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Development of a high activity HDS catalyst for diesel fuel: from basic research to commercial experience

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Abstract

Cosmo Oil and Petroleum Energy Center (PEC) have developed a new hydrodesulfurization (HDS) catalyst of high activity, C-603A, to produce clean diesel fuel, whose sulfur content is less than 0.05 mass%. The preparation of this catalyst combines the use of zeolite technology and impregnation technology to provide excellent HDS activity. C-603A possesses significantly higher activity than conventional Co–Mo/alumina catalyst. Industrial operation with this catalyst has successfully proven its high performance. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, because air pollution by exhaust gas from diesel engine has been a serious problem, much attention has been paid to deep HDS of diesel fuel. Actually, the sulfur contents of diesel fuel have been limited to 0.05 mass% in Japan since October 1997. Furthermore, the restriction of diesel fuel specifications will be more tightened in the near future [1,2]. To satisfy these requirements, it has been strongly desired to develop a new catalyst which is considerably increased in HDS activity. To attain deep HDS, it is vital to effectively remove refractory sulfur compounds such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) and 4-methyldibenzothiophene (4-MDBT) [3].

Therefore, we performed a two-step approach to increasing HDS activity as follows:

1. To increase the distribution of active metals in order to enhance the intrinsic HDS activity.
2. To add a new catalytic function in order to convert 4,6-DMDBT and 4-MDBT to sulfur compounds that are easy to be desulfurized.

By applying the technologies of Cosmo's patents [4,5], we have successfully developed a new high activity HDS catalyst containing zeolite, C-603A. Compared to conventional Co–Mo/alumina catalyst, C-603A exhibited considerably higher HDS activity and greater stability. In this contribution, progress in development of this catalyst and its catalytic performance are highlighted.

2. Experimental

2.1. Catalysts

Catalysts were prepared by pore-volume impregnation, using aqueous solutions containing the

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required amounts of cobalt, molybdenum and phosphorus on carriers composed of alumina or zeolite-including alumina. After impregnation these samples were air dried and calcined. Prior to the activity test, fresh catalysts were presulfided in situ with light gas oil under normal conditions. For comparison, an alumina-supported commercial Co–Mo catalyst was also presulfided and tested under the same conditions.

Zeolite alumina, silica alumina, and alumina without active metals were also used for model reaction (reaction of 4,6-DMDBT in *n*-decane).

2.2. Feedstock properties

Middle East straight run gas oils containing sulfur between 0.8 and 2.0 mass% were used as feedstock for this work.

4,6-DMDBT (0.05% as sulfur)/*n*-decane was also used as model feedstock. 4,6-DMDBT was synthesized according to the method given in the patent [6].

2.3. Equipment

HDS of light gas oil was carried out using both bench-scale plant and commercial HDS unit. The bench-scale plant contained a 100 ml isothermal fixed-bed reactor operating in down-flow mode. The demonstration operation with C-603A has been carried out with the commercial HDS unit (14 000 BPSD) of Cosmo Oil Sakai refinery. This unit was loaded with ca. 30 tonne of C-603A. The run was started in October, 1994.

Model reaction was carried out using a continuous flow micro-reactor.

2.4. Reaction conditions

HDS of light gas oil was carried out under the following conditions: temperature, 320–370°C; total pressure, 3–5 MPa; liquid hourly space velocity (LHSV), 1.0–4.5 h^{-1}.

Model reaction was carried out under the following conditions: temperature, 200–290°C; total pressure, 3.4 MPa; liquid hourly space velocity (LHSV), 1.5 h^{-1}.

2.5. Analytical

The amount of sulfur was determined by energy-dispersive X-ray fluorescence spectroscopy (Mitsubishi Kagaku RX-500SAH). The sulfur containing compounds were analyzed by a gas chromatograph (GC) (Hewlett-Packard 5890 II plus) equipped with a capillary column (HP-1, 25 m, 0.32 mm diameter) and an atomic emission detector (AED) (Hewlett-Packard 5921A).

2.6. Kinetic calculations

The decrease of the total sulfur content in the light gas oil was assumed in pseudo-1.5 order. The following equation was used to analyze the results of the experiment.

$$k = (1/\sqrt{S_p} - 1/\sqrt{S_f}) \times (\mathrm{LHSV}),$$

where k is intrinsic rate constant (h^{-1}), S_p is the amount of sulfur in product and S_f is the amount of sulfur in feedstock.

3. Results and discussion

3.1. Development of a high activity HDS catalyst

It is well-known from the literature [7–9] that phosphorus generally enhances the HDS activity of Co(Ni)–Mo hydroprocessing catalysts. Many researchers suggest that the addition of phosphorus increases the dispersion of the Co(Ni) and Mo active metals [10,11]. Therefore, in order to investigate the effect of phosphorus on the HDS activity of light gas oil, Co–Mo–P/alumina catalysts were prepared using aqueous solutions of $CoCO_3$ and Mo–P heteropoly compounds as starting material. Phospholic acid was added in order to control the concentration of phosphorus. Co–Mo/alumina catalyst was prepared using aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and $(NH_4)6Mo_7O_{24} \cdot 4H_2O$. Fig. 1 indicates the catalytic activity for HDS of light gas oil as a function of phosphorus content. HDS activity increases with phosphorus content, up to 0.2 $P_2O_5/(CoO+MoO_3)$ ratio, and then decreases slightly. From this result it is evident that the addition of a small amount of

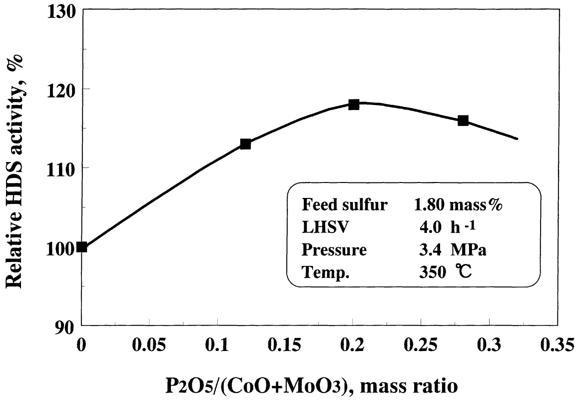

Fig. 1. The dependence of HDS activity on phosphorus content.

phosphorus enhances HDS activity. Furthermore, as mentioned in Section 1, in order to achieve deep HDS, it is necessary to effectively remove refractory sulfur containing compounds such as 4-MDBT and 4,6-DMDBT. It was proposed that the retarding effect of methyl substituents on the 4- and 6-position of DBT on the HDS rates should be ascribed to the steric hindrance in the C–S bond scission of DBTs adsorbed on the HDS active sites [12] or the direct steric hindrance of DBTs adsorption on the HDS active sites [13]. Thus, it has been suggested that isomerization or dealkylation of the alkyl groups and/or hydrogenation of one of the benzene rings of DBT could practically decrease the steric hindrance. Therefore, in order to alleviate this steric hindrance, we have focused on the use of acidic supports, particularly zeolites, which have the ability to promote isomerization reaction. However, zeolites also drastically increase the undesirable cracking activity, which accelerates the rate of coke deposition and enhances the yields of naphtha product and less diesel product. Thus, in order to overcome this drawback, it is necessary to carefully control the acidity of zeolite and the content of zeolite in catalyst. After extensive studies to resolve the above-mentioned problem, we have successfully developed an improved zeolite-containing HDS catalyst, C-603A. Chemical and physical properties of C-603A are listed in Table 1.

The promotion effect of zeolite can be studied by comparing the result with the non-zeolitic catalyst. Accordingly, reaction studies of the HDS of light gas oil were performed on the Co–Mo/alumina catalyst, the Co–Mo–P/alumina catalyst, and the developed catalyst (C-603A). From the results in Fig. 2 it can be observed that the activity of C-603A is much higher than those of the conventional catalysts. Also, to directly investigate the difference between C-603A and conventional Co–Mo/alumina catalyst, the reactivities of DBT, 4-MDBT and 4,6-DMDBT were measured by GC-AED. The distribution of sulfur compounds after HDS is shown in Fig. 3. The evident characteristics of C-603A is to improve the HDS activity, primarily by desulfurizing 4-MDBT and 4,6-DMDBT. Especially in the region of deep HDS, the HDS ability of C-603A is outstanding.

In order to investigate the effect of zeolite on the HDS activity, we examined the reactivity of 4,6-DMDBT in *n*-decane over non-active metal zeolite–alumina, silica–alumina, and alumina, respectively. As shown in Fig. 4, it can be observed that only zeolite–alumina promotes isomerization reaction. From this result, we assumed that zeolite plays a vital

Table 1
Catalyst description

Catalyst	C-603A
Active phase	Co–Mo–P
Support	Zeolite–alumina
Surface area (m^2/g)	>250
Extrudate shape	Cylinder
Diameter (in.)	1/16
Side crushing strength (lbs/mm)	3.6
Abrasion (%)	0.3

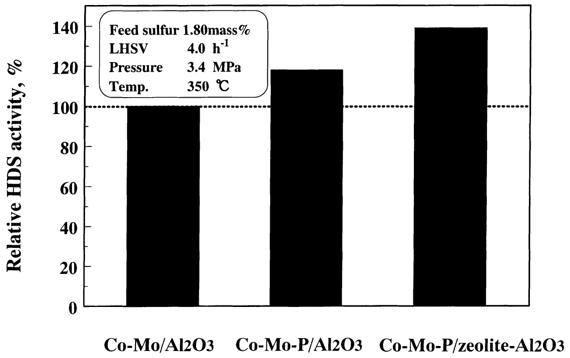

Fig. 2. The effect of phosphorus and zeolite on the HDS activity of light gas oil.

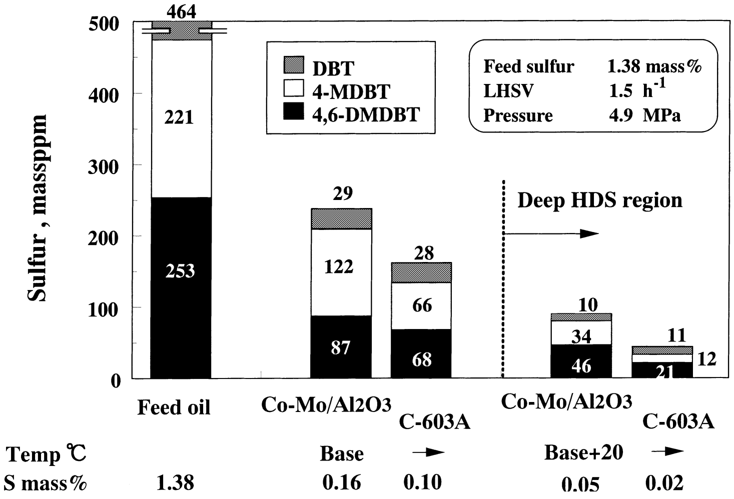

Fig. 3. The distribution of sulfur compounds after HDS of light gas oil.

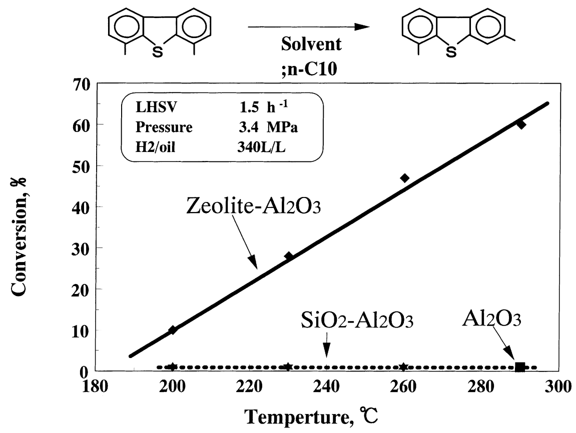

Fig. 4. Isomerization reaction of 4,6-DMDBT.

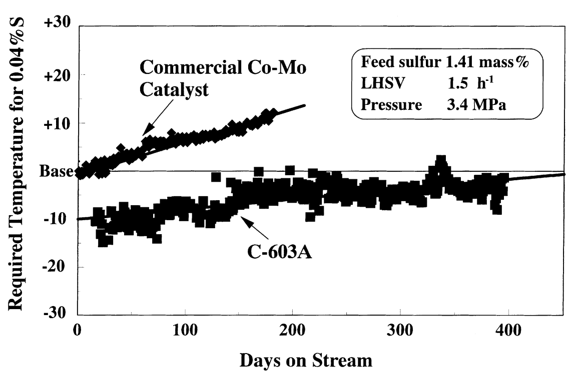

Fig. 5. Temperature required to give 0.04 mass% sulfur in product using C-603A.

role in converting 4,6-DMDBT to 3,6-DMDBT that is easy to be desulfurized.

Isoda et al. [14,15] also investigated the effect of zeolite on Co–Mo/alumina catalyst. They observed the isomerization and transalkylation of 4,6-DMDBT to 3,6-DMDBT and tri- or tetramethyldibenzothiophenes over Co–Mo/alumina-zeolite catalyst and Co–Mo/alumina + Ni-HY mixed catalyst. They concluded that the migration of methyl groups enhances the HDS reactivity of the refractory sulfur species by diminishing the steric hindrance.

3.2. *Catalyst performance of C-603A in bench-scale plant*

Extended test performed in the bench-scale plant demonstrates the stability of C-603A. Results obtained with C-603A during a 400 day test are shown in Fig. 5. The plot shows the temperature required to maintain 0.04 mass% sulfur in the product. It is shown that our newly developed catalyst C-603A enables HDS of diesel fuel to a high degree and has not shown any significant deactivation for more than a year of operation. From this result, the deactivation rate of C-603A has been calculated as 0.021°C/day, which is much lower than that of conventional Co–Mo catalyst.

Generally, coke formation is the most important cause for deactivation of zeolite [16–19]. Hence, in order to decrease the rate of coke deposition, we carefully controlled the acidity (acid strength and the amount of acid sites) and content of zeolite in catalyst. As the reason of the high stability of C-603A containing zeolite, we assumed that the rate of deactivation by coking was suppressed, since the higher activity of this catalyst could lower the reaction temperature in the mode of operation to produce the constant sulfur product and also the acidity and content of zeolite in catalyst were well-controlled.

3.3. Correlation of catalyst performance between bench-scale plant and commercial unit

The correlation of catalyst performance between bench-scale plant and commercial unit was investigated. The amounts of sulfur in product treated with both units under the same operating conditions are indicated in Fig. 6. It can be seen that the industrial performance results fully agree with the results of bench-scale plant tests.

3.4. Properties of products

Table 2 gives the properties of feedstock and products. The various values of the industrial operation are parallel with the bench-scale plant results. The products have good quality, the color has upgraded and the Cetane number has increased.

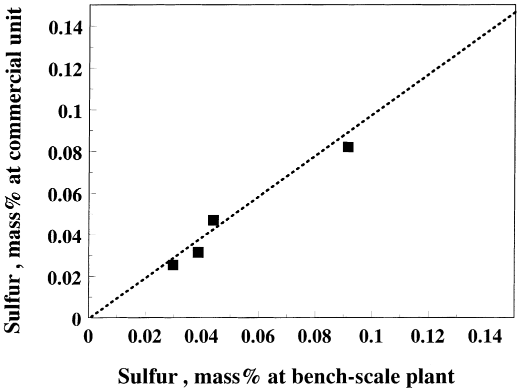

Fig. 6. The correlation of catalyst performance between bench-scale plant and commercial plant.

Table 2
Properties of product

	Feedstock	Bench-scale plant	Commercial unit
Density (g/ml)	0.8543	0.8369	0.8374
Sulfur (mass%)	0.95	0.044	0.047
Nitrogen (mass%)	0.013	0.0071	0.0062
Cetane number	56	62	62
Saybolt color	+3	+10	+7
Distillation			
IBP (°C)	161.5	186.0	171.5
50 vol% (°C)	301.0	295.0	301.0
EP (°C)	367.5	357.5	361.5

3.5. Commercial experience of C-603A

C-603A is now in service in the light gas oil HDS units of Cosmo Oil Sakai and Sakaide refineries and in the vacuum gas oil HDS units of Cosmo Oil Chiba, Yokkaichi and Sakaide refineries. Approximately 650 tonne of C-603A have been used in their units. These industrial operations have actually proven the high HDS activity and stability of C-603A. Furthermore, based on the success of the technical advantages, Cosmo Oil Yokkaichi refinery have applied C-603A to the light gas oil HDS unit since October 1997.

4. Conclusions

In this contribution, an improved, highly active HDS catalyst, C-603A, and the development and performance advantages in terms of activity and stability have been presented.

The main conclusions of this work are summarized below.

1. C-603A is a successful, zeolite-containing HDS catalyst developed by Cosmo Oil.
2. Both the bench-scale plant tests and the industrial data have proven that C-603A possesses significantly higher activity than conventional Co–Mo/alumina catalyst. Especially the deep HDS performance is outstanding.
3. The high overall HDS activity of C-603A is mainly caused by a high activity for the HDS of 4,6-DMDBT and 4-MDBT.

4. The excellent stability of C-603A has been demonstrated in bench-scale and industrial operation.

Acknowledgements

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