[Review Paper]

Selective Hydrodesulfurization of Catalytic Cracked Gasoline

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Hydrodesulfurization (HDS) of catalytic cracked gasoline (CCG) over Co-Mo/γ-Al₂O₃ catalyst was investigated to clarify the important factors for deep HDS of CCG containing 229 ppm sulfur and 30.4 vol% olefins. In the HDS reaction at 220°C, 1.6 MPa, sulfur compounds were hydrodesulfurized, whereas thiols were formed from H₂S and olefins. The reactions of thiophene HDS, isoolein and n-olefin hydrogenation (HG) were studied to clarify the active sites on the catalyst. The effects of H₂S and of Co on these three reactions were examined over catalysts with different Co/(Co + Mo) ratios. Thiophene HDS was promoted by Co, isoolein HG was little affected, and n-olefin HG was largely retarded. Three types of active sites for thiophene HDS, isoolein HG and n-olefin HG were proposed. Oligomers of isoolein were found in the isoolein hydrotreated product. The possibility of improving the HDS selectivity with carbonaceous deposit by coking pretreatment was investigated for HDS reactions of CCG and model compounds. HDS selectivity (higher activity for HDS and lower activity for olefin HG) during CCG HDS was improved. A commercial scale process of CCG HDS was designed and a simulation model was studied. To calculate the sulfur content in the hydrotreated CCG accurately, the theoretical equilibrium models for thiophene HDS, thiol formation and olefin HG were considered. The results estimated using this simulator showed good correspondence with experimental results. These investigations resulted in commercial scale plant construction. Since 2004, three plants have started operation to produce 10 ppm sulfur gasoline in Japan.

Keywords
Catalytic cracked gasoline, Hydrodesulfurization, Cobalt molybdenum catalyst, Olefin

1. Introduction

Catalytic cracked gasoline (CCG) is produced from vacuum 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 olefins1). Therefore, a selective CCG HDS process providing higher HDS activity and lower olefin HG must be developed. In 2006, more than 50 CCG HDS units were operating worldwide, and most commercial units were selective CCG HDS except for demonstration units.

Control of the HDS selectivity of the catalyst requires that the HDS active site is different from the olefin HG active site. Mo catalysts modified by various treatments show differences in the two active sites, including phosphate treatment of the Mo/carbon catalyst2).

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high temperature regeneration at 700°C with steam of the Co-Mo/γ-Al₂O₃ catalyst3), and control of degree of sulfidation of the Mo/Al₂O₃ catalyst4). HDS selectivity is decreased by such modifications, so the HDS active site is different from the olefin HG active site. However, the HDS selectivity (n_HDS/n_HG) is decreased by these modifications, and thus contradicts the objective of selective CCG HDS.

The present study tried to improve the HDS selectivity by investigating the relationship between HDS activity and olefin hydrogenation activity.

2. Experimental

2.1. Feedstocks

2.1.1. Model Compounds

Commercial grade thiophene (2.83 × 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 pyridine (0.01 mol/mol) were also
used.

2.1. 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 amounts of total sulfur and thiol-type sulfur were measured by oxidative micro-coulometry (ASTM D 3120) and potentiometric methods (ASTM D 3227), respectively. Sulfur compounds were quantitatively analyzed by GC-AED (gas chromatography equipped with atomic emission detection, Hewlett Packard 5921A) using a 50 m PONA column. Sulfur compounds were analyzed by GC-MS (gas chromatography-mass spectrometer). GC and PIONA-GC (Analytical Controls Inc.) were used for the measurement of the HG reactivity of olefins.

2.3. Catalyst and Catalyst Pretreatments

Co-Mo/γ-Al2O3 catalyst was prepared by a conventional pore-filling method. CoO and MoO3 contents were 4.6 and 15.0 mass%, respectively. A total of 60 ml of the catalyst was packed in a bench pilot reactor, and a 4 ml 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°C, 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 types of HDS (%) are defined in the present paper by the following equations. Olefin HG (%) is also defined as follows.

2.4.1. Model Compound HDS

Total HDS (%): (1 – product sulfur / feed sulfur) × 100

2.4.2. CCG HDS

Total HDS (%): (1 – product sulfur / feed sulfur) × 100

Conversion of S compounds (%):

\[1 - \left( \frac{\text{product sulfur} - \text{thiol sulfur}}{\text{feed sulfur}} \right) \times 100\]

Olefin HG (%): (1 – olefin content in product / olefin content in feed) × 100

3. Hydrodesulfurization of CCG

The GC-AED analysis of CCG is shown in Fig. 1. Eleven alkylthiophenes and 2 alkylbenzothiophenes, 3 alkylthiacyclopentanes, and 2 disulphides were observed. The compositions of these sulfur compounds are shown in Table 2. The total amount of alkylthiophenes was about half that of alkylbenzothiophenes. As shown in Table 1, CCG contained olefins, saturates and aromatics. Internal and branched olefins were dominant in the olefins of CCG. These results basically agree with the analysis of CCG containing 1000 ppm sulfur.

The HDS conditions were as follows: 210-220°C, 1.6 MPa, LHSV 3.5 h⁻¹, H2/feed ratio 338 Nl/l. The compositions of sulfur compounds in the HDS products of CCG treated in the bench pilot plant are shown in Table 2.

After HDS the total sulfur content clearly decreased from 229 ppm to 81 ppm at 220°C, whereas 17 ppm of thiols were produced. Alkylbenzothiophenes were more reactive than alkylthiophenes and the reaction rate constant of benzothiophene was 6 times larger than that of thiophene. The HDS reactivity decreased with increasing number of alkyl substitution groups. 2-Methylthiophene was less reactive than 3-methylthiophene, due to the steric hindrance of the methyl group substituted at the 2-position of thiophene.
Table 2 Sulfur Compounds in CCG before and after HDS

| GC-AED No. | Sulfur compound | Feed stock sulfur [ppm] | Reaction temperature [°C] | | | |
| --- | --- | --- | --- | --- | --- |
| | | Sulfur [ppm] | Conversion [%] | Sulfur [ppm] | Conversion [%] |
| 1 | thiophene | 7 | 4 | 43 | 3 | 57 |
| 5 | thiacyclopentane | 5 | 2 | 60 | 1 | 80 |
| 3 | 2-methylthiophene | 11 | 7 | 36 | 6 | 46 |
| 4 | 3-methylthiophene | 10 | 5 | 50 | 3 | 70 |
| 6 | 2-methylthiacyclopentane | 3 | 3 | 0 | 2 | 33 |
| 7 | 3-methylthiacyclopentane + 2-ethylthiophene | 5 | 5 | 0 | 4 | 20 |
| 10 | 2,3-dimethylthiophene | 5 | 3 | 40 | 2 | 60 |
| 9 | 2,4-dimethylthiophene | 7 | 5 | 29 | 4 | 43 |
| 8 | 2,5-dimethylthiophene + 3-ethylthiophene | 4 | 2 | 50 | 2 | 50 |
| 11 | 3,4-dimethylthiophene | 3 | 1 | 67 | 1 | 67 |
| 13 | C3-thiophenes | 15 | 15 | 0 | 12 | 20 |
| 14 | C4-thiophenes | 7 | 6 | 14 | 5 | 29 |
| 15 | benzothiophene | 63 | 2 | 97 | 0 | 100 |
| 16 | methylbenzothiophenes | 63 | 28 | 56 | 12 | 81 |
| 2 | dimethyldisulfide | 4 | 1 | 75 | 0 | 100 |
| 12 | dimethylsulfide | 1 | 1 | 0 | 0 | 100 |
| unknown | 16 | 15 | 6 | 7 | 56 |
| thiols | 0 | 22 | 17 | | |
| total sulfur | 229 | 127 | 81 | | |

HDS %: 45 65
Conversion %: 54 72

Intrinsic reactivities of the sulfur compounds contained in CCG were examined as pure sulfur compounds dissolved in toluene. The conversions at several temperatures are shown in Fig. 2. Clearly the reactivity decreased in the order benzothiophene > thiophene > 3-methylthiophene > 2-methylthiophene > 2-ethylthiophene > 2,5-methylthiophene within the temperature range examined. The order of reactivity is the same as that of sulfur compounds in CCG HDS. However, the reaction rate of sulfur compounds in toluene is much faster than that in CCG. The olefins in CCG probably reduce the HDS reactivity by competitive adsorption on the HDS active sites of the catalyst. A few studies have been reported on the effects of hydrocarbons on the HDS reaction \(^1\). No formation of thiol was observed. Therefore, thiol produced in CCG HDS is not the intermediate of the HDS of sulfur compounds. Thioles are produced by the reaction between H₂S and olefins contained in CCG.

4. Active Sites of the Catalyst

In order to improve the HDS selectivity of CCG, it is necessary to clarify the difference between the HDS active site and the olefin HG active site. Thiophene and butene have been used to investigate the HDS mechanism, and most studies have indicated that the HDS active site is different from the butene HG active site\(^2\).  

Fig. 2 HDS Conversion of Individual Sulfur Compounds and CCG

The difference in the active sites was studied by using the inhibiting effects of H₂S. As is well known\(^3\), H₂S is adsorbed on the HDS active site with coordinative unsaturation and competitively inhibits the access.
of other sulfur compounds to the HDS active site. If olefin reactions are affected by H₂S as HDS is affected, the structure of the olefin HG active site can be considered to be similar to that of the HDS active site. If olefin reactions are not affected by H₂S, the structure of the active site for olefin reactions may be different from that of the HDS active site. The effects of H₂S on HDS of thiophene, alkylthiophenes, and benzothiophene were examined in the H₂ stream with or without H₂S (Table 3). Even with a small amount of H₂S (0.1 vol% in H₂), the HDS of all thiophenes was strongly retarded, and the reaction rate constants obtained were 15-20% of the original rate constants. The reactions of disobutylene, 1-octene and 1-hexene were examined in the H₂ stream with or without H₂S (Fig. 3). With H₂S, HG of disobutylene was promoted whereas HG of 1-octene and 1-hexene was retarded. This finding shows that the isolefin HG active site is different from the HDS active site, and control of the selectivity of CCGH may be possible.

In order to further clarify the difference between the HDS active site and the isolefin HG active site, the response of the catalyst activity to the well-known promoting effects of Co was studied by using catalysts with varying Co content. The results shown in Figs. 4 and 5. As is well-known, thiophene HDS drastically increased with increasing Co/(Co + Mo) ratio.

MoS₂ 15.0 mass% (* 7.5 mass%), temperature 175°C, pressure 1.3 MPa, H₂/ feed 0.34 g-cat. min/mol, feed thiophene 2.83 × 10⁻⁴ mol/mol, toluene 80 mol%, olefin 20 mol%.

MoS₂ 15.0 mass% (* 7.5 mass%), temperature 190°C, pressure 1.3 MPa, H₂/ feed 0.34 g-cat. min/mol, feed thiophene 2.83 × 10⁻⁴ mol/mol, toluene 80 mol%, olefin 20 mol%.

Fig. 4 Effects of Co on HDS and Isolefin HG

Fig. 5 Effects of Co on HDS and n-Olefin HG

On the other hand, HG of diisobutylene slightly decreased and HG of 1-octene greatly decreased with increasing Co/(Co + Mo) ratio. Similar decreasing trends have been reported for the activity for butene HG on unsupported Co-Mo sulfide catalyst, in which thiophene HDS and successive butene HG were undertaken at 320°C and atmospheric pressure. The explanation is that the addition of Co ions blocks the coordinatively unsaturated Mo sites on the edges of MoS₂ and decreases the HG activity. If Co blocks the unsaturated Mo sites, the small effects of Co on isolefin HG suggest that isolefin HG proceeds on the unsaturated Mo sites not blocked by Co. In the case of catalyst with half metal content (* marked), thiophene conversion largely decreases, whereas olefin HG slightly decreases. A content of 7.5 mass% of MoS₂ is too small to cover the whole surface of the Al₂O₃. Uncovered Al₂O₃ surface may enhance olefin HG. These results also indicate that HDS and olefin HG proceed at different active sites. The effects of H₂S and Co are summarized in Table 4.

The effects of pyridine modification on catalyst
activity and selectivity of Co-Mo/γ-Al₂O₃ catalyst were investigated in the micro reactor. Thiophene HDS, diisobutylene HG and 1-octene HG were studied at 150°C, 1.3 MPa 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 inhibition by pyridine spike was studied. Then, the temperature was increased to 300°C to strip the pyridine and the temperature was reduced to 150°C to measure the remaining effects of pyridine. After pyridine was desorbed at 300°C, HDS activity almost recovered to the initial level. However, the activity for diisobutylene HG still remained much lower than the initial activity. The activity for 1-octene HG recovered to half of the initial activity. The persistent effect of the pyridine spike on isoolein HG was stronger than that on n-olefin HG. These observations strongly support the idea that three different types of active sites are present on the catalyst.

From these results, we proposed the following three types of active sites.

HDS active site: This site is inhibited by H₂S and promoted by Co. n- and isoolein can approach.

n-olefin HG active site: This site is inhibited by H₂S and inhibited by Co. This site has some similarity with the HDS active site.

Isoolein HG active site: This site is promoted by H₂S and is slightly inhibited by Co. This site strongly interacts with isoolein, resulting in the formation of oligomer. This site is totally different from the HDS and n-olefin active sites.

These phenomena suggest the possibility of selective CCG HDS in which the HDS reaction occurs with minimal olefin HG because most olefins contained in CCG are isoolefins.

5. HDS Selectivity Improvement

5.1. Selectivity Improvement with Optimized Co Distribution

Co addition test shows that the optimum amount of Co loaded on γ-Al₂O₃ gives good selectivity for CCG HDS by reducing the n-olefin HG activity. The Co distribution is also important for the selectivity improvement. Highly dispersed Co catalyst was prepared with CyDTA-Co (trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid-Co). The thiophene HDS and 1-octene HG reactions were examined and the activities were compared with those over conventional Co-Mo/γ-Al₂O₃ catalyst. CyDTA-Co showed higher HDS activity and lower 1-octene HG activity than the conventional catalyst.

5.2. Selectivity Improvement by Coking Pretreatment

We previously found that isoolefins were oligomerized on the isoolein HG active site. Oligomer may finally be irreversibly deposited on the active site as coke. If the isoolein HG active site is selectively deactivated by the coke, then selective CCG HDS will occur.

Three different combinations of pretreatments were carried out on the fresh catalyst: sulfiding + aging, sulfiding + aging + coking, and coking + sulfiding + aging. The coking pretreatment used a mixture of cyclohexene + 1-methylnaphthalene. The results of CCG HDS are shown in Fig. 6. The catalyst with sulfiding + aging provided a higher total HDS percentage than the catalyst with coking. The catalyst with sulfiding + aging + coking showed higher HDS selectivity than the catalyst without coking. However, the catalyst with coking + sulfiding + aging showed the same selectivity as the catalyst without coking. These results show that coking pretreatment should be performed after sulfiding to improve HDS selectivity.

The effects of coke were further examined by using refinery spent catalyst previously used in the diesel fuel HDS process for 1 year. This catalyst, containing 8.8 mass% deposited coke, was supplied for the CCG HDS activity test. This spent catalyst also showed high HDS selectivity. However, this high selectivity was lost by the regeneration procedure. This result suggests that the coke deposition improves the HDS selectivity.

Thiophene HDS was carried out over the catalyst.

Table 4 Effects of H₂S and Co

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<th>H₂S</th>
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<td>C</td>
<td>inhibition</td>
<td>promotion</td>
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<tr>
<td>C-C-C-C-C-C</td>
<td>HG</td>
<td>promotion</td>
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<tr>
<td>C-C-C-C-C</td>
<td>HG</td>
<td>inhibition</td>
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Temperature 300°C, pressure 0.4 MPa, H₂/feed 85 Nl/l, feed CCG (sulfur 157 mass ppm, olefin 36.6 vol%).

Fig. 6 Effects of Coking Pretreatment on HDS Selectivity
Temperature 175°C, pressure 1.3 MPa, H₂/feed 1.6 mol/mol, feed thiophene 2.83 × 10⁻⁴ mol/mol, toluene 80 mol %, olefin 20 mol %.

Fig. 7  Effects of Coking on HDS Selectivity in the Presence of Isoocten

Temperature 190°C, pressure 1.3 MPa, H₂/feed 1.6 mol/mol, feed thiophene 2.83 × 10⁻⁴ mol/mol, toluene 80 mol %, olefin 20 mol %.

Fig. 8  Effects of Coking on HDS Selectivity in the Presence of n-Olefin

with or without aging and coking pretreatment in the presence of disobutylene and 1-octene. Thiophene HDS was little reduced by the aging pretreatment but much reduced by the coking pretreatment. The disobutylene HG percentage is plotted against thiophene HDS in Fig. 7. Little difference was observed between the selectivity of the catalysts with or without aging. However, disobutylene HG of the catalyst with coking was much lower than those of catalysts without coking.

The 1-octene HG percentage is plotted against thiophene HDS in Fig. 8. 1-Octene HG of the catalyst with coking was much higher than those of catalysts without coking. The effects of coking pretreatment on the three different types of active sites decreased in the order isoocten HG active site > thiophene HDS active site > n-olefin HG active site. This order also suggests that the coking pretreatment effectively reduces isoocten HG activity but hardly reduces n-olefin HG activity. As most olefins in CCG are isoolefins, the CCG HDS selectivity can be improved by coking pretreatment.

6. Simulation Model of CCG HDS

6.1. Theoretical Model

The CCG HDS test was conducted and the simulation model was studied. The reaction conditions were: temperature = 200-300°C, pressure = 1.0-5.0 MPa, hydrogen/feed = 100-500 m³/l, HHSV = 2-6 h⁻¹.

6.1.1. Thiol Formation

The thiol formation model is shown in Fig. 9. The equilibrium constant is given by Eqs. (1) and (2):

\[ K_p = \frac{[\text{Thioli}]([\text{Olefin}][\text{H}_2][\text{S}])}{\theta} \]  
\[ K_p = \exp(-\Delta H + T\Delta S/RT) \]  

where \( K_p \) is the equilibrium constant, \([\ ] \) is the partial pressure of a component, and \( \theta \) is the H₂S coverage rate of catalyst. \( \theta \) is calculated from Eq. (3):

\[ \theta = \frac{K[H_2S]/(1 + K[H_2S])}{[\text{H}_2][\text{S}]} \]  

where \( K \) is the adsorption equilibrium constant of H₂S. In Eq. (2), \( \Delta H \) and \( \Delta S \) denote the enthalpy and entropy of thiol formation, respectively. These values were calculated employing the NASA thermochromic polynomials shown in Eqs. (4) and (5):

\[ \Delta H/RT = a_1 + a_2T^2 + a_3T^3/3 + a_4T^4 + a_5T^5 + a_6T^6 \]  
\[ \Delta S/R = a_1\ln T + a_2T^2 + a_3T^3/2 + a_4T^4/4 + a_5T^5 \]  

Each constant \( a_i \), through \( a_7 \) was calculated using THERGAS²⁰(²¹), which is a program for calculating the thermochromic properties of organic compounds in the gas and liquid phases. In this paper, we used 2-methyl-1-hexylthiol as a typical thiol contained in heavy CCG.

6.1.2. HDS and Olefin HG

For CCG HDS, thiophene HDS and olefin HG ratios were calculated from Eqs. (6) and (7), respectively.

\[ -d[\text{Olefin}]/dt = [\text{Olefin}]^{\alpha[H_2]}A_1\exp(-E/RT) \]  
\[ (1/1+\alpha[H_2][\text{S}]) \]  

\[ -d[\text{Thiophene}]/dt = [\text{Thiophene}]^{\alpha[H_2]}A_2\exp \]  
\[ (-E/RT)(1/1+\alpha[H_2][\text{S}]) \]  

In Eqs. (6) and (7), \( A \) is the frequency factor and \( E \) is the activation energy. The sulfur and olefin contents in hydrotreated CCG can be estimated by including these equations in the simulation model.

6.2. Verification of Simulator Model

Figure 10 shows the effects of temperature on the estimated and experimental results for thiol production. The theoretical calculations showed good correspondence with the experimental results. It is clear that higher temperature results in lower thiol formation. In general, the equilibrium constant $K_p$ depends on the temperature. $K_p$ decreases with increasing temperature in this reaction.

The effects of pressure are shown in Fig. 11. For most HDS reactions, higher reaction pressure results in lower sulfur content. On the other hand, the sulfur content of hydrotreated CCG increases as the reaction pressure increases. The reason is that the thiol content increases as the pressure increases. Therefore, this experimental result shows that lower pressure is favorable for reducing the sulfur content in hydrotreated CCG. In this case, our calculated results agree very closely with the experimental results. Most total sulfur in hydrotreated CCG derives from the generated thiol. Therefore, the simulation model must account for thiol formation.

Most of the $\Delta T$ comes from olefin HG in CCG HDS. The olefin HG ratio is calculated by Eq. (6). Figure 12 shows the effects of the hydrogen/feed in olefin HG. The theoretical calculations showed good correspondence with the experimental results. Figure 13 shows the reactor temperature profile for the reaction. In this case, the estimated results obtained by our simulator agree with the experimental results as measured in an adiabatic reactor^{221}.

7. CCG HDS Process

Process development of CCG HDS was started as a research project of Japan Petroleum Energy Center with a subsidy from the METI, Japan. In August 2004, a 20,000 BPSD demonstration plant started operation to produce 10 ppm sulfur gasoline in Sendai, Japan.
Catalyst Activity Trend in Sendai CCG HDS Plant (Fig. 14). The plant has smoothly operated for two years and catalyst life is expected to be 4 years based on the catalyst deactivation rate (Fig. 15). Two more plants were constructed in Negishi and Mizushima in 2004.

References

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要  旨

接触分解ガソリンの選択的水素化脱硫

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FCC ガソリン（CCG）の水素化脱硫を Co-Mo/γ-Al₂O₃ 触媒を使用して検討した。硫黄化合物は脱硫されたが、硫化水素とオレフィンの反応によりチオールが生成した。

チオフェン、n-オレフィン、イソオレフィンを使用したモデル反応で、硫化水素と Co のこれら反応に与える影響を調べた。
Co の添加により、脱硫反応は促進されたが、n-オレフィンの水素化反応は阻害され、イソオレフィンの水素化反応はほとんど影響を受けなかった。この実験に基づき、触媒上にチオフェンの脱硫活性点、n-オレフィンの水素化活性点、イソオレフィンの水素化活性点という三つの異なる活性点の存在を提案した。イソオレフィンの反応において、オリゴマーの生成を確認し、これを応用してコーミング処理による脱硫選択性（脱硫活性とオレフィン水素化活性の比）の向上を検討した。

商業規模の CCG 脱硫プロセスを設計し、反応シミュレーションモデルを検討した。脱硫された CCG 中のチオフェン、チオール、オレフィンの量を計算できる式を作成し、その精度を検証した。

これら研究成果は、20,000 BPSD の商業規模実証化装置に結実し、2004 年より硫黄分 10 ppm のサルファーフリー-ガソリンの製造が開始された。