Hydrogenation by CoMo/Al₂O₃ Catalyst (Part 5)
Effect of H₂S on the Hydrodenitrogenation of Quinoline

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The hydrodenitrogenation (HDN) of quinoline (Qn) was studied over sulfided CoMo/Al₂O₃ catalysts, using a trickle bed reactor, at 400 °C, 5MPa, in a stream of H₂ or in flowing H₂S/H₂. The main products observed in the reaction were 1,2,3,4-tetrahydroquinoline (4HQn), 5,6,7,8-tetrahydroquinoline (4H'Qn), decahydroquinoline (10HQn), o-propylaniline (OPA), propylcyclohexane (PrCH), and propylbenzene (PrBz). The contact time dependency of the product distribution of reactions in a stream of H₂ showed that the ring hydrogenation of Qn to 4HQn occurred readily, and that the HDN of Qn proceeded via aromatic and/or heteroring saturation. The conversion of HDN in a stream of H₂ was about 5-15%. When the reaction was carried out in a stream of 5 mol% H₂S/H₂, the conversion of HDN increased greatly (about 50%). From the results of reactions of several hydrogenated intermediates observed in the reaction path of the HDN of Qn, the increase in the conversion of HDN of Qn due to H₂S addition seems to be effected by the promotion of the aliphatic C-N bond-cleavage leading to nitrogen elimination. The addition of H₂S was also effective to enhance the HDN activity of the catalyst which was exposed to the reaction atmosphere in a stream of H₂ for a certain period of time. The HDN activity of variously pretreated catalysts was in the following order: presulfided>prereduced-then-sulfided>prereduced under H₂S/H₂ atmosphere. This order was consistent with the IR-absorption intensity of nitric oxide (NO) adsorbed on Co sites. The effects of Mo and Co were evaluated by performing the test runs over a series of laboratory prepared CoMo/Al₂O₃, Co/Al₂O₃, and Mo/Al₂O₃. In a stream of 5 mol% H₂S/H₂, it was found that HDN activity of CoMo/Al₂O₃ was much higher than the sum of the activities of Co/Al₂O₃ and Mo/Al₂O₃. The maximum HDN activity was obtained at r(Co/(Co+Mo))=ca. 0.5. The present results allow us to consider that the promoting effect of the H₂S addition is strongly related with both Mo and Co species.

1. Introduction
Catalysts which are currently used in hydro-treating of heavy oils are composed of oxides of molybdenum as the active component and oxides of cobalt or nickel as a promoter supported on alumina. Usually, the catalysts must be presulfided for activation. Since the most expensive process among the hydrotreating processes of heavy oils is hydrodenitrogenation (HDN), much effort has been made to improve the activity of HDN catalysts. Recently, it has been reported that a high catalytic-HDN activity was achieved by introducing H₂S to the reaction system of HDN of coal-derived oils.¹ To date, however, the effect of H₂S addition on HDN reactions over CoMo/Al₂O₃, which is an important hydrotreating catalyst has been scarcely investigated for the model compounds. Moreover, the role of Mo and Co involved in the promoting effect of H₂S on HDN reactions over molybdenum-based catalysts has not yet been discussed.

In a previous paper of this series, we have discussed effects of catalyst pretreatments on the HDN activity of a CoMo/Al₂O₃ catalyst in hydroprocessing of coal-liquid.² We have also shown that H₂S addition enhanced the HDN conversion of coal derived liquid over CoMo/Al₂O₃ and that it was especially effective for the removal of strong base component in coal liquids.² In the present paper, we will discuss in more detail the promoting effect of H₂S on HDN of Qn, as a model of a strong base, over CoMo/Al₂O₃ catalysts. We will also demonstrate...
that such promoting effect of H₂S is strongly related with both Mo and Co species in the catalyst.

2. Experimental

Catalyst A commercial CoMo/Al₂O₃ catalyst, KF-742 supplied by Nippon Ketjen Co., was generally used.

Mo/Al₂O₃ or Co/Al₂O₃ component catalysts were prepared by impregnating gamma-Al₂O₃ (CK-300; Nippon Ketjen Co.) with ammonium heptamolybdate or cobalt nitrate, respectively. These were followed by drying at 105 °C and calcining at 550 °C. A series of CoMo/Al₂O₃ combined catalysts with different Co contents was also prepared by impregnating the above Mo/Al₂O₃ with cobalt nitrate, followed by drying and calcining. Compositions of the catalysts studied are listed in Table 1.

Apparatus and procedure Details of the reactor and procedure were described in our preceding paper.⁹ 1.0 gram of catalyst (32-60 mesh) diluted with gamma-Al₂O₃ to 1:5 was charged. Presulfidation of the catalyst was carried out in flowing 5 mol% H₂S/H₂ (1 MPa) at 400 °C for 2 hr. Prereducing was carried out at 400 °C in flowing H₂ (5 MPa) for 10 hr. Reactions were carried out at 375 °C, LHSV=15 min⁻¹, in flowing 5 MPa H₂ or 5 mol% H₂S/H₂ and a gas/lean ratio of 1000 vol/vol. The 5 mol%-Qn/heptane solution was metered into the system at a rate of 0.3 cm³/min from a measuring burette using a high pressure pump. Liquid products were collected after they were separated from the gaseous effluent with a train of separators.

All reagents were high-grade commercial chemicals and used without further purification.

Analysis Products were identified using a JEOL JMS-D300 GC-MS Spectrometer. Hitachi 063 Gas Chromatograph, equipped with a 50 m

Table 1 Chemical Composition and BET Surface Area of the Catalysts

<table>
<thead>
<tr>
<th>Cat. No</th>
<th>CoO (wt%)</th>
<th>MoO₃ (wt%)</th>
<th>r²(mol%)/</th>
<th>area²</th>
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<tr>
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<td>0.36</td>
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<td>M</td>
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<td>0.48</td>
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</tr>
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<td>1.00</td>
<td>182</td>
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</tbody>
</table>

1): r²=Co/(Co+Mo)
2): BET surface area
3): commercial CoMo/Al₂O₃

Fig. 1 Effect of Contact Time on Reaction of Quinoline at 375 °C in H₂ Stream over Presulfided CoMo/Al₂O₃ (■: Qn, ▲: 4HQn, ●: 4’HQn, △: 10HQn, O: OPA, Δ: PrCH, ▽: PrBz)

3. Results

Reaction in a stream of H₂ Typical products observed in the reaction of Qn over presulfided catalyst were 4HQn, 4’HQn, 10HQn, OPA, PrCH, and PrBz.

Effects of contact time on product distribution was investigated by changing the amount of the catalyst charged. The catalyst used was commercial CoMo/Al₂O₃. As shown in Fig. 1, a sharp increase in 4HQn and a rapid decrease in the remaining Qn were observed for short contact times. It should be noticed that the ratio of 4HQn to Qn is almost constant (3.2—3.6). This suggests that, in the reaction of Qn, the hydrogenation of Qn to 4HQn could occur readily, and Qn and 4HQn could be equilibrated under the present reaction conditions. As the contact time was increased, the amount of the ring-saturated product (4HQn, 4’HQn, and 10HQn) passed its maximum, and then decreased. OPA, however, was formed only in a limited amount. PrCH, the main HDN product, increased linearly after its induction period.
The reaction formed fewer kinds of products at 275 °C than at 375 °C. No denitrogenated products such as PrCH or PrBz were recognized in the testing runs. The product distribution is shown in Fig. 2(a). In a stream of H₂, 4HQn was produced overwhelmingly.

**Reaction in a stream of 5 mol% H₂S/H₂** Fig. 3 illustrates the effect of contact time on product distribution. When Fig. 3 was compared to Fig. 1, 4HQn, and 10HQn decreased rapidly with increasing contact time. OPA became dominant and behaved as intermediate in the denitrogenation process. It was also found that the amount of PrCH increased greatly with contact time. The amount of PrBz was also increased to some extent compared to the reaction in a stream of H₂.

The results of the reaction at 275°C are shown in Fig. 2(b). Compared with the results of the reaction in a stream of H₂ (Fig. 2(a)), a higher amount of OPA is noticeable. Moreover, 10HQn is not produced under atmosphere of H₂S/H₂.

**Reaction of 4HQn, 4’HQn, and o-ethylaniline (OEA)** To understand the HDN mechanism of Qn in more detail, reactions of several intermediates in the Qn HDN process, such as 4HQn and 4’HQn, were carried out under both H₂ and 5 mol% H₂S/H₂ streams. Instead of OPA, the reaction of OEA was investigated. The results are
To evaluate the reactivity quantitatively, the conversion of HDN, defined here by 100×[mol% of nonpolymer hydrocarbon products not containing nitrogen]/[mol% of total products (including unconverted reactant)] as registered on gas chromatograms was used. In a stream of H₂, the conversion of HDN of OEA was very high compared with the conversions of Qn, 4HQn, and 4'HQn. This may suggest that if Qn is converted to OPA, the denitrogenation process could occur readily.

In a stream of 5 mol% H₂S/H₂, the increase in the conversion of HDN due to H₂S addition was observed for the two ring-saturated compounds, especially it was significant in the case of 4'HQn. The conversion of HDN of OEA, however, decreased slightly.

**Reproducibility of the effect of H₂S addition**

The effect of H₂S addition was investigated by alternately performing the reaction in a stream of H₂ and in that of 5 mol% H₂S/H₂. As shown in Fig. 5, it is evident that the introduction of H₂S was also effective in raising the HDN activity of the catalyst which had been exposed to the reaction atmosphere in a stream of H₂ for a certain period of time. When this introduction was stopped, however, the HDN activity dropped quickly to its former level. These phenomena are completely reversible.

**Effects of concentration of H₂S**

As shown in Fig. 6(a), ring-hydrogenated products were formed at the region of lower concentrations of H₂S (<2 mol%), and disappeared with increasing concentration of H₂S. On the other hand, both OPA and PrCH increased with increasing concentration of H₂S up to 5 mol%. Beyond 5 mol% H₂S/H₂, OPA still continued to increase, but PrCH tended to decrease. The conversion of HDN attained its maximum at 5 mol% H₂S/H₂ (Fig. 6(b)).

**Effects of catalyst pretreatments**

Effects of catalyst pretreatments on HDN reaction were investigated, using presulfided, prereduced-then-sulfided and prereduced commercial CoMo/Al₂O₃. The results are shown in Fig. 7. In a stream of H₂, although the conversion of HDN over all catalysts was low, there seems to exist some difference among the pretreatments in the early stages of the time on stream. The results of the reaction in a stream of 5 mol% H₂S/H₂ for these variously
Table 2 Products Distribution of the Reaction of Quinoline over Presulfided Catalysts (mol%)

<table>
<thead>
<tr>
<th>Cat. No</th>
<th>Qn</th>
<th>4HQN</th>
<th>4'HQN</th>
<th>10HQN</th>
<th>OPA</th>
<th>PrCH</th>
<th>PrBz</th>
</tr>
</thead>
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<tr>
<td>CK-300^1</td>
<td>32.0</td>
<td>57.1</td>
<td>4.8</td>
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<td>0.2</td>
</tr>
<tr>
<td>C</td>
<td>17.0</td>
<td>60.0</td>
<td>7.0</td>
<td>1.2</td>
<td>1.0</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>M</td>
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<td>0.9</td>
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<td>CM-45</td>
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<tr>
<td>KF-742^2</td>
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<td>26.7</td>
<td>8.4</td>
<td>4.3</td>
<td>2.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

a) in H₂ stream

b) in 5 mol% H₂S/H₂ stream

1): gamma-Al₂O₃
2): commercial CoMo/Al₂O₃

Fig. 7 HDN of Quinoline over Variously Pretreated CoMo/Al₂O₃ (○: presulfided, △: prereduced-then-sulfided, □: prereduced, in H₂ stream; ●: presulfided, ▲: prereduced-then-sulfided, ■: prereduced, in 5 mol% H₂S/H₂ stream)

Fig. 8 HDN of Quinoline over Presulfided Catalysts in: a) H₂ stream; b) 5 mol% H₂S/H₂ stream (catalysts: ▲; C, △; M, ■; CM-45, ○; KF-742)
pretreated catalysts are also shown in Fig. 3. The order of HDN activity was: presulfided>prereduced-then-sulfided>prereduced. The fact that the sequence of pretreatments also influenced the catalytic HDN activity was interesting.

**Reaction over Co/Al₂O₃, Mo/Al₂O₃, and CoMo/Al₂O₃** Table 2(a) shows the product distribution of the reaction over the laboratory prepared Co/Al₂O₃, Mo/Al₂O₃, CoMo/Al₂O₃ catalysts. The results for commercial CoMo/Al₂O₃ and gamma-Al₂O₃ are also included in this table. From the fact that the concentration of 4HQn was so high (57%) even in the case of Al₂O₃, it was evident that the heterocyclic ring of Qn was hydrogenated very easily under the present reaction conditions. The remarkable point in the product distribution among the catalysts is the difference in the concentration of 4HQn and 4’HQn, although the sum of 4HQn and 4’HQn is almost identical in all cases. The formation of denitrogenated products (PrCH, PrBz) over all the catalysts was limited.

The results of conversion of HDN are shown in Fig. 8(a). In a stream of H₂, the behavior of HDN activities of Mo/Al₂O₃, CoMo/Al₂O₃, and commercial CoMo/Al₂O₃ was very similar. The HDN activity of each catalyst dropped in early stages of the reaction, then it became constant. The HDN activity of the Co/Al₂O₃ catalyst did not actually change at all with time on stream. With all the catalysts examined, the conversion of HDN was maintained at relatively low levels, mostly under 10%.

The results of product distribution in the reaction in a stream of 5 mol% H₂S/H₂ are shown in Table 2(b). Compared with the results listed in Table 2(a), product distribution scarcely changed in the case of Co/Al₂O₃ catalyst. In respect of the Mo/Al₂O₃ catalyst, a remarkable decrease in the concentration of 4HQn was observed by H₂S addition. Concentration of OPA and PrCH, a typical aliphatic C-N bond-cleaved product and a denitrogenation product, respectively, increased greatly. This tendency was further strengthened in the case of CoMo/Al₂O₃ catalysts. Moreover, it is worth noting that the concentration of Qn dropped to zero and that the amount of OPA and PrCH were almost identical in the case of CoMo/Al₂O₃ catalysts.

The results of HDN activity are shown in Fig. 8(b). Compared to Fig. 8(a), no obvious change in activity of Co/Al₂O₃ was observed. However, the addition of H₂S led to a certain increase in the conversion of HDN in Mo/Al₂O₃. The increase in the conversion of HDN for two CoMo/Al₂O₃ catalysts was most remarkable. It should be noticed that the conversion of HDN over CoMo/Al₂O₃ catalysts was much higher than even the sum of the conversions of HDN over Co/Al₂O₃ and Mo/Al₂O₃ catalysts. It can be said that the promoting effect of H₂S is remarkable when both Co and Mo are present in the catalyst.

To evaluate the effect of Co in Mo-based catalyst on HDN reaction of Qn under the atmosphere of H₂S/H₂ in more detail, a series of laboratory prepared CoMo/Al₂O₃ (Table 1) catalysts with different Co contents was tested in a stream of 5 mol% H₂S/H₂. Because of the slightly different Mo content in each catalyst [mol% of products/mol% of loading Mo] (apparent turnover number) vs atomic ratio of Co (r=Co/(Co+Mo)) are plotted in Fig. 9(a). The ring-hydrogenated products were observed at the region of low Co contents and they disappeared with increasing content of Co. At the region of r>0.2, almost all of the reaction products were OPA, PrCH and PrBz. The conversion of HDN vs the atomic ratio of Co is plotted in Fig. 9(b). With increasing content of Co, the conversion of HDN increased to its maximum and then decreased slightly.

**4. Discussion**

**Mechanism of quinoline HDN** Satterfield et
al. have earlier proposed the mechanism of the HDN reaction of Qn under the atmosphere of H2 over presulfided NiMo/Al2O3 catalysts, as shown in Fig. 10. This means that the aromatic and/or heteroring of Qn was firstly hydrogenated, then the aliphatic carbon-nitrogen bond broken, and finally denitrogenated. Although no cyclic olefins (observed by Satterfield et al.) were found in the present work, the product distribution pattern vs contact time illustrated in Fig. 1 is quite similar to the pattern reported by Satterfield et al. This suggests that above HDN mechanism in Fig. 10 is also adaptable to the case of CoMo/Al2O3 catalyst.

When the reaction was carried out in a stream of 5 mol% H2S/H2, the concentration of OPA attained its maximum, then decrease with increasing contact time (Fig. 3). That is, OPA behaves as intermediates in the HDN process. However, the concentration of PrCH increased with contact time. Furthermore, considering the ring saturation of Qn to 4HQn to be very easy, in a stream of 5 mol% H2S/H2, the HDN reaction of Qn might mainly occur via the following path: Qn--4HQn--OPA--PrCH. As shown in Fig. 4, the conversion of HDN of OEA was inhibited slightly by H2S introduction. On the basis of these results, it seems reasonable to assume that the concentration of PrCH increased with contact time. Furthermore, considering the ring saturation of Qn to 4HQn to be very easy, in a stream of 5 mol% H2S/H2, the HDN reaction of Qn might mainly occur via the following path: Qn--4HQn--OPA--PrCH. As shown in Fig. 4, the conversion of HDN of OEA was inhibited slightly by H2S introduction. On the basis of these results, it seems reasonable to assume that in the reaction of Qn, the introduction of H2S may principally promote the step of aliphatic C-N bond-breakage (4HQn--OPA), and this increases consequently the conversion of HDN. In addition, from the fact that HDN of 4'HQn occurred more readily than the HDN of 4HQn under H2S atmosphere (Fig. 4), the route via 4'HQn may, to some degree, increase the conversion of HDN of Qn due to the addition of H2S.

**Effects of H2S addition** As shown in Fig. 6(b), the maximum conversion of HDN was attained at the concentration of 5 mol% H2S/H2. Increasing further the concentration of H2S, however, caused some decrease in the conversion of HDN. From the results in Fig. 6(a), the addition of higher concentration of H2S seems to be unfavorable for the step from OPA to PrCH. The same observation was reported also by Satterfield et al. with respect to the HDN of Qn over NiMo/Al2O3 using CS2 instead of H2S. The authors have previously reported that the addition of higher concentration of H2S (>5 mol%) inhibited hydrogenation of o-xylene. The decrease in the conversion of HDN of Qn caused by introducing a higher concentration of H2S could therefore be due to the inhibition of hydrogenation of OPA.

We have earlier reported that the weight of the commercial CoMo/Al2O3 was increased by presulfiding (0.1 MPa, 5 mol% H2S/H2). By subsequent reduction of the above catalyst with H2, about 30 wt% of sulfur was easily eliminated as H2S. Resulfiding of the catalyst, the weight (i.e., the amount of sulfur) was restored to the level before reduction. This process was found to be completely reversible. Strikingly, when H2 and H2S/H2 were alternately introduced, the behavior of the conversion of HDN (Fig. 5), is quite similar to the weight change of the catalyst. This means that a high sulfidation state seems to be necessary for obtaining higher HDN activity. When this highly sulfided state is broken (by carrying out the reaction in a stream of H2), the HDN activity is decreased. Also, the sulfur contents (XPS) in the used catalysts exposed to the reaction atmosphere, 5 mol% H2S/H2 and H2, were measured as 2.68 and 2.22, respectively. These XPS results support the above speculation.

**Effects of pretreatments and the role of Mo and Co species** As mentioned above, the effect of catalyst pretreatments of the HDN activity was found to be in the following order: presulfided>prereduced-then-sulfided>prereduced when the HDN of Qn was carried out in a stream of 5 mol% H2S/H2. Although the HDN activity of prereduced catalyst is increased by successive sulfiding, it is still lower than that of the initially sulfided catalyst. We have already reported such observation with respect to the effect of pretreatments, i.e., the same order was also observed in the HDN conversion of coal-liquids. These results suggest that a certain irreversible change of the state of the catalyst surface occur by prereducing the catalyst at the beginning, resulting in the alteration in the HDN activity. An FT-IR study of NO adsorbed on pretreated catalysts demonstrated that this irreversible change occurred mainly on Co site. Combining the results of FT-IR study with the effect of pretreatment on HDN activity,
the active site for HDN is sensitive to the change in Co site.

The present results reveal further information about the role of Co in CoMo/Al₂O₃ catalysts. As shown in Fig. 8(b), although no effect of H₂S addition was observed for Co/Al₂O₃, the promoting effect of H₂S addition was much more significant for both prepared and commercial CoMo/Al₂O₃ than for Mo/Al₂O₃. It can be said that coexistence of Co strongly increases the promoting effect of H₂S addition. With increasing Co content, the HDN activity increased almost linearly to its maximum at \( r (=\text{Co}/(\text{Co+Mo})) = \text{ca.} 0.5 \), then it tended to decrease slightly (Fig. 9(b)). This result may indicate that a kind of Co-Mo paired species, strongly promoting the HDN reaction under atmosphere of H₂S/H₂, has been formed in the CoMo/Al₂O₃ catalysts.

In our earlier report, we have shown that in the reaction of monoaromatic hydrocarbons over a CoMo/Al₂O₃ catalyst, the skeletal isomerization of the hydrogenated products of benzene, toluene, and xylene was promoted by introducing H₂S to the reaction system.¹⁰ This result suggests that the acidic property of the CoMo/Al₂O₃ catalyst surface is increased by H₂S addition, since the skeletal isomerization is believed to be associated strongly with the Bronsted acid sites. The induced acidity of Mo-based catalysts by H₂S addition has been pointed out earlier.¹³,¹⁴ Two possible explanations have already been proposed. One is that the Bronsted acid sites are formed afresh by the dissociative adsorption of H₂S on the anion vacancy of Mo.¹⁴ Such acid site can act as the active site for HDN, since the C-N bond cleavage leading to nitrogen removal is claimed to be through the Hoffmann degradation, namely, that the nitrogen leaving needs to be quaternized before rupturing of the C-N bond.¹⁴ The other explanation is that the surface sulfur makes a path through which the partially hydrogenated intermediate diffuses from Mo site to the Al₂O₃ support where it becomes a carbonium ion and subsequently decomposes (denitrogenating) or isomerizes on the acidic site of the support as in the case of Pt/Al₂O₃ bifunctional catalysts. The gas phase H₂S increases the number of this path from the Mo site to the acidic site of Al₂O₃ support.¹⁰ In either case, reproducibility of the effects of H₂S addition on HDN activity (Fig. 5) can be accounted for by assuming the dynamic equilibrium between the gas phase H₂S and the adsorbed sulfur species on the surface. This dynamic equilibrium has already been observed in H₂S/H₂-CoMo/Al₂O₃ system.¹⁰ Our present results indicate that the acidic properties induced afresh under the atmosphere of H₂S are strongly correlated not only with Mo sites but also with Co site.

References

CoMo/Al₂O₃触媒による水素化反応（第5報）
キノリンの水素化脱窒素に及ぼす硫化水素の影響

東北工業大学工学部化学工学科，980 仙台市荒巻青葉

本研究では，CoMo/Al₂O₃触媒によるキノリン（Qn）の水素化脱窒素反応（HDN）を400°C，5 MPa，水素あるいは5 mol%硫化水素/水素気流中で行い，反応に基づく硫化水素の添加効果及びその作用を検討した。

QnのHDN反応における主生成物は，1,2,3,4-テトラヒドロキノリン（4 HQn），5,6,7,8-テトラヒドロキノリン（6 HQn），δ-プロピオルニリン（OPA），プロピロキシンヘキサノ（PrCH），プロピベンゾン（PrBz）であった。触媒の量を変えることによって接觸時間を変えた実験の結果をFig. 1に示した。接觸時間が増すにつれて，4 HQn，10 HQnなどの環状水素化合物は共に最大値を経て減少するが，主な生成物であるPrCHは有する誘導期間の後に増大している。Satterfieldらは，NiMo/Al₂O₃触媒を用いて，水素気流中でQnのHDN行い，Fig. 10に示すような反応機構を提案した。本研究においてFig. 1の結果は，Satterfieldらが報告した接觸時間を変えたときの生成物の挙動をほぼ同じ傾向を示していたので，本研究でのHDN反応機構も本質的にはFig. 10と差異のないものと考えられる。

硫化水素/水素気流中における接觸時間と生成物分布との関係をFig. 3に示した。OPAは極大値を取る傾向を示し，PrCHは接觸時間と共に増大した。Fig. 10のHDN過程におけるいくつかの中間生成物である4 HQn，4 HQn，さらにOPAの代用としてのα-エチルアリジン（OEA）の反応を水素および硫化水素/水素気流中で行った。Fig. 4に示すように，水素気流中では，OEAのHDN反応は他のものに比べて特によかった。一方，硫化水素/水素気流中では，OEAのHDN反応は水素気流中のときと比べて若干低下している。これらの結果から，Qnの反応を硫化水素/水素気流中で行った際にみられたHDN反応の幅大な上昇（Fig. 4: 50%）は，Fig. 10における4 HQnからOPAへの水素化分解の段階が促進されたことに由来するものと考えられる。このことは，Qnの反応を低温の275°Cで行ったときの結果（Fig. 2a），（b）によってもある程度支持される。また，Fig. 4から4 HQnのHDN反応も硫化水素/水素気流中でかなり進行しやすいことが分かった。水素気流中でのQnの反応において，4 HQnもかなり生成していることを考慮すると，硫化水素希釈気流中でのHDN反応の促進には，4 HQnを経由する経路も関与している可能性がある。

QnのHDN反応への硫化水素濃度の影響をFig. 6に示した。HDN反応は硫化水素濃度が5 mol%のところで最大となっている。生成物分布については，環状水素化合物である4 HQn，4 HQnと10 HQn等は硫化水素濃度が低い（2 mol%）範囲内で生成しているが，やがて消失している。一方，OPAとPrCHは硫化水素濃度と共に増加しているが，5 mol%を境にOPAは更に増え続け，PrCHは減少している。このことから，高濃度（＞5 mol%）の硫化水素の添加によるQnのHDN転化率の減少はOPA除却後の水素化が抑制されたことに由来すると考えられる。Fig. 5に硫化水素の添加効果の再現性についての結果を示した。われわれが既に報告した触媒表面の吸着NOの量をFT-IRで観測した結果から考えると，この前処理法による触媒のHDN活性の違いは，触媒表面のCo種と深く関係していることが推測される。

自製のCoMo/Al₂O₃およびCo/Al₂O₃，Mo/Al₂O₃触媒（Table 1）を使って，触媒のHDN活性とCo種との関係について調べた。水素気流中において，QnのHDN転化率は515%と低かった（Fig. 8a）。硫化水素/水素気流中では，CoMo/Al₂O₃触媒の活性はCo/Al₂O₃およびMo/Al₂O₃触媒の活性の和よりもかなり高くなっている（Fig. 8b）。このことから，触媒中にCoとMoが共存すると硫化水素の添加効果が最も顕著になることが分かる。Fig. 9a，（b）にはCoの原子分率（r = Co/(Co + Mo)）の異なる一連の自製CoMo/Al₂O₃触媒を使って，硫化水素/水素気流中で反応した結果を示した。HDN活性とCoの原子分率との間にある程度の相関関係が存在することが分かる。

触媒のHDN活性に対する硫化水素の添加効果については，触媒の表面酸性と結び付けて次のように推測している。すなわち，Mo上のアミオンの存在が硫化水素が吸着する重要な役割を果たすと考えられる。このアミオンの存在が触媒のHDN活性を制限するため，硫化水素が吸着すると，触媒表面の酸性が低下して，硫黄化合物の生成が促進されることになる。さらに，硫化水素の添加が触媒表面の酸性を低下させると，触媒表面の酸性が低下することになる。このことから，触媒のHDN活性に及ぼす硫化水素の添加効果は，触媒表面の酸性と深く関連していることが示唆される。