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Facile ultra-deep desulfurization of gas oil through two-stage or -layer catalyst bed

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Abstract

Ultra-deep hydrodesulfurization (HDS) was attempted to achieve the sulfur level less than 15 ppm S by staged and layered catalyst beds over commercially available catalysts. It was confirmed that two-stage and two-layer reaction schemes can attain the targeted sulfur level. Two-stage reaction with hydrogen refreshment between stages could provide the sulfur content lower than 15 ppm S over most of the catalysts examined in the present study where the first stage desulfurized the feed oil to be of 300–400 ppm S. Two-layer reaction, where two layers were connected directly without gas renewal, suffered severe inhibition of H_2S and NH_3. Nevertheless, NiMo sulfides on alumina support with sufficient acidity or zeolite achieved the sulfur level lower than 15 ppm S by two-layer scheme. Nitrogen species survived in the first layer reaction were found to strongly affect the extent of desulfurization in the subsequent second layer reaction.

Keywords: Hydrodesulfurization; Catalyst; Gas oil; Multiple bed

1. Introduction

Stricter regulation on the sulfur content in diesel fuel will be implemented with the increasing concerns on the public health. Sulfur species in diesel arise several kinds of environmental problems. First of all, SO_x emitted from the oxidation of sulfur species is a cause of acid rain. Furthermore, oxidized sulfur species are poisons for de-NO_x catalyst and diesel particulate filter (DPF), resulting in the increase of NO_x and particulate matter. It requires novel strategy in catalyst and process designing to remove the sulfur species in the gas oil to be less than 15 ppm of sulfur content. Refractory species in gas oil, such as 4,6-dimethyldibenzothiophene, has been reported to survive after the conventional desulfurization, focusing the difficulty to achieve the required regulation [1]. There are two main obstacles to achieve the target, structural inertness of the refractory sulfur species and their susceptibility to inhibitions by several kinds of compounds [2].

The present authors proposed the staged reaction scheme to achieve the deep hydrodesulfurization (HDS) [2,3]. Reactive sulfur species, most abundant sulfur species in gas oil, are hydrodesulfurized in the first stage with the production of large amount of H_2S and NH_3, which have been recognized as notorious inhibitors for HDS [2,4,5]. Both H_2S and NH_3 can be removed or diluted with fresh H_2 between the first and second stages with an aim to accelerate the activity

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for deep HDS in the second stage. Hence, the refractory sulfur species can be hydrodesulfurized without the intervention by inhibitors. Such a scheme has been verified to be very effective to lower the sulfur content down to a few tens of ppm over very conventional catalysts in the laboratory scale batch reactor [2,3]. Recently, it was reported that the two-stage process could provide the sulfur free ($S < 10$ ppm S) diesel oil in the flow type reaction system equipped with the gas stripper between the stages to refresh the gas phase fed into the second stage [6]. Although the two-stage reaction scheme is a very reasonable approach to achieve the ultra-clean diesel fuel, there must be significant cost increase in installing one more reactor and the gas stripper between the stages and necessity of more hydrogen volume.

Two catalyst beds are directly connected in the two-layer reaction scheme, where the best catalysts are installed in the respective layers. The feed oil of the second layer must carry H_2S and NH_3 produced in the first layer but much less content of sulfur and nitrogen species. Thus, the second layer catalyst is focused to desulfurize effectively the small amount of the refractory sulfur species which are left with some inhibitors in the desulfurized gas oil in the first layer.

Novel HDS catalysts with higher activity have been practiced to follow the stepwisely tightened regulation by dispersing sulfide active species well on the better supports [7,8]. The acidity has been recognized to be important for high HDS activity [4,9]. Some catalysts were suggested to have higher activity to hydrodesulfurize the refractory sulfur species and resistivity to the inhibitors [10,11].

The objectives of this study are thus to find the best catalysts for the first and second layers. The catalyst of the first layer is required to remove all reactive sulfur species and refractory sulfur species as much as possible. The catalyst of the second layer must remove refractory sulfur species of the very low concentration to less than 15 ppm in the presence of inhibitors produced and surviving in the first layer. The optimum catalysts for the second layer must be different from the best one for the first layer in terms of surface area, pore size, and acidity of the supports. Hence, the present study is attempted to confirm the significance of two-layer catalyst bed with the best catalysts for each layer. The products of each layer were identified at molecular levels by GC-AED.

2. Experimental

HDS was conducted by using an autoclave type reactor (100 ml internal volume). The amount of gas oil, catalyst, and hydrogen gas charged into the reactor were 10 g, 1 g and 50 kg/cm^2, respectively. Reactor pressure increased to about 70 kg/cm^2 at reaction temperature. Straight run gas oil (SRGO) (11,780 ppm S) and two commercially available hydrodesulfurized gas oils (HSRGO) (340 ppm S) and DSGO (350 ppm S) were used as the feed for the first and second stage/layer reactions, respectively. HSRGO was treated with active carbon to remove nitrogen species. Such oils are defined as DN-HSRGO (326 ppm S).

To simulate the second layer reaction, 1.66 vol.% H_2S containing H_2 was used as gas feed and diethyl amine was added to the feed oil to produce 200 ppm NH_3 in the reactor. The reaction scheme used in this study is depicted in Fig. 1. All reactants and products were analyzed by GC-AED, which provided carbon-, sulfur-, and nitrogen-specific chromatograms [12]. AED utilizes very confined plasma to breakdown the effluents from GC down to elemental state, which emits its particular atomic emission light. Spectrometer equipped in AED analyzes the emission spectrum and monitors the emission line

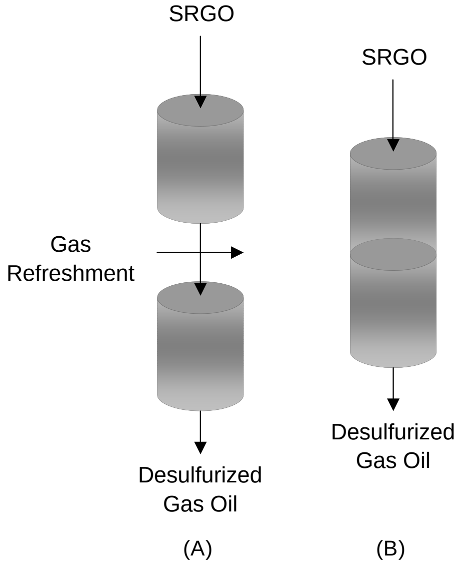

Fig. 1. Schematic diagrams of reaction schemes examined in the present study: (A) two-stage scheme and (B) two-layer scheme.

Table 1
Properties of catalysts and their catalytic activity

Name	Support type	Surface area (m^2/g)	Average pore size, 4*V*/*S* (Å)[a]	Amount of adsorbed NH_3 (mmol/g)[b]
CoMo-A	Alumina	217	75	0.48
NiMo-A		193	61	0.62
CoMo-SA	Silica–alumina	234	70	0.49
NiMo-SA		228	67	0.56
CoMo-AZ	Alumina–zeolite	264	51	0.81
NiMo-AZ		234	52	0.66

[a] *V*: total pore volume; *S*: surface area.

[b] Amount of NH_3 desorbed from room temperature to 620 °C.

of particular wavelength ascribed to each elements, such as sulfur (181 nm), carbon (179 nm) and nitrogen (388 nm). Identification of each peak on sulfur- and nitrogen-specific chromatograms was done by comparing the chromatograms with those reported [12]. Each peak on sulfur- and nitrogen-specific chromatograms were integrated to calculate its content by using calibration factor, which was obtained from standard sample. Total sulfur and nitrogen content were quantified by integrating whole chromatograms. The detection limits of GC-AED for sulfur and nitrogen analyses were estimated to ca. 10 ppb S and N.

The catalysts used in this study were CoMo and NiMo supported on alumina (A), silica–alumina (SA) and alumina–zeolite composite (AZ), all of which were provided by commercial catalyst suppliers. Their specific surface area, average pore size, and acidity are summarized in Table 1 which were measured by conventional N_2 physisorption method and NH_3 TPD, respectively.

3. Result

3.1. Catalyst characterization

The catalysts used in this study carried various surface area, pore size and acidity as shown in Table 1. Silica–alumina supported catalysts had larger surface area than alumina supported ones while alumina–zeolite supported catalysts showed the largest surface area and smallest pore size among the catalysts. NH_3 desorption started at ca. 100 °C to show its maximum peak at ca. 200 °C over all catalysts as shown in Fig. 2. The amount of desorbed NH_3 from each catalyst was estimated from the NH_3 TPD spectrum from room temperature to 620 °C and summarized in Table 1. Alumina–zeolite supported catalysts showed more desorption at 300–500 °C than the other catalysts, showing their stronger acidity than the other catalysts.

3.2. Feed oils characterization

Fig. 3 shows sulfur- and nitrogen-specific chromatograms of feed oils, SRGO and HSRGO. Sulfur species present in SRGO ranged from benzothiophenes (BTs) to alkylated dibenzothiophenes (DBTs). In contrast, HSRGO contained only alkylated DBTs. Sulfur species having shorter retention time than 4-MDBT was not found in HSRGO. It must be noted that almost all reactive sulfur species and 88% of refractory sulfur species had been removed from SRGO through commercial HDS process. Nitrogen species in SRGO (155 ppm N) and HSRGO (30 ppm N) were analyzed as mainly carbazoles as shown in Fig. 3. 1,4,8-trimethylcarbazole, 3,4,6-trimethylcarbazole and some trialkyl-carbazoles were found in HSRGO, indicating their inertness in hydrodenitrogenation (HDN) reaction.

3.3. Activities of the catalysts

Table 2 summarizes total sulfur contents left in the desulfurized products from SRGO (first stage or layer HDS), HSRGO in the absence of H_2S and NH_3 (second stage reaction), and with both NH_3 and H_2S (second layer reaction).

As for the HDS of SRGO, NiMo-AZ showed the highest activity (242 ppm S) among six catalysts, and the remaining sulfur content in the product was less

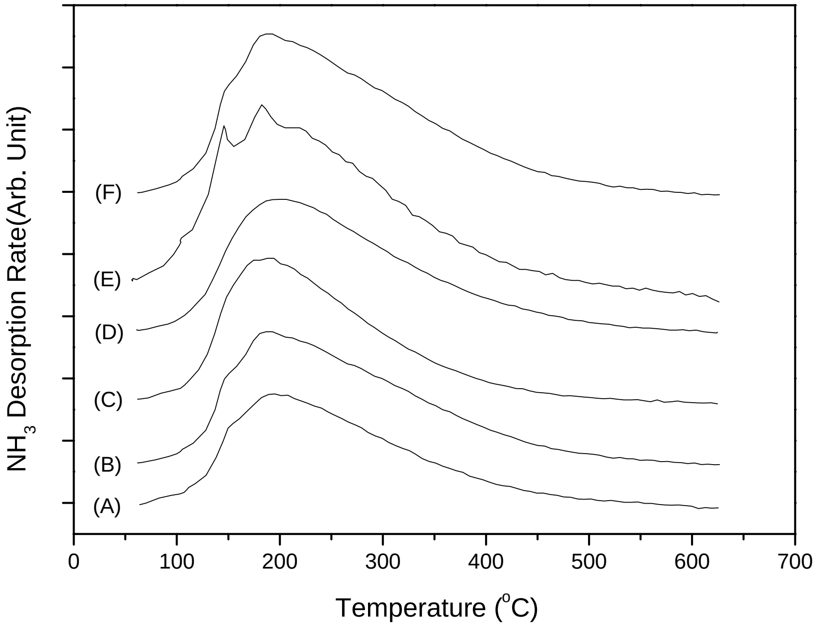

Fig. 2. NH_3 TPD spectra of (A) CoMo-A, (B) NiMo-A, (C) CoMo-SA, (D) NiMo-SA, (E) CoMo-AZ, and (F) NiMo-AZ.

than 300 ppm S. Zeolite containing catalysts showed always higher activity than SA- and A-series catalysts for HDS of SRGO. Fig. 4 shows the sulfur-specific chromatograms of HDS product from SRGO over the catalysts. Reactive sulfur species, such as BTs and DBT, could not be found in the HDS products of less than 500 ppm S (Fig. 4(E)–(G)). In contrast, the large amount of DBT and BTs remained after 1 h reaction over a catalyst of low activity such as NiMo-A catalyst which allowed 2229 ppm S left in the product. The refractory sulfur species such as 4-MDBT and 4,6-DMDBT and 4,6-alkylated DBT survived more or less the first layer HDS over all catalysts. NiMo-SA, CoMo-AZ and NiMo-AZ removed almost of all reactive sulfur species and about 83, 88 and 91% of refractory sulfur species, respectively, to achieve sulfur level of less than 500 ppm S.

Activities of all catalysts except for NiMo-A in HDN were proportional to those for HDS as indicated in Table 2. NiMo-A showed much better HDN activity than HDS activity. NiMo-AZ provided the lowest nitrogen content in the desulfurized product to be 5.4 ppm N. The reactivities of nitrogen species depended on the position of methyl substituents on carbazole (Cz). 1-MethylCz, 1,8-dimethylCz, 1,4,8-trimethylCz, 2,3-dimethylCz and 1,4,5-trimethylCz

Table 2
Remaining sulfur and nitrogen content (ppm S, ppm N) over catalysts after 1 h reaction at 340 °C[a]

Name	SRGO (ppm S)	SRGO (ppm N)	HSRGO in the absence of H_2S and NH_3 (ppm S)	HSRGO in the presence of H_2S and NH_3 (ppm S)
CoMo-A	1118 (56.3%)	81.0	22.5 (6.7%)	36.7 (4.6%)
NiMo-A	2229 (53.4%)	12.2	2.1 (0.62%)	5.9 (0.6%)
CoMo-SA	576 (47.7%)	41.6	7.1 (3.9%)	36.4 (12.4%)
NiMo-SA	477 (36.9%)	19.6	4.4 (0.1%)	32.7 (8.4%)
CoMo-AZ	323 (20.3%)	17.1	5.3 (3.5%)	17.8 (5.3%)
NiMo-AZ	242 (16.4%)	5.4	3.6 (4.3%)	15.5 (1.2%)

[a] % value in parenthesis is the remaining content of 4,6-DMDBT.

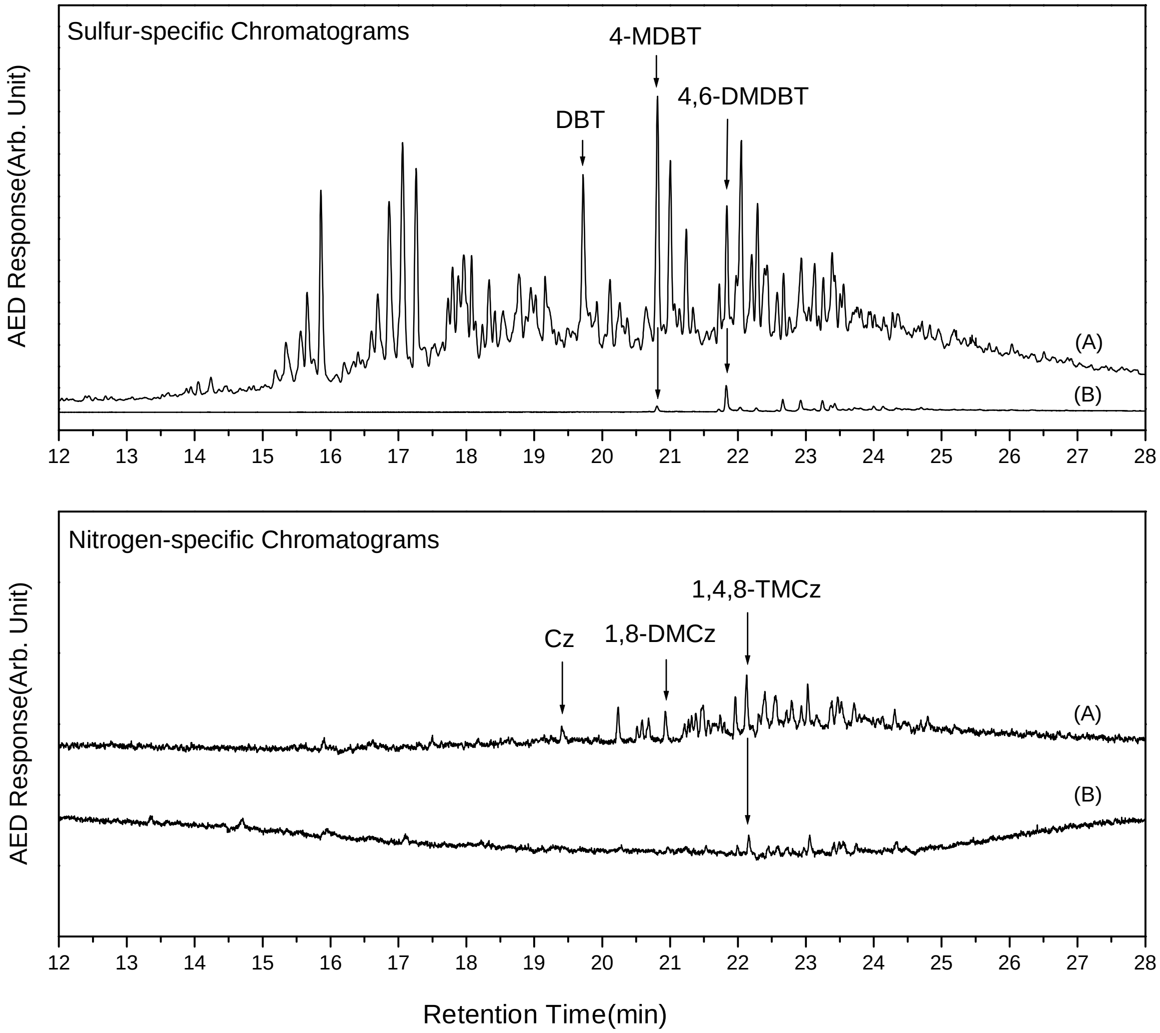

Fig. 3. Sulfur- and nitrogen-specific chromatograms of (A) SRGO and (B) HSRGO. Some of sulfur and nitrogen species are indicated at their position on chromatograms.

were found in hydrodenitrogenated products over CoMo-A (81.0 ppm N) and CoMo-SA (41.6 ppm N). The hydrodenitrogenated products of very low nitrogen content showed the dominant presence of 1,4,8-trimethylCz.

Results on the HDS of HSRGO without H_2S and NH_3 over NiMo or CoMo catalysts are summarized also in Table 2. HDS of HSRGO alone can simulate the second stage HDS after separation of gas-phase inhibitors such as H_2S and NH_3. All of the catalysts, except for CoMo-A, achieved sulfur level less than 10 ppm S. It must be noted that NiMo-A, the least active catalyst in the HDS of SRGO, showed the highest activity in the HDS of HSRGO. The remaining sulfur species in the HDS product from HSRGO were found to be 4,6-DMDBT and 4,6,X-TMDBTs as in Fig. 5.

Fig. 6 shows sulfur-specific chromatograms of desulfurized HSRGO in the presence of both H_2S and NH_3. This reaction scheme simulates the second layer reaction. NiMo-A found very active for HDS of refractory sulfur species in the presence of H_2S and NH_3 to achieve less than 6 ppm S. In contrast, CoMo-A,

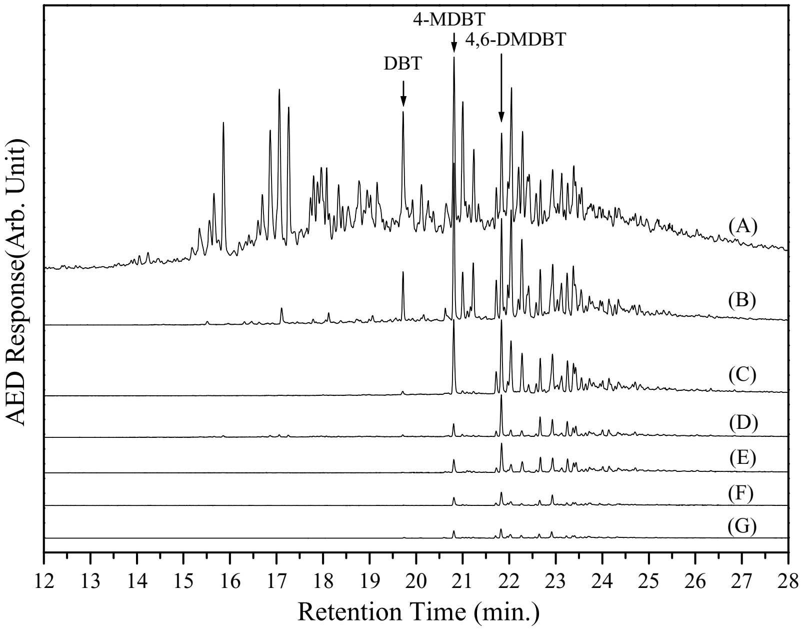

Fig. 4. Sulfur-specific chromatograms of (A) SRGO and desulfurized products of SRGO over (B) NiMo-A, (C) CoMo-A, (D) CoMo-SA, (E) NiMo-SA, (F) CoMo-AZ, and (G) NiMo-AZ. Some of sulfur are indicated at their position on chromatograms.

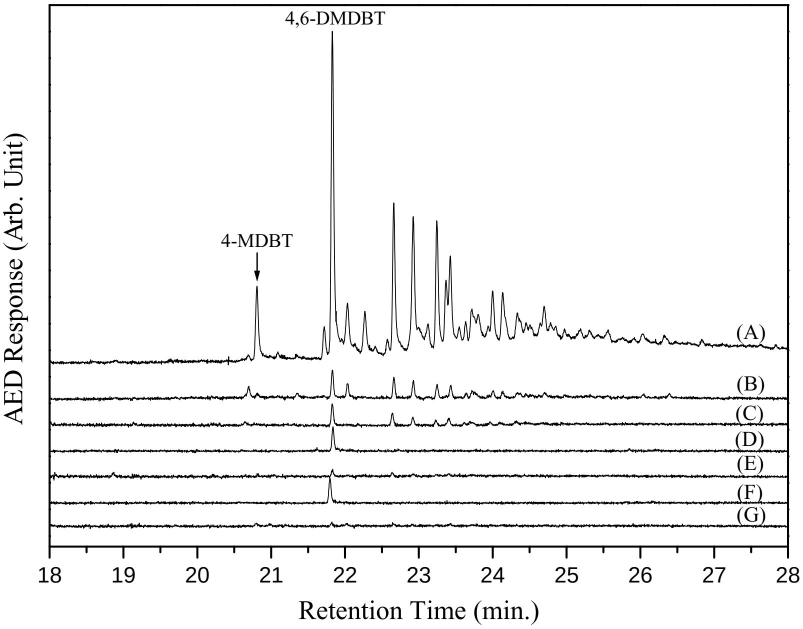

Fig. 5. Sulfur-specific chromatograms of (A) HSRGO and desulfurized products of HSRGO over (B) CoMo-A, (C) CoMo-SA, (D) CoMo-AZ, (E) NiMo-SA, (F) NiMo-AZ, and (G) NiMo-A. Some of sulfur are indicated at their position on chromatograms.

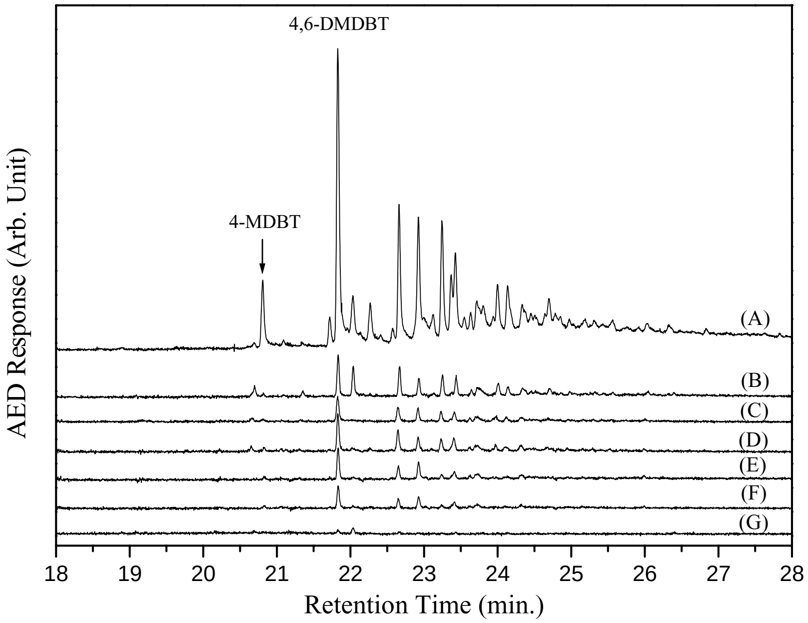

Fig. 6. Sulfur-specific chromatograms of (A) HSRGO and desulfurized products of HSRGO over (B) CoMo-A, (C) CoMo-SA, (D) CoMo-AZ, (E) NiMo-SA, (F) NiMo-AZ, and (G) NiMo-A in the presence of H_2S and NH_3. Some of sulfur are indicated at their position on chromatograms.

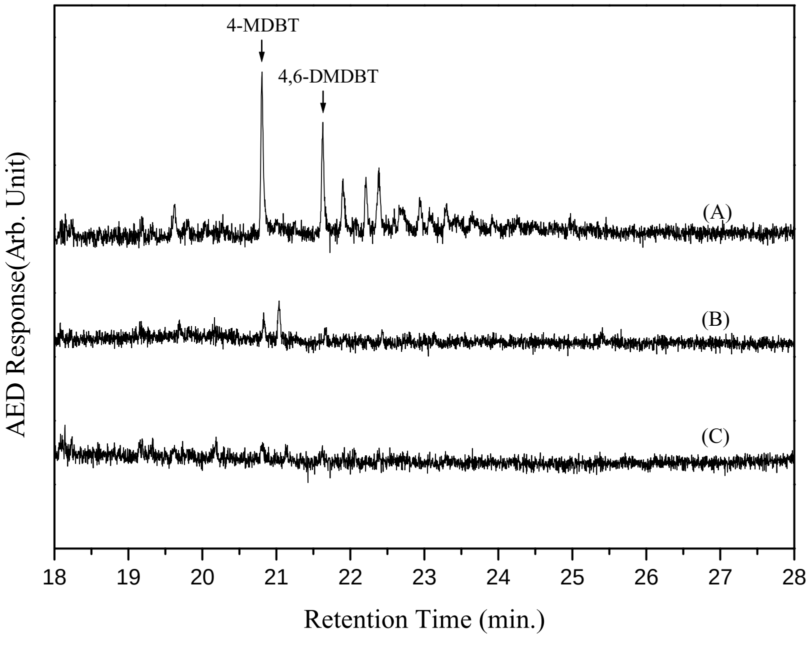

Fig. 7. Sulfur-specific chromatograms of desulfurized products of (A) DSGO (60 ppm N), (B) HSRGO (30 ppm N), and (C) adsorptive-treated HSRGO (2 ppm N) over NiMo-A catalyst in the presence of H_2S and NH_3. Some of sulfur are indicated at their position on chromatograms.

NiMo-SA and CoMo-SA were less active. Although NiMo-AZ and CoMo-AZ appeared much inhibited by the inhibitors, the former catalyst still achieved 15 ppm S. The sulfur species in the product were analyzed to be 4,6-DMDBT and 4,6,X-TMDBTs.

A series of desulfurized gas oil with various nitrogen content was further desulfurized over second layer catalyst. DSGO, HSRGO, and DN-HSRGO contained 57, 30 and 2 ppm N species, respectively. All of nitrogen species contained in the feed oils were found carbazoles. Their sulfur contents were 350, 340 and 326 ppm S, respectively, being much the same with each other. The HDS results of these GOs over NiMo-A catalyst in the presence of H_2S and NH_3 were very striking. As can be seen in Fig. 7, DN-HSRGO with 2 ppm N left only 1 ppm S (Fig. 7(C)) after the HDS over NiMo-A while feed oil with 60 ppm N left 15.9 ppm S (Fig. 7(A)) in the HDS product. The remaining sulfur contents in the three gas oils were certainly influenced by the nitrogen content in the feed oil. The strong inhibition of nitrogen species around 60 ppm N confirmed very definitely that the extent of HDN in the first stage is very influential on the very deep HDS at the second layer.

4. Discussion

The present study revealed that the two-stage and -layer catalyst beds, with the best HDS catalysts of respective stages or layers under respective conditions can be a logical approach to achieve deep HDS of gas oil at acceptable reaction temperature and space velocity.

The first stage or layer aims to desulfurize completely the reactive sulfur species and additionally refractory sulfur species as much as possible. Nitrogen species is also removed as much as possible because they inhibit the HDS of refractory sulfur species of 300–500 ppm S to lower than 15 ppm S. The catalysts examined in the present study exhibited their catalytic activities which depended on the types of their support and kinds of active sulfides. Alumina–zeolite mixed supports provided the highest catalytic activities in the first stage (layer) while silica–alumina did the next. The alumina-supported NiMo (NiMo-A) showed the lowest activity for the first stage HDS, being less active than CoMo on the same supports although NiMo was not always inferior to CoMo depending upon the supports. NiMoS supported on alumina–zeolite (NiMo-AZ) and silica–alumina (NiMo-SA) were more active in the first layer HDS than CoMo on the same supports as observed in the present study. The larger surface area and higher acidity appear to enhance the activity for the first stage and layer HDS.

The activity for the first stage must be examined in terms of HDS of the reactive and refractory sulfur species, respectively, except for NiMo-A. All reactive sulfur species are completely desulfurized over all catalysts of the present study except for NiMo-A. The extent of HDS of the refractory sulfur species are 30, 64, 82, 81, 91 and 88% over NiMo-A, CoMo-A, NiMo-SA, CoMo-SA, NiMo-AZ, and CoMo-AZ catalyst, respectively. Acidic nature of the support is certainly helpful for deeper desulfurization of refractory sulfur species in the first stage. NiMo-A failed to desulfurize all of the reactive sulfur species, leaving 339 ppm S of reactive sulfur species, while the catalyst removed the least extent of refractory species. Hence, the less activity of NiMo-A is due to lower activity for the reactive sulfur species and strong inhibition on the desulfurization of the refractory sulfur species. The smaller surface area of the support appears the most reasonable explanation for its lower activity for the reactive sulfur species.

It must be noted that the active catalysts except for alumina-supported ones examined in the present study, desulfurized all reactive species and over 80% of refractory sulfur species. This fact is very indicative for the difficulty in the deep desulfurization. The real task is how to reduce the 300–500 ppm S of refractory sulfur species left in the desulfurized gas oil to be less than 15 ppm. Inhibition of the further desulfurization must be intensified at this level of the sulfur concentration. The reactivities of themselves are certainly low but allows their significant desulfurization in the first stage where the inhibition of co-present species of the feed gas oil must be moderated at the higher concentration of refractory sulfur species by selecting the catalysts as well as the reaction conditions.

Nitrogen species which can be inhibitors in the second-layer catalyst bed were also eliminated in the first stage. The catalysts examined in the present study reduced the nitrogen level from 155 ppm N to less than 20 ppm N over NiMo-A, NiMo-SA, CoMo-AZ, and NiMo-AZ catalysts. The influences of remaining nitrogen species in the second stage or layer must be concerned to achieve deep desulfurization.

HSRGO alone was easily desulfurized to less than 7 ppm S over all the catalysts examined in the present study, except for CoMo-A (23 ppm S). The major sulfur species were desulfurized, some very refractory sulfur species such as 4,6-DMDBT and 4,6,*X*-TMDBT being left in the HDS product. Thus, the two-stage HDS which is equipped with hydrogen renewal or enrichment system to reduce the concentration of gaseous inhibitors, such as H_2S and NH_3, is very effective to achieve the ultra-deep desulfurization to less than 15 ppm S.

The catalytic activities of the present catalysts were in the order of NiMo-A(2.1) $>$ NiMo-AZ(3.6) $>$ NiMo-SA(4.4) $>$ CoMo-AZ(5.3) $>$ CoMo-SA(7.1) $>$ CoMo-A(22.5) as shown in the Table 2 (number in the paranthesis indicates the sulfur content of the HDS product over each catalyst). The very high activity of NiMo-A must be noted because it is not a good catalyst for the first stage. Its low activity against the reactive and refractory sulfur species due to the abundant inhibitors present in the feed gas oil must be counted. Except for NiMo-A, the activities of the present catalysts in each layer are proportional to each other.

H_2S, NH_3 and other gaseous products are sent to the second-layer catalyst bed where the bed is directly connected to the first layer catalyst bed. HDS of HSRGO in the presence of H_2S and NH_3 can simulate the HDS of the second-layer catalyst bed. Such species certainly inhibited the deep desulfurization, the extent of inhibition being dependent on the catalyst type. NiMo catalysts tended to suffer more inhibition than CoMo ones. Nevertheless, NiMo-A and NiMo-AZ achieved the sulfur level less than 15 ppm S, proving the effectiveness of the two-layer catalyst beds for the ultra-deep desulfurization. NiMo-A is the best catalyst for the second layer bed. Silica–alumina-supported catalysts suffered the largest inhibition of H_2S and NH_3, failing to achieve the ultra-deep desulfurization under the present condition.

The acidic supports have been observed to reduce the H_2S inhibition. Acidity of the catalyst support may enhance the desorption of H_2S from the active sulfide site through weakening metal–sulfur bond or spillover to the acidic site of the support [13]. Strong acidity is also effective to desulfurize the refractory sulfur species through enhancing the hydrogenation, isomerization or trans-alkylation of the neighboring phenyl rings of the refractory sulfur species [4,9]. However, it must be noted that the strong acidity tends to suffer the strong inhibition of NH_3 and nitrogen species. Nitrogen species, even neutral and acidic, appears to inhibit the desulfurization of the refractory sulfur species of low concentration at the second layer. Silica–alumina appears the case. CoMo is certainly resistive to the inhibition of H_2S and NH_3 as observed in the present study. Acidic property of catalyst should be more investigated. The role of Brønsted and Lewis acidic sites will be discussed in another paper about their contribution to deep HDS.

HSRGO selected as the model feed for the second-layer catalyst bed carried only 30 ppm nitrogen species which are basically carbazole and its methyl-substituted derivatives. The first stage HDS of SRGO eliminated concurrently nitrogen species to the levels of 80–5 ppm, depending on the HDN activity of the catalysts. HDS and HDN appear to progress concurrently but not always so. Their inhibition at their concentration in HSRGO is negligible to achieve the deep desulfurization at the second layer as shown in Fig. 6. The lower nitrogen content is left, deeper HDS is obtained. 60 ppm N of nitrogen species appears the highest level of allowed nitrogen species to achieve

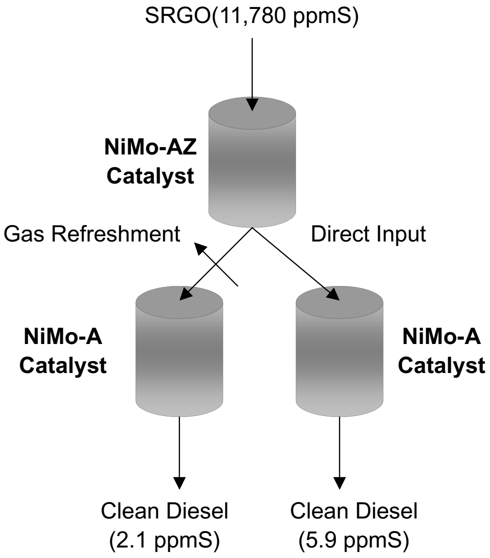

Fig. 8. Optimum combination of catalysts for two-stage (left) and two-layer (right) reaction schemes. Reaction temperature is 340 °C.

the sulfur content less than 15 ppm S. Hence, the denitrogenation extent must be concerned carefully when the catalyst for the first stage is evaluated.

Optimum combinations of catalysts for two-stage and -layer schemes were illustrated in Fig. 8.

5. Conclusion

The present study proved the effectiveness of two-stage and layer catalyst bed to achieve ultra-deep HDS lower than 15 ppm S by optimizing the catalysts for the respective stage or layer. The first stage for removal of all reactive sulfur species and 50% of refractory sulfur species, nitrogen species are reduced to lower than 20 ppm N. NiMo catalysts with high acidity and large surface area were proved to achieve the targeted level of desulfurization of the first stage.

The second stage with fresh hydrogen, excluding the gaseous inhibitors in the first stage, achieved the sulfur level lower than 15 ppm S with most of the catalysts examined in the present study. Difficulty for ultra-deep HDS is ascribed to the inhibited HDS of refractory sulfur species for less than 15 ppm S. Strong competition of the remaining refractory sulfur species is counted to be difficult for the ultra-deep desulfurization in the second-layer catalyst bed. Nevertheless, NiMoS supported on a particular alumina with sufficient acidity on zeolite were confirmed to achieve the sulfur level lower than 15 ppm S. In contrast, silica–alumina supports suffer very strong inhibition of H_2S and NH_3, failing to achieve the ultra-deep HDS.

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