[Regular Paper]

Inhibition Effect of Hydrogen Sulfide and Ammonia on NiMo/Al₂O₃, CoMo/Al₂O₃, NiCoMo/Al₂O₃ Catalysts in Hydrodesulfurization of Dibenzothiophene and 4,6-Dimethyldibenzothiophene

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(Received August 24, 2004)

Model hydrodesulfurization catalysts (Co2.75Mo11, Ni2.75Mo11 and Ni0.9Co1.85Mo11 wt%/γ-Al₂O₃) prepared by impregnation of similar supports with similar starting materials were used in the following test reactions: hydrodesulfurization (HDS) of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene, with and without addition of H₂S or NH₃. The presence of H₂S or NH₃ has a profound effect on the catalyst ranking and the activities of various reaction pathways, *e.g.*, the hydrogenation (HYD) route and the direct desulfurization (DDS) route. In the case of the HDS of DBT and 4,6-DMDBT, hydrogen sulfide only weakly poisoned CoMo and NiCoMo catalyst, whereas a NiMo catalyst is poisoned more strongly. On the other hand, ammonia strongly poisoned HYD route of CoMo catalyst, whereas DDS route of NiMo catalyst is not at all poisoned in the case of the HDS of DBT. The trimetallic NiCoMo catalyst exhibited the best performance in the conversion of DBT. A comparison of the HYD and DDS rate constants among CoMo, NiMo and NiCoMo catalysts shows that in the presence of rich H₂S, the activity of HYD and DDS of the NiCoMo catalyst equals the sum of the activity of the HYD of NiMo catalyst and of the DDS of CoMo catalyst. On the other hand, in the presence of rich NH₃, the activity of the NiCoMo catalyst equals the sum of the HYD and DDS of NiMo catalyst, which each in turn are higher than those of CoMo catalyst. This dual promoting effect of NiCoMo catalyst causes higher activity than either NiMo or CoMo catalyst in the presence of either rich H₂S or rich NH₃.

Keywords

Hydrodesulfurization, Inhibition effect, Nickel molybdenum catalyst, Cobalt molybdenum catalyst, Hydrogen sulfide, Ammonia

1. Introduction

The development of more active catalysts for more efficient hydrotreating processes is important in view of upcoming oil regulations. Further tightening of diesel fuel sulfur restrictions has been proposed and will be implemented worldwide in the near future. In order to reduce particulate matter and NO_x emission from diesel-fueled vehicles, the maximum permissible sulfur content of diesel fuel will be 50 wt ppm by the end of the year 2004 in Japan. Requirement of substantially “sulfur free” diesel fuel (10 wt ppm or less) has been proposed for the future. The European Commission proposed a mandatory “zero sulfur” restriction (10 wt ppm or less) from 2011. Japan is also considering requiring “sulfur free” diesel fuel by 2007. Therefore, much attention is given to effective technological solutions for ultra-low sulfur diesel fuel, particularly sulfur-

free diesel fuel production. In deep hydrodesulfurization (HDS), employed to accomplish this goal, the most refractory sulfur compounds in gas oil are alkyl-dibenzothiophenes with alkyl groups near the sulfur atom (in positions 4 and 6)^{1,2)}. The other problem is inhibition by H₂S^{3,4)} and nitrogen compounds including NH₃^{5,6)}. These inhibitors are generated during HDS and HDN reactions and their concentration is higher under the conditions of deep HDS.

Two solutions for ultra-low sulfur diesel fuel production have been developed by the authors. A simple solution known as the “CoMo/NiMo Catalyst Relay” system was described in ref.7. This solution can achieve 50 wt ppm sulfur production without major revamp of conventional deep HDS units. In this system, the first part of the catalyst bed is the CoMo type, which is the pretreatment catalyst for ultra deep HDS, arranged over the main NiMo catalyst which is the second part. The main function of the CoMo catalyst is to achieve HDS of reactive sulfur compounds such as dibenzothiophene (DBT). The NiMo catalyst in the

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second bed is the main catalyst for ultra-low sulfur diesel fuel production and achieves HDS of refractory sulfur compounds such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), even in the presence of high concentrations of catalyst poisoning materials such as hydrogen sulfide and ammonia.

A more effective solution is a two-stage process with gas/liquid separation (GLSP) in the middle of the unit⁸⁾. This process has a great potential for producing sulfur-free diesel fuel production ($S = 10$ wt ppm or less). Removal of produced H_2S and NH_3 in the middle of the unit accelerates HDS in the second-stage reactor here described. Typical straight gas oil derived from Middle East heavy oil contains 1.2 wt% of sulfur and 100–300 wt ppm of nitrogen compounds. During ultra-deep HDS, in the first-stage reactor most of the nitrogen compounds are converted to NH_3 , and some 1.0% of sulfur compounds is converted to H_2S . The authors will examine the inhibition effect of these substances on ultra-deep HDS in the second-stage reactor.

We have also developed a new HDS catalyst, using the promotion effect of both Ni and Co⁹⁾. The activity of the catalyst on HDS and HDN is higher than that of conventional NiMo and CoMo catalysts in a limited range of Ni/Co ratio, $0.5 < Co/(Co + Ni) < 0.75$.

In this work, this promoter effect was examined in more detail, special attention being paid to the inhibition of NH_3 and H_2S . The Ni-, Co- and NiCo-promoted Mo catalysts were prepared by pore-volume impregnation, each in a similar support. In this way, we were able to clearly understand the inhibition of NH_3 and H_2S on the HDS catalysts in conversion of DBT and 4,6-DMDBT.

2. Experimental

2.1. Catalyst Preparation

Catalysts were prepared by successive incipient wetness impregnations of $\gamma-Al_2O_3$ (pore volume: $0.78\text{ cm}^3 \cdot g^{-1}$, specific surface area: $380\text{ m}^2 \cdot g^{-1}$) with an aqueous solution of MoO_3 and Ni carbonate or Co carbonate and with an aqueous solution of phosphoric acid. The catalysts contained 11 wt% Mo and 2.75 wt% Co or 2.75 wt% Ni, or 1.85 wt% Co + 0.9 wt% Ni.

After the impregnation, each catalyst was dried in an oven at 393 K for 15 h and finally calcined at 773 K for 30 min. The catalysts were crushed and sieved to the desired particle size before use. A sample of 0.5 g of a catalyst was diluted with 9 cm^3 $\alpha-Al_2O_3$ to achieve continuous up-flow in a fixed bed reactor, thereby preventing incomplete catalyst wetting and bypass flow.

2.2. Model Feed Experiments

The model feed consisted of a solution of either 0.20 wt% of 4,6-DMDBT (Acros Organics, purity > 95%) which contains 300 wt ppm sulfur, or 0.58 wt% DBT (Kanto Chemical Co., Inc., purity > 98%) which con-

Scheme 1 Reaction Scheme for HDS Reaction of DBT (from ref. 10)

tains 1000 wt ppm sulfur, in a decaline solution. The amount of the sulfur compounds referred to here is that measured in the inlet of the second-stage reactor in our two stage process incorporating gas/liquid separation. The effect of H_2S on the catalyst performance was tested by addition of 0.05 wt% of a hydrogen sulfide-generating compound (dimethyldisulfide, DMDS, Kanto Chemical Co., Inc., purity > 99%, sulfur amount corresponding to 10,000 wt ppm of H_2S). To explore the effect of NH_3 on the catalyst activity in the HDS of 4,6-DMDBT and DBT, 0.13 wt% of a NH_3 -generating compound (tri-*n*-butyl amine, TBA, Kanto Chemical Co., Inc., purity > 99%, sulfur amount corresponding to 300 wt ppm of NH_3) was added to the reactant mixture. The mixed catalysts (Co(2.75)Mo(11)/Ni(2.75)Mo(11)/ and Ni(0.9)Co(1.85)Mo(11)/ $\gamma-Al_2O_3$, amount in parentheses after a metal is wt%—hereafter the same) were pre-sulfided *in-situ* with a decaline solution of 2 wt% DMDS at 5.0 MPa and 573 K for 8 h.

The catalysts were tested at 563–603 K at a total pressure of 5.0 MPa, weight hourly space velocity of 30 h^{-1} , under $6\text{ l} \cdot \text{h}^{-1}$ hydrogen flow for 4,6-DMDBT reactions.

For the reactions of DBT, the catalysts were tested at 583–623 K at a total pressure of 5.0 MPa, weight hourly space velocity of 60 h^{-1} under $6\text{ l} \cdot \text{h}^{-1}$ hydrogen flow.

2.3. Catalyst Activity and Reaction Pathways

The reaction products were quantitatively analyzed by gas chromatography with a Shimadzu GC-17A equipped with a 60 m WCOT fused silica capillary column, a CP-Sil 8 CB column (VARIAN, 0.25 mm i.d., 0.25 μm film thickness), and a flame ionization detector (FID) and also identified by GC-MS (Shimadzu 17A/QP-5000) and GC-SCD (Sulfur chemiluminescent detector, ANTEK7090 with FID-GC, Shimadzu GC2010). On the other hand, the result of sulfur stripping of the product oil was checked by XRF (X-ray fluorescence ZSX101e, RIKEN) to correct the FID results.

All the HDS activities are characterized by their first order reaction rate (k_{HDS}) for DBT or 4,6-DMDBT.

The HDS of DBT proceeds through two different parallel pathways¹⁰⁾ (Scheme 1): the so-called direct desulfurization pathway (DDS), where a direct C–S bond cleavage of the DBT molecule leads to production

of biphenyl (BP), or the hydrogenation pathway (HYD), which yields cyclohexylbenzene (CHB) by an initial hydrogenation of one of the aromatic rings of the DBT followed by C–S bond cleavage.

The HYD and the DDS selectivity are based on the product concentration ratio ((CHB)/(BP + CHB)) and (BP/(BP + CHB)), respectively. The HDS of 4,6-DMDBT proceeds through similar pathways (Scheme 2)¹¹. In the 4,6-DMDBT case, the DDS pathway leads to production of 3,3'-biphenyl (BPs) and the HYD pathway leads to 3,3'-dimethylcyclohexylbenzene (CHBs) and 3,3'-dimethylbicyclohexyl (BCHs).

In this case, the HYD and the DDS selectivity are based on the product concentration ratio (CHBs + BCHs)/(BPs + CHBs + BCHs) and (BPs/(BPs + CHBs + BCHs)), respectively.

It should be noted that an intermediate primary hydrogenated product, like tetrahydrodibenzothiophenes (THDBTs), and an intermediate secondary hydrogenated product, like hexahydrodibenzothiophenes (HHDBTs), are formed along the HYD pathway. These concentrations are very low and are not detected in the most

cases, and therefore, they were omitted in the calculation of the conversion or selectivity.

We estimated the first order reaction rate constant for the conversion of DBT or 4,6-DMDBT (k_{HDS}) is the summation of the first order reaction rate constant for the DDS route (k_{D}) and the first order reaction rate constant for the HYD route (k_{H}), k_{D} and k_{H} being defined as follows,

$$k_{\text{D}} = (\text{HYD selectivity}) \times k_{\text{HDS}} \quad (1)$$

$$k_{\text{H}} = (\text{DDS selectivity}) \times k_{\text{HDS}} \quad (2)$$

$$k_{\text{HDS}} = k_{\text{D}} + k_{\text{H}} \quad (3)$$

3. Results

3.1. Model Feed Experiments with 4,6-DMDBT

The first order overall reaction rate constants of the different catalysts for the conversion of 4,6-DMDBT with and without additives are shown in Table 1A.

NiMo is by far the most active catalyst in the blank test. The ratio of the first order reaction rate constant of NiMo to that of the blank test at the same temperature strongly decreases. The first order reaction rates of other catalysts also decrease in the presence of H₂S. The apparent activation energy of CoMo catalysts is lower than the other catalysts (Table 2).

The presence of NH₃ significantly decreases the overall reaction rate constant for the conversion of 4,6-DMDBT for all tested catalysts to a greater extent than that for the blank test. Interestingly, the reaction rate constant of CoMo catalyst significantly decreases with addition of NH₃. The apparent activation energy of NiMo is lower than the other catalysts (Table 2).

3.2. Model Feed Experiments with DBT

The first order overall reaction rate constants of the different catalysts for the conversion of DBT with and without additives are shown in Table 1B.

The rate constant of NiCoMo catalyst in the blank

Scheme 2 Reaction Scheme for HDS Reaction of 4,6-DMDBT (from ref. 11)

Table 1A The First Order Rate Constants of the Conversion for 4,6-DMDBT

Temperature	Blank				Addition of H ₂ S (+H ₂ S)				Addition of NH ₃ (+NH ₃)			
	563 K	573 K	583 K	593 K	583 K	593 K	603 K	613 K	583 K	593 K	603 K	613 K
NiCoMo	19.1	23.0	32.4	46.1	16.6	31.8	53.8	76.4	14.7	25.1	40.1	79.2
NiMo	39.1	43.3	61.5	86.6	21.0	31.2	57.6	90.9	29.0	44.8	61.5	72.0
CoMo	17.5	22.6	30.4	43.9	20.6	31.3	41.2	56.3	6.6	8.4	18.1	40.9

Table 1B The First Order Rate Constants of the Conversion for DBT

Temperature	Blank				Addition of H ₂ S (+H ₂ S)				Addition of NH ₃ (+NH ₃)			
	583 K	593 K	603 K	613 K	593 K	603 K	613 K	623 K	593 K	603 K	613 K	623 K
NiCoMo	82.9	104.6	121.2	141.4	47.0	74.8	108.8	152.5	65.5	90.2	132.2	178.0
NiMo	66.7	87.2	104.8	125.2	25.9	40.7	59.2	78.4	73.0	98.8	139.6	152.3
CoMo	58.1	86.6	109.8	129.5	44.8	66.6	85.4	93.6	50.1	82.4	106.1	120.5

Table 2 Apparent Activation Energy for HDS of 4,6-DMDBT and DBT
[kcal·mol⁻¹]

Catalyst	4,6-DMDBT			DBT		
	NiMo	NiCoMo	CoMo	NiMo	NiCoMo	CoMo
Blank test	17.8	19.7	20.0	14.5	12.1	18.5
+H ₂ S	35.0	35.7	23.1	26.9	28.2	17.9
+NH ₃	21.4	38.3	43.7	18.5	24.4	21.0

k_H (black bar), the first order reaction rate constant for HYD route; k_D (white bar), the first order reaction rate constant for DDS route; $k_{HDS} = k_H + k_D$. A: NiMo, B: CoMo, C: NiCoMo.

Fig. 1 The First Order Reaction Rate Constant for the Conversion of 4,6-DMDBT

test is slightly higher than those of the other catalysts, the rate constants of the catalysts being the almost the same.

The presence of H₂S significantly decreases the overall reaction rate constant for the conversion of DBT for all tested catalysts to a greater extent than that for the blank test (Table 1B). NiCoMo is the most active catalyst for the conversion of DBT in the presence of H₂S. The apparent activation energy of CoMo is lower than those of the other catalysts (Table 2).

The presence of NH₃ significantly decreases the activity of CoMo; the rates of the NiMo and NiCoMo

catalyst are not decreased by NH₃ as much.

3. 3. Reaction Pathway

The first order reaction rate constants for the conversion of 4,6-DMDBT and DBT were calculated separately for the HYD route (k_H) and for the DDS route (k_D).

The rate constant divided into k_H and k_D components for each catalyst for the conversion of 4,6-DMDBT are shown in Figs. 1A-1C. The HYD route (k_H) is dominant in all the test results of 4,6-DMDBT.

The k_H and k_D of each catalyst for the conversion of DBT are shown in Figs. 2A-2C. The DDS route is

k_H (black bar), HYD activity; k_D (white bar), DDS activity; $k_{HDS} = k_H + k_D$. A: NiMo, B: CoMo, C: NiCoMo.

Fig. 2 The First Order Reaction Rate Constant for the Conversion of DBT

Fig. 3 The Average Inhibition Degree of the Activity for the Conversion of 4,6-DMDBT and DBT against Each Blank Test at the Same Temperature in the Presence of H_2S and NH_3

dominant in all the test results of DBT. The HYD selectivity of NiMo and NiCoMo catalysts is higher than that of CoMo.

We observed the differences resulting from different routes among the catalysts, and found that the degree of inhibition by H_2S and NH_3 are different according to the route. The reason for these differences will be discussed in the following section.

3. 4. Inhibition Effect of H_2S and NH_3

Each first order reaction rate constant is compared to the rate constant of the blank test at the same temperature. The average of the activity relative to the blank test is shown as relative activity in Fig. 3.

The ranking of the inhibition effect of H_2S on the conversion of 4,6-DMDBT is as follows,

CoMo < NiCoMo < NiMo

The ranking of the inhibition effect of NH_3 on the conversion of 4,6-DMDBT is as follows,

NiMo, NiCoMo << CoMo

The ranking of the inhibition effect of H_2S on the conversion of DBT is as follows,

CoMo, NiCoMo < NiMo

■ : NiMo, ■ : NiCoMo, □ : CoMo.

Fig. 4 The Average Inhibition Degree of k_H and k_D for the Conversion of 4,6-DMDBT against Each Blank Test at the Same Temperature in the Presence of H₂S and NH₃

■ : NiMo, ■ : NiCoMo, □ : CoMo.

Fig. 5 The Average Inhibition Degree of k_H and k_D for the Conversion of DBT against Each Blank Test at the Same Temperature in the Presence of H₂S and NH₃

The ranking of the inhibition effect of NH₃ on the conversion of DBT is as follows,

NiMo < NiCoMo < CoMo

4. Discussion

4.1. Inhibition Effect of H₂S and NH₃ on HYD and DDS Reaction Pathways

To identify the active site of each promoted catalyst, we estimated which route was poisoned by H₂S and NH₃ by comparing separately k_H and k_D activity of the blank test with the tests using H₂S- and NH₃-containing feeds.

Figure 4 shows the average inhibition degree of k_H and k_D for the conversion of 4,6-DMDBT, against each blank test at the same temperature in the presence of H₂S and in the presence of NH₃.

The inhibition of H₂S in the HYD route on NiMo catalyst is clearly shown. CoMo catalyst is weakly poisoned by H₂S. NiCoMo poisoning is moderate, between NiMo and CoMo.

On the other hand, direct desulfurization route of CoMo and NiCoMo are strongly poisoned by H₂S. This implies H₂S is adsorbed on the active site of DDS.

The inhibition effect of H₂S and NH₃ is more clearly shown in the conversion of 4,6-DMDBT than in the conversion of DBT. The sulfur atom in 4,6-DMDBT is difficult to remove because of the steric hindrance of the methyl groups¹². The reaction route for HDS of 4,6-DMDBT is usually HYD; therefore, this cause of the difference in inhibition has clearer effect than in the reaction route for HDS of DBT.

The inhibition effect of H₂S on each catalyst in the HDS of DBT is shown in Fig. 5.

The role of H₂S on hydrotreating sulfide catalysts

has been studied extensively in the literature^{2)~4)}. In general, by adsorption of H₂S, DDS active sites may be converted into HYD active sites, which can change the rate of elementary reaction steps¹³⁾. Texier *et al.*¹⁴⁾ reported that the addition of H₂S increases hydrodesulfurization activity. Reinhoudt *et al.*⁵⁾ also reported that the addition of DMDS, which means H₂S addition, increases CoMo catalyst activity of HDS for 4,6-alkylated DBT and DBT. In our study, we did not observe such an increase; however, the high tolerance to H₂S poisoning of NiCoMo and CoMo has the same mechanism as this increase in activity. The adsorption of H₂S on the CoMo catalyst surface may form a HYD active site.

Raybaud *et al.*¹⁵⁾ reported the most stable Co-promoted MoS₂ (10 $\bar{1}$ 0) surfaces, found using *ab initio* quantum chemical calculation. The study shows that Co atoms are apt to be substituted for Mo atoms on the MoS₂ (10 $\bar{1}$ 0) edge and the most stable surface is not covered at all by sulfur and presents only four-fold coordinated Co atoms. There are many coordinatively unsaturated (CUS) sites where a sulfur atom can adsorb are located on the most stable Co-promoted MoS₂ surface.

Travert *et al.*¹⁶⁾ also reported the most stable CoMo and NiMo catalyst surfaces under actual working conditions, calculating the adsorption energy of hydrogen using the same calculation program as Raybaud *et al.*¹⁵⁾ and considering the thermodynamic equilibrium of these surfaces with H₂S and H₂ in the gas phase. The results show that hydrogen is easily dissociated on CoMo catalyst surfaces of the Co-S-Co bridge site which is one of the most stable Co-promoted MoS₂ surfaces under actual working conditions, while hydrogen breaks Ni-S bonds on the NiMo catalyst surface edge of the S-Ni-S

Table 3 Comparison of k_H and k_D for the Conversion of 4,6-DMDBT or DBT between the Proportional Distribution and the NiCoMo Catalyst (k_H ; $\text{h}^{-1} \cdot \text{g}^{-1}$, k_D ; $\text{h}^{-1} \cdot \text{g}^{-1}$)

Feed	Reaction temperature [K]	CoMo		NiMo		NiCoMo		Proportional distribution ^{a)}	
		k_H	k_D	k_H	k_D	k_H	k_D	k_H	k_D
Blank test	583	8	51	26	41	17	66	14	47
	593	13	74	36	52	22	83	20	66
	603	12	97	35	70	30	91	20	88
+H ₂ S	593	9	36	12	14	12	35	10	29
	603	13	54	18	23	19	55	14	43
	613	17	69	25	34	21	88	20	57
+NH ₃	593	7	44	16	57	9	56	10	48
	603	12	71	27	71	15	75	17	71
	613	16	90	47	93	28	110	26	91

a) The proportional distribution of 66%CoMo and 33%NiMo.

Mesh: Higher k_H and k_D values between CoMo and NiMo.

bridge structure.

The CUS site is a DDS active site, and after the adsorption of S atom on the CUS site, a Co-S-Co bridge structure is formed on the Co-promoted MoS₂ (1010) surface. This Co-S-Co bridge structure activates hydrogen¹⁶⁾ and likely influences the HYD active site.

The inhibition effect of NH₃ is shown in **Figs. 4** and **5**. NH₃ poisoned strongly both the HYD and DDS active site on CoMo catalyst in the case both of DBT and 4,6-DMDBT. In the case of 4,6-DBT poisoned with NH₃, NiCoMo catalyst behaves like NiMo catalyst. In the case of DBT poisoned with NH₃, NiMo catalyst shows a high tolerance for NH₃. Especially, k_D of NiMo catalyst exhibits almost the same activity as the blank test in the case of DBT poisoned with NH₃.

4.2. The Activity of NiMo Catalyst

NiMo catalyst causes the highest level of HDS conversion of 4,6-DMDBT blank test. Among our experimental conditions, this is the case where H₂S concentration is the lowest. An ideal gas/liquid separation system with high HDS-promoting catalyst in the first-stage reactor realizes such a lean H₂S condition. Hensen *et al.*¹⁷⁾ also reported high activity of NiMo catalyst under lean H₂S conditions.

The NiMo catalyst has a high tolerance for NH₃. **Figure 5** shows that the HYD active site on NiMo catalyst is poisoned by NH₃ as are the other catalysts; however, the DDS active site on NiMo catalyst is not poisoned at all. This phenomenon suggests that the DDS active site on NiMo catalyst has a high tolerance for NH₃.

4.3. The Activity of CoMo Catalyst

The CoMo catalyst is not as active as the other two catalysts except under H₂S rich conditions. However, H₂S rich conditions are the most typical actual conditions for HDS of straight-run gas oil, and therefore CoMo catalyst is commonly used for actual HDS of

straight-run gas oil. The activity of CoMo catalyst is strongly poisoned by NH₃. Reinhoudt *et al.*⁵⁾ also reported the poisoning effect of carbazole on CoMo catalyst in the case of 4,6-alkylated DBT. If the feed contains a lot of nitrogen compounds, CoMo catalyst is not suitable for HDS.

4.4. The Activity of NiCoMo Catalyst

NiCoMo catalyst is the best catalyst for DBT conversion in all cases. After calculating HYD and DDS activity, we found an interesting result in the summation of k_H and k_D .

NiCoMo catalyst comprises Ni, Co and Mo impregnated in the same support. On this surface, there are two active sites located together. Examining the inhibition effect of H₂S and NH₃, we found that the nature of NiMo catalyst and of CoMo catalyst are quite different from each other. CoMo catalyst has a high tolerance for H₂S and NiMo catalyst has a high tolerance for NH₃. If there are two different active sites on NiCoMo catalyst, and k_H and k_D are different for NiMo and CoMo, the NiCoMo HDS activity should be the summation of higher values of k_H and k_D .

We list the higher of the values of k_H and k_D for NiMo and for CoMo, and compare the calculated values of NiCoMo catalyst in **Table 3**.

Although there are some variations at higher temperatures, the activity of NiCoMo catalyst is the summation of the higher values of k_H and k_D for NiMo and for CoMo in the presence of rich H₂S and NH₃ conditions.

The CoMo catalyst has a higher k_D value than the NiMo catalyst while the NiMo catalyst has a higher value of k_H . NiCoMo catalyst activity is a summation of k_D of CoMo and k_H of NiMo; therefore the total HDS activity is higher than either or CoMo. It is known that catalytic reactions proceed through the lowest barrier. NiCoMo catalyst has two kinds of active sites, and the reaction pathway proceeds through the active site with the lower barrier. Thus, NiCoMo catalyst

activity is the sum of the higher values of k_H and k_D for CoMo and for NiMo.

The variation of k_H among catalysts in the presence of NH_3 is larger than in the presence of H_2S . As shown in **Table 3**, the HYD route of all catalysts is poisoned by NH_3 . If we find the proportion of CoMo and NiMo and incorporate this in calculations, the estimated HYD activity of NiCoMo is much more accurate. This implies that the HYD active sites are poisoned by NH_3 .

If the NiCoMo catalyst is just a mixture of NiMo and CoMo catalyst, the activity should be the proportional distribution of NiMo and CoMo activity. The NiCoMo catalyst comprising 1.9 wt% Co and 0.85 wt% Ni is loaded on an Al_2O_3 support. Co and Ni atoms are intended to substitute for atoms at the MoS_2 edge surface¹⁵⁾, and for this reason the NiCoMo catalyst surface is 1/3 NiMo and 2/3 CoMo.

We compared the k_H and k_D calculated based on the proportion of NiMo and CoMo catalyst with the actual k_H and k_D of NiCoMo catalyst. **Table 3** also shows a comparison between k_H and k_D for the conversion of 4,6-DMDBT or DBT computed from the proportional distribution and those of the actual NiCoMo catalyst. The k_H and k_D value of NiCoMo catalyst is higher than those calculated from the proportional distribution between NiMo and CoMo except in the case of the blank test of HDS for 4,6-DMDBT. The blank test for the conversion of 4,6-DMDBT (300 wt ppm as S atoms) generates very low H_2S concentration. The other cases generate conditions rich in H_2S or NH_3 , and therefore NiCoMo catalyst shows higher activity than the proportional distribution would indicate. These results imply the NiCoMo catalyst causes high activity of both HYD and DDS in the presence of rich H_2S or NH_3 conditions.

Finally, we determined the best combination for the two-stage process with gas/liquid separation as follows. NiCoMo catalyst is the best catalyst for the first-stage reactor because NiCoMo has the high tolerance for both H_2S and NH_3 . NiMo catalyst is the best catalyst for the second-stage reactor because NiMo has high HDS activity under lean H_2S conditions.

5. Conclusion

It was demonstrated that the presence of H_2S and NH_3 has a large effect on the catalyst ranking and relative importance of reaction pathways, *i.e.* the activity of HYD route (k_H) and the activity of DDS route (k_D), of various catalysts for the conversion of both DBT and 4,6-DMDBT.

In the presence of H_2S , NiCoMo catalyst is the best catalyst for the conversion of DBT. We examined the HYD and DDS activity of NiCoMo, and found that the NiCoMo catalyst activity is the sum of the higher of the

HYD values for NiMo and CoMo, and the higher of the DDS values for NiMo and CoMo. This implies the dual promoting effect of Ni and Co on NiCoMo catalyst.

The best combination of catalysts in the first-stage and second-stage reactor for the two-stage process with gas/liquid separation is considered to be as follows.

In the first-stage reactor, NiCoMo catalyst is the best catalyst because of the high tolerance for both H_2S and NH_3 . In the second-stage reactor, NiMo catalyst is the best catalyst because of the high HDS activity under lean H_2S conditions. Among industrial hydrotreating catalysts, a NiW catalyst would be an alternative for a NiMo catalyst because NiW catalyst is well known its high hydrogenation activity in lean H_2S conditions.

Acknowledgment

The research of the two-stage process with gas/liquid separation was entrusted by the New Energy and Industrial Technology Development Organization (NEDO) under a subsidy of the Ministry of Economy, Trade and Industry and this research was partially commissioned by NEDO.

References

- 1) Houalla, M., Broderick, D., Sapre, A. V., Nag, N. K., de Beer, V. J. H., Gates, B. C., Kwart, H., *J. Catal.*, **61**, 523 (1980).
- 2) Kabe, T., Ishihara, A., Tajima, H., *Ind. Eng. Chem. Res.*, **31**, 1577 (1992).
- 3) Isoda, T., Ma, X., Mochida, I., *Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.)*, **37**, (5), 506 (1994).
- 4) Zhang, Q., Qian, W., Ishihara, A., Kabe, T., *Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.)*, **40**, (3), 185 (1997).
- 5) Reinhoudt, H. R., van Gorsel, M., van Langeveld, A. D., van Veen, J. A. R., Sie, S. T., Moulijn, J. A., *Stud. Surf. Sci. and Catal.*, **127**, 211 (1999).
- 6) LaVopa, V., Satterfield, C. N., *J. Catal.*, **110**, 375 (1988).
- 7) Koide, R., Goto, Y., Kawabata, M., Ishida, K., *Prep. Petrol. Chem. Div., Am. Chem. Soc.*, **46**, 398 (2001).
- 8) Amemiya, M., Minatoya, M., Koide, R., Goto, Y., Kawabata, M., Ishida, K., Segawa, H., *Prepr. Div. Fuel Chem., Am. Chem. Soc.*, **47**, 461 (2002).
- 9) Nakamura, H., JP3545943.
- 10) Houalla, M., Broderick, D., de Beer, V. H. J., Gates, B. C., Kwart, H., *Prepr. Div. Petrol. Chem., Am. Chem. Soc.*, **22**, 941 (1977).
- 11) Isoda, T., Ma, X., Mochida, I., *Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.)*, **37**, (4), 368 (1994).
- 12) Isoda, T., Takase, Y., Isumi, N., Kusakabe, K., Morooka, S., *Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.)*, **41**, (5), 318 (1998).
- 13) Yang, S. H., Satterfield, C. N., *J. Catal.*, **81**, 168 (1993).
- 14) Texier, S., Berhault, G., Pérot, G., Harlé, V., Diehl, F., *J. Catal.*, **223**, 404 (2004).
- 15) Raybaud, P., Hafner, J., Kresse, G., Toulhoat, H., *J. Catal.*, **190**, 128 (2000).
- 16) Travert, A., Nakamura, H., van Santen, R. A., Cristol, S., Paul, J.-F., Payen, E., *J. Am. Chem. Soc.*, **124**, 7084 (2002).
- 17) Hensen, E. J. M., de Beer, V. H. J., van Veen, J. A. R., van Santen, R. A., *J. Catal.*, **215**, 353 (2003).

要 旨

ジベンゾチオフエンおよび4,6-ジメチルジベンゾチオフエンの脱硫反応におけるNiMo/Al₂O₃, CoMo/Al₂O₃, NiCoMo/Al₂O₃触媒への硫化水素とアンモニアの阻害効果

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出発原料, 担体, 担持方法の影響の少ないモデル触媒 (Co_{2.75}Mo₁₁, Ni_{2.75}Mo₁₁ および Ni_{0.9}Co_{1.85}Mo₁₁ wt %/ γ -Al₂O₃) を調製して, 4,6-ジメチルジベンゾチオフエンとジベンゾチオフエンの脱硫反応における H₂S, NH₃ の影響を検討した。脱硫反応で考えられている水素化脱硫および直接脱硫ルートごとの性能を NiMo, CoMo, NiCoMo 触媒で比較した。その結果, CoMo 触媒と NiCoMo 触媒は H₂S に対する被毒の影響が少なかったのに対して, H₂S は NiMo 触媒の両反応ルートの活性を大きく低下させた。一方, CoMo 触媒の水素化脱硫ルートが

NH₃ により強く被毒されるが, NiMo 触媒の直接脱硫ルートは NH₃ に被毒されないことを明らかにした。また, NiCoMo 触媒に関しては, NiMo と CoMo の担持比率から計算される水素化および直接脱硫ルートの反応速度定数の比例配分値より高い性能を示し, その値は NiMo 触媒, CoMo 触媒の各反応ルートのより高い値の和に近い値を示すことが分かり, 被毒物質のある雰囲気では NiMo 単独あるいは CoMo 単独より高い活性を示すことを明らかにした。

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