Hydrodesulfurization of 4,6-DMDBT in the High Boiling Fraction of Gas Oil

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A high boiling fraction of straight run gas oil, which contained 4,6-DMDBT by addition but free from dimethylbiphenyl and dimethylcyclohexylbenzene of its HDS products, was desulfurized over commercial catalysts to find principal products of 4,6-DMDBT. Thus, HDS of 4,6-DMDBT in the high boiling fraction of real feed was proved to proceed principally through hydrogenative route. During the HDS of the fraction, 4,6-DMDBT was found to be produced from trimethyldibenzothiophenes. This activity depended very much on the acidity of the catalyst.

Strict regulation on the sulfur content in the diesel fuel lower than 15 ppmS requires deep hydrodesulfurization of refractory sulfur species such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) and 4,6,x-trimethyldibenzothiophene (4,6,x-TMDBT) which survive in the oil after conventional hydrodesulfurization process.[1–3] Their HDS has been reported to proceed principally through the hydrogenation of one phenyl ring of dibenzothiophene in the model feed at around 300 °C while higher reaction temperature at 380 °C enhanced the direct desulfurization.[2] Such a scheme is a key information for the design of the better catalyst and process for practical deep desulfurization below 350 °C under the strong influences of inhibitors present in real feed. It is easy in principle to distinguish the mechanism by identifying products, dimethylbiphenyl (DMBP) and dimethyl cyclohexylbenzene (DMCHB) from 4,6-DMDBT in the HDS products. However, it is not practically easy since the gas oil contains a variety of hydrocarbons in relatively high concentrations compared to those of 4,6-DMDBT at a few hundreds of ppm. Hence, no literature is found on the HDS mechanism of 4,6-DMDBT in real feed although there has been many reports on the reaction network of 4,6-DMDBT in model feeds.[2]

The contribution of each pathways to desulfurization depends on the reaction conditions and catalysts type.[2] Recently acidic catalyst showed higher activity on HDS of 4,6-DMDBT[4,5]. Such a high activity is ascribed in the model study partly to the migration of methyl groups at 4- or 6-position to reduce their steric hindrance.[4] Such results indicates the significance of interconversion of methyl groups substituted on the DBT ring. Hydrogenation is also enhanced by the acidity of the catalyst.[6]

The aim of this study is to confirm the reaction network of 4,6-DMDBT in the practical desulfurization. On this objective, cut fraction of gas oil free from 4,6-DMDBT above 345 °C was hydrodesulfurized over CoMoS catalysts by adding 4,6-DMDBT to identify the biphenyls and cyclohexylbenzenes by GC-AED in its products since the fraction was free from such species. Characteristic features of the catalysts can be identified by measuring the particular products. Reactivities of high boiling sulfur species were also concerned since they may suffer the methyl migration as well as desulfurization. Thus the HDS reactivity of the sulfur containing products may influence the deep desulfurization.

Fractionated feed oil (345 °C+, 1.87 wt% S) used in this study was prepared from straight run gas oil (SRGO, 1.54 wt% S). 4,6-DMDBT (Aldrich Chem.) was added to the fractionated oil to obtain the total sulfur content of 1.93 wt% S. The catalysts, which were supplied from commercial catalyst vendors, were CoMoS supported on alumina (CM3, CMMS, CMML) and silica-alumina (CMLX) with different specific surface area and acidity as shown in Table 1. 10 g of feed oil, 2 g of pre-sulfided catalyst and 60 kg/cm^2 of H_2 were charged into 100 mL of an autoclave-type reactor. Reaction temperature and time were 340 °C and 2 h, respectively. Reaction products were analyzed by GC (HP 6890+) coupled with atomic emission detector (AED, HP G2350).[7]

Table 1. Characteristics of Catalysts Used in This Study

Name	CM3	CMLX	CMML	CMMS
Support	Alumina	Silica-Alumina	Alumina	Alumina
Surface Area	217 m^2/g	234 m^2/g	148 m^2/g	202 m^2/g
Average Pore Size	3.8 nm	3.5 nm	5.4 nm	3.2 nm
Acidity[a]	0.48	0.56	0.36	0.18

[a] Amount of NH_3 Desorbed (mmol NH_3/g catalyst)

A feed of 345 °C+ fraction contained high boiling point sulfur species whose retention times were longer than that of 4,6-DMDBT. Benzothiophenes (BT), dibenzothiophene (DBT), mono methyl substituted DBT (C1-DBT) and 4,6-DMDBT were absent in the 345 °C+ fraction.

Figure 1 is the sulfur chromatogram of the reaction product from 345 °C+ fraction over CMLX catalyst. The product certainly contained 4,6-DMDBT as a product. Furthermore new peaks besides 4,6-DMDBT, which were not observed in the feed oil, were found in the product. Such peaks, which survived 2 h reaction, were regarded as refractory sulfur species having alkyl substituents at 4- and 6-positions of dibenzothiophene.

The amount of 4,6-DMDBT detected in the products depended on catalyst types. As shown in Figure 1, CMLX and CM3 catalysts produced the largest amount of 4,6-DMDBT in the product.

The addition of 4,6-DMDBT to 345 °C+ fraction slowed down the HDS of the fraction. The product from 345 °C+ fraction with added 4,6-DMDBT (600 ppmS) was analyzed as in Figure 2. The sulfur chromatogram of the HDS product of 0.1 wt% 4,6-DMDBT in n-decane was also illustrated to indicate the peak positions of HDS products. The product from 4,6-DMDBT in n-decane showed two peaks assigned to DMCHB and another peak to DMBP. DMCHB appeared to carry two isomers such as cis and trans-forms.[8] DMCHB stayed always the dominant product regardless of the reaction time over all catalysts. No methyl group migration with 4,6-DMDBT was

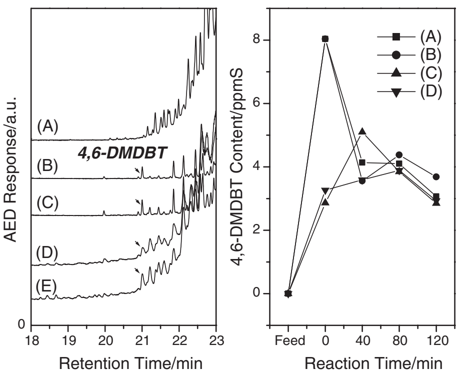

Figure 1. Left: sulfur chromatograms of (A) 345 °C+ fraction and HDS products over CMLX catalyst, (B) 0 min, (C) 40 min, (D) 80 min, (E) 120 min. Right: Amount of 4,6-DMDBT during the reaction over the catalysts. (A) CM3, (B) CMLX, (C) CMML, (D) CMMS.

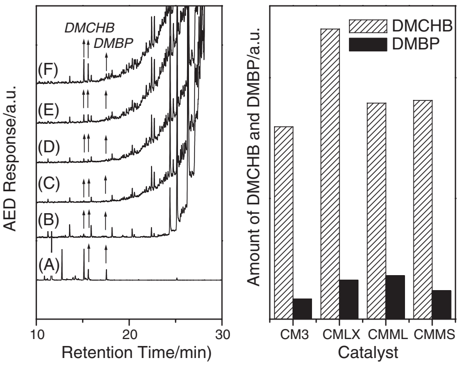

Figure 2. Left: hydrogen chromatograms of (A) HDS product of 4,6-DMDBT model feed, (B) 4,6-DMDBT-added 345 °C+ fraction and its HDS products over CMLX catalyst, (C) 0 min, (D) 40 min, (E) 80 min, (F) 120 m. Right: Amount of DMCHB and DMBP after 120 min reaction over the catalysts.

detected. 4,6-DMDBT contents in HDS product of 345 °C+ fraction added with 4,6-DMDBT were 203, 154, 184, and 186 ppmS over CM3, CMLX, CMML, and CMMS catalysts, respectively. Thus the amounts of DMCHB in the product were in the order of CM3 < CMML < CMMS < CMLX.

Figure 1 indicates that some species in 345 °C+ fraction were transformed into 4,6-DMDBT increasing its content during reaction. The formation of 4,6-DMDBT exceeds its hydrodesulfurization during 2 h reaction at 340 °C. CMLX and CM3, which were more acidic than the others, provided more amount of 4,6-DMDBT at the start of the reaction. The relative kinetic constants for hydrodesulfurization of 345 °C+ fraction were estimated as 0.55 (CM3), 0.78 (CMML), 0.51 (CMMS), and 1.00 (CMLX) by assuming second order kinetics, while CMLX gave the maximum amount of 4,6-DMDBT at the start of the reaction. This fact also suggests the important role of acidity of catalyst for the formation of 4,6-DMDBT. CMML with larger pores and high acidity, showed the second highest activity. Large sulfur molecules contained in the 345 °C+ fraction may be more favorably activated in the larger pores.

In spite of the presence of strong inhibitors for HDS such as aromatic and nitrogen species, 4,6-DMDBT in the high boiling fraction was proved to be hydrodesulfurized principally through the hydrogenative route at 340 °C as observed in model feed HDS. The most acidic catalyst, CMLX resulted in the largest amount of DMCHB while the amount of its DMBP was almost same to that of CMML. Hence the hydrogenation activity was concluded to be enhanced by acidic site of the HDS catalyst. Thus the acidic function of the HDS catalyst is favored to enhance the HDS of refractory sulfur species in the real feed through the hydrogenation route. At the same time, the acidity tends to enhance the production of refractory 4,6-DMDBT and 4,6-dialkyl DBTs, disturbing the deep HDS. Thus the acidity of the HDS catalysts must be moderated to enhance relatively the hydrogenation.

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