactive than alkylthiophenes. With increasing the number of alkyl substitution groups, the HDS reactivity decreases. 2-methylthiophene is less reactive than 3-methylthiophene, being due to the steric hindrance of a methyl group substituted at the 2-position of thiophene. Intrinsic reactivity of sulfur compounds contained in CCG was examined by pure sulfur compounds dissolved in toluene. The order of the reactivity is the same as that of sulfur compounds in CCGHDS. However, the reaction speed of sulfur
compounds in toluene is much faster than that in CCG. It is considered that olefins in CCG depress the HDS reactivity by competitive adsorption on HDS active sites of the catalyst. It is noted that no formation of thiol was observed. Therefore, thiol produced in CCGHDS is not the intermediate of the HDS of sulfur compounds. Thiols are produced by the reaction between H$_2$S and olefins contained in CCG.

3.2. Active Sites of the Catalyst

In order to improve the HDS selectivity of CCG, it is necessary to make clear the difference between the HDS active site and the olefin hydrogenation active site.

The difference of the active sites was studied by using the inhibiting effects of H$_2$S. As is well known, H$_2$S is adsorbed on the HDS active site having coordinative unsaturation and competitively inhibits the other sulfur compounds’ access to the HDS active site. If olefin reactions are affected by H$_2$S as HDS is affected, the structure of the olefin hydrogenation active site is considered to be similar to that of the HDS active site. If olefin reactions are not affected by H$_2$S, the structure of the active site for olefin reactions may be different from that of HDS active site. The effects of H$_2$S on HDS of thiophene, alkylthiophenes, and benzothiophene were examined in the H$_2$ stream with of without H$_2$S (Table 3).

Even with a small amount of H$_2$S (0.1 vol% in H$_2$), all thiophenes’ HDS was strongly retarded, and the reaction rate constants obtained were 15-20% of the original. The reaction of diisobutylene, 1-octene and 1-hexene were examined in the H$_2$ stream with of without H$_2$S (Figure 2). With H$_2$S, hydrogenation of diisobutylene is promoted while hydrogenation of 1-octene and 1-hexene are retarded. This finding shows that the isoolefin hydrogenation active site is different from the HDS active site, and it may possible to control the selectivity of CCGHDS.

<table>
<thead>
<tr>
<th>sulfur compound</th>
<th>H$_2$S%</th>
<th>H$_2$S%</th>
</tr>
</thead>
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<tr>
<td>thiophene</td>
<td>86.0</td>
<td>27.0</td>
</tr>
<tr>
<td>2-methylthiophene</td>
<td>63.8</td>
<td>10.9</td>
</tr>
<tr>
<td>3-methylthiophene</td>
<td>75.3</td>
<td>22.3</td>
</tr>
<tr>
<td>benzothiophene</td>
<td>99.4</td>
<td>63.8</td>
</tr>
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</table>

Table 3. Effects of H$_2$S on HDS reaction

Figure 2. Effects of H$_2$S on olefin hydrogenation. temperature 150 $^\circ$C, pressure 1.3MPa, H$_2$/feed 0.34g of cat min/mol, feed toluene 80mol% olefin 20mol%
In order to further clarify the difference between the HDS active site and the isoolefin active site, the response of the catalyst activity to the well-known promoting effects of Co was studied by using the catalysts with varying Co content. The results are shown in Figure 3 and 4. As is well-known, thiophene HDS drastically increased with increasing Co/(Co+Mo) ratio. On the other hand, with increasing Co/(Co+Mo) ratio, it is noted that the hydrogenation of diisobutylene decreases a little and that of 1-octene largely decreases. The similar decreasing trend has been reported about the activity for butane hydrogenation on unsupported Co-Mo sulfide catalyst, in which thiophene HDS and successive butene hydrogenation were undertaken at 320 °C and atmospheric pressure. 6) They have explained about the phenomena that the addition of Co ions blocks the coordinatively unsaturated Mo sites on the edges of MoS₂ and decreases the hydrogenation activity. If Co blocks the unsaturated Mo sites, the small effects of Co on isoolefin hydrogenation suggest that isoolefin hydrogenation proceeds on the unsaturated Mo sites not blocked by Co. In the case of catalyst having half metal content(*marked), thiophene percent conversion largely decreases, however percentage of olefin hydrogenation slightly decreases. These results also indicate that HDS and olefin hydrogenation proceed at the different active sites.

Figure 3. Effects of Co on HDS and isoolefin hydrogenation.
MoO₃ 15.0mass%(*7.5mass%), temperature 175 °C, pressure 1.3MPa, H₂/feed 0.34g of cat min/mol, feed thiophene 2.83x10⁻⁴mol/mol, toluene 80mol% olefin 20mol%

Figure 4. Effects of Co on HDS and n-olefin hydrogenation.
MoO₃ 15.0mass%(*7.5mass%), temperature 190 °C, pressure 1.3MPa, H₂/feed 0.34g of cat min/mol, feed thiophene 2.83x10⁻⁴mol/mol, toluene 80mol% olefin 20mol%

Table 4. Effects of H₂S and Co HDS hydro.

<table>
<thead>
<tr>
<th>H₂S</th>
<th>Co</th>
<th>HDS hydro.</th>
</tr>
</thead>
<tbody>
<tr>
<td>inhibition</td>
<td>promotion</td>
<td>inhibition</td>
</tr>
<tr>
<td>S₈C-C-C=C-C</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>C₄-C-C-C=Chydro.</td>
<td>promotion</td>
<td>no effect</td>
</tr>
</tbody>
</table>
The studies of the effects of H$_2$S and Co are summarized in Table 4. From these results, we speculated on the following three types of active sites.

HDS active site: This site is inhibited by H$_2$S and promoted by Co. n- and isoolefin can approach.

n-olefin hydrogenation active site: This site is inhibited by H$_2$S and is also inhibited by Co. This site has some similarity with HDS active site.

isoolefin hydrogenation active site: This site is promoted by H$_2$S and is slightly inhibited by Co. This site is strongly interact with isoolefin, resulting in the formation of oligomer. This site is totally different from HDS site and n-olefin active site.

These phenomena suggest the possibility of selective CCGHDS in which HDS reaction performs with minimizing olefin hydrogenation because most of olefins contained in CCG are isoolefins.

3.3. Selectivity Improvement by Coking Pretreatment

We found that isoolefins are oligomerized on the isoolefin hydrogenation active site. Oligomer may finally be irreversibly deposited on the active site as a coke. If it is possible that isoolefin hydrogenation active site is selectively deactivated by the oligomer and coke, it leads to selective CCGHDS.

Three different combinations of the pretreatments were carried out on the fresh catalyst. They were sulfiding + aging, sulfiding + aging + coking, and coking + sulfiding + aging. The coking pretreatment was done by using a mixture of cyclohexene + 1-methylnaphthalene. The result of CCGHDS is shown in Figure 5. The catalyst with sulfiding + aging gives a higher total HDS percentage than the catalyst with coking. selectivity, the catalyst with sulfiding + aging + coking shows higher selectivity than the catalyst without coking. However, the catalyst with coking + sulfiding + aging shows the same selectivity as the catalyst without coking. These results show that coking pretreatment should be done after sulfiding to improve HDS selectivity.

The effects of coke were further examined by using a refinery spent catalyst which was used for 1 year in the diesel fuel HDS process. This catalyst, having 8.8 mass% deposited coke, was supplied for CCGHDS activity test. This spent catalyst also shows high HDS selectivity. However, this high selectivity is lost by a regeneration procedure. This result suggests that coke deposit improves the HDS selectivity.

![Figure 5. Effects of coking pretreatment on HDS selectivity.](image-url)
Thiophene HDS was carried out over the catalyst with or without aging and coking pretreatment in the presence of diisobutylene and 1-octene. Thiophene HDS are little reduced by the aging pretreatment but are much reduced by the coking pretreatment. The diisobutylene hydrogenation percentage is plotted against thiophene HDS in Figure 6. Little difference is observed between the selectivity of the catalyst with or without aging. However, it is noted that diisobutylene hydrogenation of the catalyst with coking is much lower than those of catalysts without coking. The 1-octene hydrogenation percentage is plotted against thiophene HDS in Figure 7. 1-octene hydrogenation of the catalyst with coking is much higher than those of catalysts without coking. The effects of coking pretreatment on the three different types of active sites are follows, isoolefin hydrogenation active site > thiophene HDS active site > n-olefin hydrogenation active site. This order also suggests that the coking pretreatment effectively reduces isoolefin hydrogenation activity but hardly reduces n-olefin hydrogenation activity. As most of olefins in CCG are isoolefin, it is considered CCGHDS selectivity is improved by coking pretreatment.

3.3. Selectivity Improvement by Pyridine Modification

The effects of pyridine modification on the catalyst activity and selectivity of Co-Mo/γ-Al₂O₃ catalyst were investigated by micro reactor. Thiophene HDS, diisobutylene hydrogenation and 1-octene hydrogenation were studied at 150 ºC, 1.3MPa to measure the original activity. Thiophene (2.83 × 10⁻⁴ mol/mol) /pyridine (0.01 mol/mol)/toluene, diisobutylene (0.25 mol/mol)/toluene and 1-octene (0.25 mol/mol)/toluene were passed into the reactor and the inhibition by pyridine spike was studied. Feedstocks were backed to the system without pyridine and the activities...
were measured again. Then, the temperature was up to 200 °C to strip some pyridine and the temperature was again backed to 150 °C to measure the activities. Finally, the temperature was up to 300 °C to strip much pyridine and the temperature was backed to 150 °C to measure the activities. The changes of the activities were shown in Figure 8. All three reactions were strongly inhibited by pyridine spike. After the reactions were brought back to the pyridine free system (desorption at 150 °C), the effects of pyridine spike still persist clearly. After pyridine was desorbed at 300 °C, HDS activity has almost recovered to the initial level. However, the activity for diisobutylene hydrogenation was still remained much lower than the initial activity. The activity for 1-octene hydrogenation recovered to half of the initial activity. Increasing the temperature to 300 °C resulted in the inhibiting effect of pyridine spike persisting for olefin hydrogenation but not thiophene HDS. The remaining effect of the pyridine spike on isooolefin hydrogenation was stronger than that on n-olefin hydrogenation. These observations strongly support the idea that three different types of active sites are present on the catalyst.

![Bar chart showing the effects of pyridine spike on thiophene HDS and olefin hydrogenation](image)

**Figure 8. Effects of pyridine spike on thiophene HDS and olefin hydrogenation**

CCGHDS was investigated at 240 °C with or without pyridine modification (Table 5).

<table>
<thead>
<tr>
<th>Pyridine modification</th>
<th>Total sulfur mass ppm</th>
<th>Thiol sulfur mass ppm</th>
<th>Total HDS %</th>
<th>Olefin hydrogenation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>49</td>
<td>21</td>
<td>78.6</td>
<td>11.5</td>
</tr>
<tr>
<td>yes</td>
<td>53</td>
<td>15</td>
<td>76.9</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Pyridine modification decreased conversion of sulfur compounds from 87.7 to 83.4%. GC-AED analysis found that thiophene HDS was not inhibited, but benzothiophene HDS was slightly inhibited. Thiol yield is decreased from 21ppm to 15ppm. As a result
of these two factors, total HDS was slightly decreased. Olefin hydrogenation % was reduced from 11.5 to 7.2%.

4. Conclusions

The present study investigated the possibility of improving CCGHDS selectivity on Co-Mo/\(\gamma\)-Al\(_2\)O\(_3\) catalyst. The difference of the active sites was studied and three different active sites were proposed (i.e. HDS active site, isoo-olefin hydrogenation active site and n-olefin active site). Coke pretreatment and pyridine modification improve HDS selectivity by selectively deactivation olefin hydrogenation active sites.

This study also suggests the possible direction for commercial CCGHDS catalyst. Those are,

a) Improvement Co distribution
b) Decrease of acidic sites

Acknowledgement

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References