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Development of a Cosmo deep HDS catalyst for diesel fuel

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Abstract

A new type of catalyst for deep hydrodesulfurization (HDS) has been developed. This catalyst was effective for removal of refractory sulfur compounds such as 4,6-dimethyldibenzothiophene. The addition of a small amount of zeolite which had well-controlled acidity has afforded a characteristic performance to deep HDS. We think that the zeolite added accelerates the hydrogenation rate of the dibenzothiophene ring. The developed catalyst has been manufactured on an industrial scale without any problems. The catalyst was loaded on an actual HDS unit as a demonstration run. The expected performance and stability have been obtained.

Keywords: Deep HDS catalyst; Diesel fuel; Desulfurization

1. Introduction

Sulfur control in diesel fuel is one of the most important problems for environmental protection as well as NO_x exhaust control. Sulfur content in diesel fuel has been restricted to 0.2 mass% or less in Japan since 1992. Besides, in 1997, this regulation will be tightened up to 0.05 mass% or less. But existing hydrodesulfurization (HDS) technology is not satisfactory to produce such very low sulfur diesel fuel without investment in new units. Development of a deep HDS catalyst is strongly needed.

It is well known that refractory sulfur compounds for HDS such as 4-methyldibenzothiophene(4-MDBT) or 4,6-dimethyldibenzothiophene (4,6-DMDBT) are contained in gas oil fractions [1,2]. They are hard to remove under normal HDS conditions, so it is difficult for a conventional HDS unit to achieve such deep HDS and to maintain its activity for a long time without any renewal.

The development of deep HDS catalyst for diesel fuel was started in 1990 at the Petroleum Energy Center (PEC) which is sponsored by MITI (Ministry of International Trade and Industry). Several petroleum companies and catalyst manufacturers have participated in this investigation project. The Cosmo Research Institute also joined it, and we have tried to remove those compounds by various methods. Finally we have succeeded in developing a new type of catalyst for deep HDS. Our catalyst has a special ability for effective removal of refractory sulfur compounds.

Some investigations have tried to clarify the

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reasons why the developed catalyst had a high activity for removal of refractory sulfur compounds.

2. Experimental

2.1. Feedstock

The feedstock used in the bench plant was obtained from a Middle East crude oil with a sulfur content of 1.38 mass%, density of 0.851 g/ml and a 50% distillation point of 574 K.

Model feedstocks were also used to analyze the reaction rate constants. Decalin was used as a solvent in each case, and each solution had a 0.29 mass% of DBT (dibenzothiophene, 0.05% as sulfur), 0.33 mass% of 4,6-DMDBT (0.05% as sulfur) or 0.05% of biphenyl (BP), respectively.

2.2. Reaction

The HDS reaction using actual gas oil was performed in a bench plant in the temperature range of 573–633 K at LHSV of 1.5–4.2 1/h. Total reaction pressure was kept at 2.9 MPa by using pure hydrogen. The catalyst was presulfided before use.

The model reaction was carried out under the following conditions: temperature 473 K, total pressure 2.9 MPa, LHSV 1.5–10 1/h.

2.3. Analysis

The quantity of total sulfur was analyzed by energy-dispersive X-ray fluorescence spectroscopy (Mitsubishi Kagaku RX-500SAH). The distribution of sulfur or carbon atom in feedstock or desulfurized oil was also analyzed by gas chromatography with an atomic emission detector (Hewlett Packard HP-5890A).

3. Results and discussion

3.1. Reactivity of each sulfur compound

Fig. 1 shows the distribution of sulfur compounds in the feedstock or the desulfurized oil. The feedstock has a lot of sulfur compounds such as benzothiophene (BT) or DBT group, but

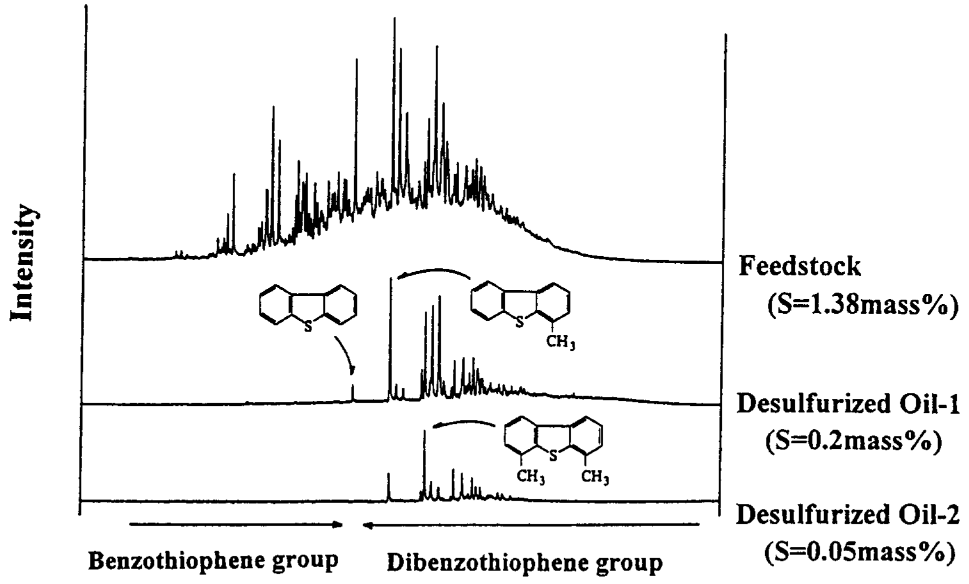

Fig. 1. Distribution of sulfur compounds in feedstock or desulfurized oil.

in the desulfurized oil, all sulfur in the BT group has been removed, and a large part of the DBT groups has been also removed. In the 0.05% sulfur case, small amounts of 4-MDBT, 4,6-DMDBT and diethyl-substituted DBT remained. Those compounds are called refractory sulfur compounds [3]. As some researchers have reported, the HDS reactivity is divided into several groups: BT group, DBT group, refractory sulfur compounds group, and so on [2,4].

3.2. Development of Cosmo deep HDS catalyst

It is explained that a sulfur atom in the refractory sulfur compounds cannot easily adsorb to a catalyst active site for HDS because of significant steric effects [3] or electronic effects [5]. Thus it is difficult for them to remove sulfur atoms. Therefore the following methods are suggested for accelerating a HDS reaction:

1. Hydrogenation of DBT ring occurs predominantly to make a hydrogenated DBT group which has extra-high reactivity of HDS.
2. Isomerization of substituents at the 4- or 6-positions occurs to avoid such steric effects.
3. Hydrocracking of refractory sulfur compounds occurs selectively.

In order to solve the problems, several kinds of acid components were evaluated as a second component toward the alumina carrier which was often used for the HDS catalyst carrier. Table 1 shows the results of HDS reactivities in the deep HDS region with several kinds of catalyst to which the 2nd component was added (the content of the 2nd component is less than 10% with regard to alumina). The addition of a type of zeolite (zeolite-A), which has a well controlled acidity by precise control of the SiO_2/Al_2O_3 ratio, had the most effective in the deep HDS region. The SiO_2/Al_2O_3 ratio of zeolite-A is smaller than that of zeolite-B.

Table 1
Results of HDS reactivities in the deep HDS region[a]

2nd component	None	MgO	SiO_2	TiO_2	Zeolite-A	Zeolite-B
Relative activity (%)[b]	100	90	105	107	140	125

[a] The main component as carrier is alumina.

[b] Relative activities (RA) were measured under the same reaction conditions, and calculated by the following equation: RA (%) = $[K(\mathrm{i})/K(\mathrm{none})] \times 100$, $K(\mathrm{i}) = (1/\mathrm{Sp}^{0.5} - 1/\mathrm{Sf}^{0.5}) \times (\mathrm{LHSV})$ where Sp is the sulfur in product and Sf the sulfur in feedstock.

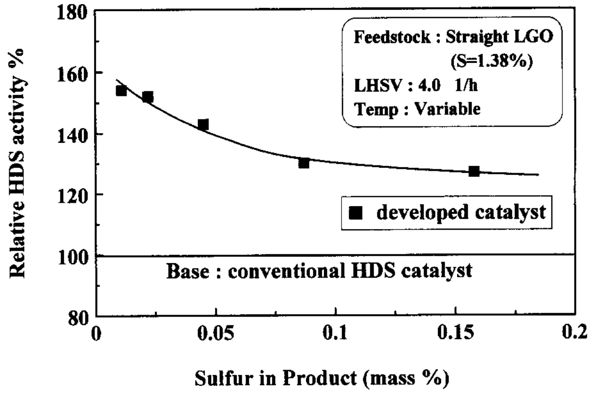

Fig. 2. HDS Performance of the developed catalyst.

An excellent catalyst for deep HDS was obtained when a small amount of the zeolite was added to the catalyst. This developed catalyst has a higher HDS reactivity than a typical conventional catalyst over the entire reaction range. And the difference of HDS activity between them becomes larger and larger when the sulfur content in the product is decreasing (Fig. 2). This is most characteristic of our developed catalyst.

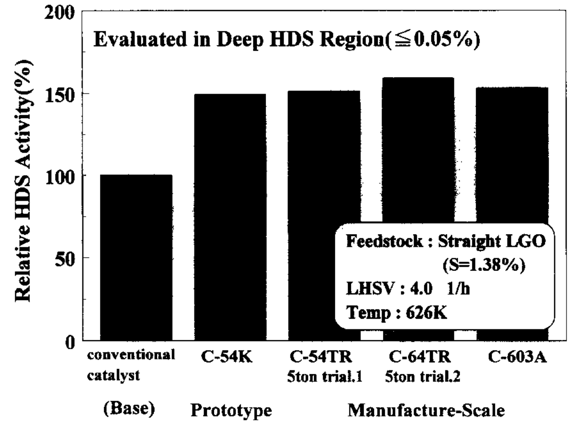

Fig. 3. HDS Activity in various developed levels.

Table 2
Properties of the C-603A catalyst

Shape	Metals	Side crushing strength (lb/mm)	Compacted bulk density (g/ml)
1/16″-Extrudate	Co-Mo	3.6	0.84

3.3. Establishment of catalyst manufacture on a commercial scale

The scale-up effect of the developed catalyst was studied for commercial production. There were some difficulties for scale-up when our developed catalyst was produced on a commercial scale because of the zeolite it contained. Improvement of crushing strength of the catalyst itself or reproducibility of surface area or pore size distribution, etc., are examples of the problems. Many trials have been done with the catalyst manufacturer, and it has been confirmed that an excellent catalyst, which has shown the same performance as the prototype (sample size of kilogram), has been produced in commercial scale (size of several 10 tons). Fig. 3 shows the HDS activities in various developed levels as examples of good reproducibility.

Some properties of C-603A which is the Cosmo deep HDS catalyst for commercial use are shown in Table 2.

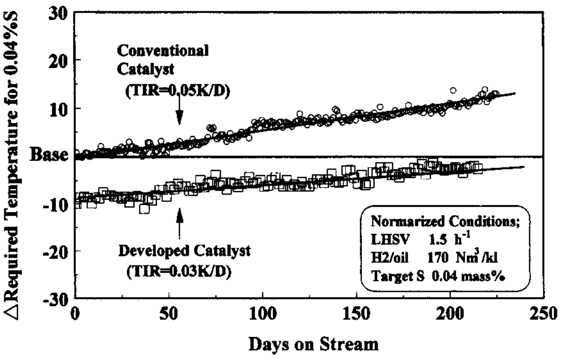

Fig. 4. Long term evaluation of developed catalyst against a conventional catalyst.

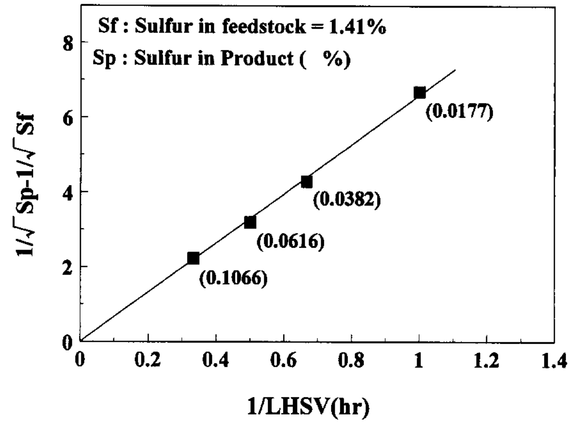

Fig. 5. Determination of HDS reaction order (as 1.5 order reaction).

3.4. Long term evaluation with bench plant

C-603A and the typical conventional catalyst have been evaluated in the deep HDS region for more than 200 days (Fig. 4). Our developed catalyst could be operated ca. 10 K lower than the conventional one, and the deactivation rate (means TIR [temperature increasing rate] in Fig. 4) was also much smaller. When the performance tests of these two catalysts will be carried out for 2 years, the activity difference between them is estimated to be more than 20 K. This means a very large difference in commercial operation. So it was confirmed that the C-603A catalyst was particularly effective for the deep HDS region.

3.5. Kinetic analyses

Kinetic analyses of the C-603A catalyst have been carried out in order to estimate the HDS reactivity under various conditions. Fig. 5 suggests that the HDS reaction in the more than 0.02% product sulfur range is expressed as 1.5

Table 3
Rate constants of each reaction step (DBT case)

Catalyst	$k_0 \times 0.1$/h	$k_1 \times 0.1$/h	$k_2 \times 0.1$/h	$k_3 \times 0.1$/h	k_2/k_0
Conventional	1.8	large	9.0	0.05	5.0
Developed	2.3	large	8.8	0.08	3.8

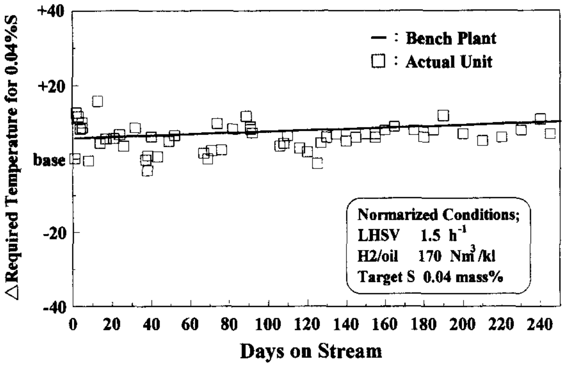

Fig. 6. Comparison of HDS activity between an actual unit and the bench plant.

order kinetics against reaction time (1/LHSV), as under conventional conditions. And the relationship between HDS rate constants (Ks) and hydrogen partial pressure (Hpp) or hydrogen/oil ratio (H/O) was calculated by the following:

$$K\text{s} \,\alpha\, (\text{Hpp})^{0.5} \times (\text{H/O})^{0.4}$$

3.6. Demonstration run in actual HDS unit

The C-603A catalyst was loaded in to an actual HDS unit in the Cosmo Sakai refinery, and the trial started in October 1994. Fig. 6 shows the results of the trial run against the bench plant data. However, the data from the actual unit are a little scattered, the tendency between the actual unit and the bench test correlates well. It was also found that many important process variables are almost the same. Therefore, it is estimated that the HDS activity will be kept for 2 or more years, because no rapid deactivation has been observed at all in the long term evaluation shown in Fig. 6.

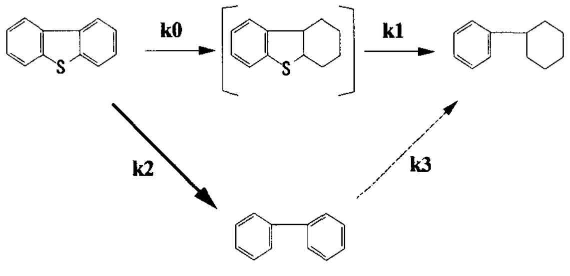

Fig. 7. Reaction scheme of the DBT.

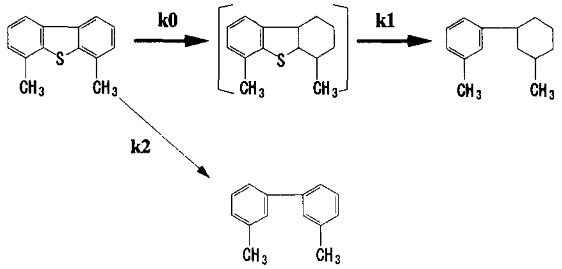

Fig. 8. Reaction scheme of the 4,6-DMDBT.

3.7. Study of reaction scheme in DBT group compounds

The C-603A catalyst which has a small amount of acidity shows high reactivity in the deep HDS region as mentioned before. The comparison of each rate constant between C-603A and the conventional HDS catalyst (alumina carrier) has been studied by using a model reaction. A decalin solution containing DBT or 4,6-DMDBT was prepared, and each reaction rate constant was calculated as pseudo-first order.

The reaction scheme of DBT is shown in Fig. 7. The rate constant of direct HDS to give biphenyl was 4 or 5 times as large as its hydrogenation step in both cases (k_2/k_0) as many researchers reported [1,6] (Table 3). This suggests the main reaction path of HDS is the step of k_2 in the case of DBT. And direct HDS rate constants (k_2) between C-603A and the conventional catalyst were almost the same, but in the k_0 path which hydrogenated DBT, C-603A was slightly larger than the conventional one.

The reaction scheme of 4,6-DMDBT is shown in Fig. 8. In this reaction, k_2, which is the direct

Table 4
Rate constants of each reaction step (4,6-DMDBT case)

Catalyst	$k_0 \times 0.1$/h	$k_1 \times 0.1$/h	$k_2 \times 0.1$/h	$k_3 \times 0.1$/h	k_2/k_0
Conventional	1.4	large	0.037		0.026
Developed	3.2	large	0.038		0.012

HDS step, was two orders of magnitude smaller than in the case of DBT (Table 4). The methyl substituents at the 4- and 6-positions decrease the rate constant of k_2 (direct HDS). On the other hand, the hydrogenation step (k_0) in C-603A was 2 times as large as the conventional case. So there is a large difference in the value of k_2/k_0 between these two cases. In the case of 4,6-DMDBT the main reaction path of HDS might be the step of k_0.

In these experiments, nothing like an isomer of 4,6-DMDBT has been detected. It is considered that the acidity from the zeolite causes the promotion of the hydrogenation rate. It could be surmised that the DBT ring can be adsorbed more easily with the electronic effect from the proton of the zeolite. This is the reason why our new catalyst (C-603A) is suitable for the deep HDS of diesel fuel.

4. Conclusions

(1) A new type of catalyst for the deep HDS region has been developed. The catalyst has a strong ability for removal of refractory sulfur compounds.

(2) The addition of a small amount of zeolite which has a well-controlled acidity has afforded the characteristic performance for deep HDS.

(3) The developed catalyst (C-603A) has been manufactured on an industrial scale without any problems.

(4) It was confirmed that the C-603A catalyst had a higher initial activity especially in the deep HDS region and is stable for a longer time.

(5) The expected performance and stability was obtained with an existing unit.

(6) It is considered that the added zeolite accelerates the hydrogenation rate of the DBT ring. This is the reason why the catalyst is suitable for the deep HDS region.

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References

[1] M. Houalla, B.C. Gates, AIChE J., 24 (1978) 1015.
[2] X. Ma, K. Sakanishi and I. Mochida, Ind. Eng. Chem. Res., 33(2) (1994) 218.
[3] T. Isoda, X. Ma and I. Mochida, Sekiyu, Gakkaishi, 37(4) (1994) 368.
[4] A. Sugimoto, F. Tsuchiya and H. Sagara, NPRA Annual Meeting, AM-92-18, 1992.
[5] M. Girgis and B.C. Gates, Ind. Eng. Chem. Res., 30(9) (1991) 2021.
[6] M.V. Bhinde, Ph.D. Dissertation, University of Delaware, 1979.