산성 및 염기성 물질이 메틸기로 치환된 디벤조티오펜의 탈황 반응에 미치는 영향

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Effect of Acidic and Basic Species on the Hydrodesulfurization of Methyl-substituted Dibenzothiophenes

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Introduction

Deep hydrodesulfurization (HDS) of gas oil is important because the tolerable sulfur concentration in the product must be reduced to low levels in the near future due to environmental concerns. Many efforts have been made to develop catalysts that are particularly active with respect to the HDS of alkyl-substituted heavy sulfur compounds [1].

The modification of HDS catalysts with acidic species represents one of the methods for improving their activity. In the case of zeolite-added catalysts, the migration of methyl groups in the aromatic ring enhanced the HDS rate of the refractory sulfur species by diminishing the steric hindrance exerted by the methyl groups, but the reactants were simultaneously cracked due to the strong acidity of zeolite.

Accordingly, it would be highly desirable to modify catalysts with relatively mild acidic species, for which fluorine and phosphoric acid are candidates. However, most of the previous studies reported on mild acidic species used thiophene as the reactant and only a few used heavier compounds such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT).

In parallel with our efforts to develop active catalysts for deep HDS, it is simultaneously important to understand the effect of nitrogen impurities included in the reaction mixture on catalyst activity because industrial feedstock inevitably contains such impurities, which, in many cases, poison catalysts even at low concentrations.

The origin of the inhibition of activity by nitrogen compounds is the poisoning of two major catalytic sites: the hydrogenolysis and hydrogenation sites [2]. However, in the case of deep HDS of gas oil, which includes such refractory reactants, an additional site should be considered that is responsible for the migration of the alkyl groups in the ring. Because nitrogen compounds are basic, they would be expected to poison the acidic sites of catalysts and, consequently, retard the migration of methyl groups in the ring.

This article summarizes the results of work carried out in this laboratory related to the issues described above [2-4]. The effect of acidic species on the performance of promoted MoS_2 catalysts in the HDS of methyl-substituted DBT compounds is explained, along with an analysis of changes in the rates of individual steps involved in the HDS mechanism. The effect of basic species is summarized in a similar manner, and, lastly, the combined effects of acidic and basic species are discussed.

Effect of Acidic Species

Table 1 compares the conversions and product distributions obtained in the HDS of DBT, 4-methyldibenzothiophene (4-MDBT), and 4,6-DMDBT on $CoMoS/Al_2O_3$ catalysts prepared by using Al_2O_3 treated with different amounts of fluorine [3]. Details of the catalyst preparation conditions can be found in a reference [3]. The catalysts are designated as FCoMoX in Table 1, with X denoting the amount of fluorine added to the catalysts in 0.1 wt.% units.

Table 1. HDS of DBT, 4-MDBT and 4,6-DMDBT on FCoMoX[(a)] at 593 K under 4.0 MPa H_2 pressure

	Catalyst	Conversion	Product concentrations (relative concentrations)	
			BP[(b)] (10^{-5} mol/cm^3) MBP[(c)] (10^{-5} mol/cm^3) DMBP[(d)](10^{-6}mol/cm^3)	CHB[(b)] (10^{-5} mol/cm^3) MCHB[(c)] and CHT[(c)] (10^{-5} mol/cm^3) MCHT[(d)] (10^{-6} mol/cm^3)
DBT[(b)]	FCoMo00	0.55 (1.00)	2.46 (1.00)	0.39 (1.00)
	FCoMo10	0.65 (1.18)	2.99 (1.16)	0.55 (1.40)
	FCoMo25	0.67 (1.22)	3.04 (1.18)	0.60 (1.53)
4-MDBT[(c)]	FCoMo00	0.39 (1.00)	1.26 (1.00)	0.70 (1.00)
	FCoMo10	0.46 (1.18)	1.54 (1.23)	0.77 (1.10)
	FCoMo25	0.51 (1.30)	1.73 (1.37)	0.81 (1.16)
	FCoMo50	0.54 (1.38)	1.89 (1.50)	0.81 (1.15)
4,6-DMDBT[(d)]	FCoMo00	0.39 (1.00)	0.32 (1.00)	1.21 (1.00)
	FCoMo10	0.48 (1.23)	0.44 (1.37)	1.47 (1.22)
	FCoMo25	0.59 (1.51)	0.54 (1.69)	1.77 (1.46)
	FCoMo50	0.62 (1.59)	0.57 (1.77)	1.89 (1.56)

(a) FCoMoX designates CoMo/Al_2O_3 catalyst containing X times 0.1 wt.% of fluorine.
(b) Biphenyl (BP) and cyclohexylbenzene (CHB) were obtained by the HDS of DBT.
(c) Methylbiphenyl (MBP), methylcyclohexylbenzene (MCHB) and cyclohexyltoluene (CHT) were obtained by the HDS of 4-MDBT.
(d) Dimethylbiphenyl (DMBP) and methylcyclohexyltoluene (MCHT) were obtained by the HDS of 4,6-DMDBT.

The conversion increases with fluorine content, by 18% on FCoMo10, and then nearly levels off for FCoMo25. Two major products in the reaction are biphenyl (BP) and cyclohexylbenzene (CHB), both of which increase with fluorine addition. The amounts of BP are 5 - 6 times larger than those of CHB, but the production of CHB is enhanced to a greater extent than that of BP as the result of catalyst fluorination, e. g., 1.53 versus 1.18 at 2.5 wt.% of fluorine.

The conversion of 4-MDBT increases with increasing fluorine content, which is similar to the case of DBT. The amounts of products also increase with fluorine content up to 5.0 wt.%. However, the relative increase of methylbiphenyl (MBP) is larger than that of methylcyclohexylbenzene (MCHB) and cyclohexyltoluene (CHT), e. g., 1.50 versus 1.15 at 5.0 wt.% of fluorine, a trend which is opposite to that observed for DBT. The conversion of 4,6-DMDBT increases with fluorine content, similar to the cases of DBT and 4-MDBT. The amounts of both dimethylbiphenyl (DMBP) and methylcyclohexyltoluene (MCHT) also increase with fluorine content. The extents of their increase are nearly the same, e. g., 1.77 versus 1.56 at 5.0 wt.% fluorine. Accordingly, the trend for the HDS of 4,6-DMDBT falls between two opposite trends observed for the HDS of DBT and 4-MDBT.

The HDS of dibenzothiophenic (DBT) compounds proceeds via two main pathways: direct desulfurization (DDS) by the hydrogenolysis of the C-S bond and hydrogenation (HYD) of the aromatic ring followed by the C-S bond hydrogenolysis. DBT, which contains no methyl substituents, is desulfurized largely via the DDS route. When methyl groups are attached to the aromatic ring as in 4-MDBT and 4,6-DMDBT, steric hindrance by these groups reduces the HDS rates, and HYD instead of DDS becomes the major route in the HDS process [5].

Fluorine addition increases the number of active sites due to enhanced dispersion of the molybdenum and cobalt species, which generates numerous corners and edges that are responsible for catalyst activity, as evidenced by our nitric oxide chemisorption results. Enhanced metal dispersion also induces a greater incorporation of cobalt into molybdenum, thus promoting the Co-Mo-O phase, as confirmed by separate experiments of temperature-programmed reduction (TPR) and temperature-programmed sulfidation (TPS) [3].

Increased acidity due to fluorine addition is another factor that affects the conversions of particularly 4-MDBT and 4,6-DMDBT [3]. The acidity originating from fluorine is largely of the Brönsted type, as evidenced by infrared spectra of pyridine adsorbed on the catalysts. It has been confirmed by separate studies of 2,2'-DMBP isomerization, carried out using fluorinated catalysts that the acidic sites assist in the methyl migration in alkyldibenzothiophenes, which increases the rates of 4-MDBT and 4,6-DMDBT HDS because it removes the screening effect by the substituents.

Fluorine addition results in different product distributions depending on the reactants [3]. In DBT HDS, CHB increases more sensitively by fluorination because the dispersion of the MoS_2 crystallites is enhanced, resulting in numerous corners, rims, and edges. 4-MDBT HDS shows an opposite trend in the product distribution to that observed for the DBT HDS. That is, MBP levels increase at the expense of CHT as a result of fluorine addition. In 4,6-DMDBT HDS, both DMBP and MCHT are enhanced to similar extents by fluorine addition, indicating that the characteristic product distribution falls between

those in the HDS of DBT and 4-MDBT. Accordingly, the DDS pathway in the HDS of 4-MDBT is the most sensitive to, or enhanced by, catalyst acidic sites, followed by that of 4,6-DMDBT and lastly DBT, which has no methyl group, is the least sensitive.

Effect of Basic Species

The poisoning effect of typical nitrogen impurities in gas oil, as represented by carbazole and quinoline, on the activity of $CoMoS/Al_2O_3$ was examined for the HDS of methyl-substituted DBT compounds [2]. The DBT conversion remains nearly constant when the reaction mixture contains up to 50 – 65 ppm of carbazole and quinoline, but decreases when larger amounts, viz. 500 – 650 ppm, are added to the mixture. The amount of CHB decreases to greater extents than that of BP, i. e., HYD is retarded more than DDS, in the presence of the nitrogen compounds.

The HDS of 4-MDBT is more sensitive to the basic species than that of DBT. The conversion of 4-MDBT decreases even at low levels of nitrogen compounds and to below 0.5 in the case of 500 ppm of quinoline. The inhibiting effect of quinoline is larger than that of carbazole, in contrast to the case of DBT HDS which shows only a slight difference in the effect between the two nitrogen compounds. MBP decreases more than the sum of MCHB and CHT, i. e., DDS is retarded more than HYD, in the presence of the compounds, which is an opposite trend to the case of DBT.

The nitrogen compounds inhibit the HDS of 4,6-DMDBT to greater extents than in the cases of DBT and 4-MDBT. The conversion decreases for small amounts of compounds similar to the case of 4-MDBT HDS, and drops to below 0.5 for 500 ppm of quinoline. The inhibiting effect of quinoline is larger than that of carbazole, but the difference in the effect between the two compounds is not as large as in the case of 4-MDBT HDS. DMBP is inhibited more than MCHT by the nitrogen compounds, but the extents to which DMBP and MCHT are suppressed become almost the same when high levels of the compounds are present.

$CoMoS/Al_2O_3$ prepared in this study contains some amounts of acidic sites, even when no acidic compounds have been added to the catalyst. The catalyst loses its acidic sites after exposure to the basic nitrogen compounds, as evidenced by IR spectra of pyridine adsorbed on the catalyst. The nitrogen compounds also lead to a reduction in the amounts of nitric oxide adsorbed on the catalyst

To demonstrate the relationship between catalyst acidity and the HDS reaction, the results obtained with acidic and basic species are plotted together in Fig. 1. In Fig. 1, the catalysts are arranged in increasing order of acid content, as measured by pyridine adsorption. That is, the catalyst modified with 2.5 wt.% fluorine contains the largest amounts of acid while that poisoned by 500 ppm of quinoline has nearly none. The conversion of DBT is not changed significantly, but that of 4,6-DMDBT is significantly affected by acidity. Accordingly, the large change in the HDS of 4,6-DMDBT can be attributed to methyl-group migration in the ring rather than enhanced metal dispersion.

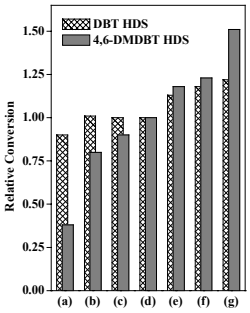

Fig. 1. Relative conversions in the HDS of DBT and 4,6-DMDBT obtained by using different $CoMo/Al_2O_3$ catalysts. Catalysts: (a) poisoned in a feedstock containing 500 ppm quinoline, (b) poisoned in a feedstock containing 50 ppm quinoline, (c) poisoned in a feedstock containing 10 ppm quinoline, (d) fresh and not modified, (e) modified by 3.0 wt.% P_2O_5, (f) modified by 1.0 wt.% fluorine, (g) modified by 2.5 wt.% fluorine.

The effect of acidity is more distinct in the product distributions. In the HDS of 4,6-DMDBT, the relative fraction of DMBP increases while that of MCHT decreases with catalyst acidity, suggesting that steric hindrance to the C-S-C bond is sensitively affected by the acidity. An opposite trend is observed in the HDS of DBT, where the promotion of HYD, as the result of an enhanced dispersion of MoS_2 crystallites [2, 3], is more important than methyl-group migration (MIG). In fact, MIG does not occur in the DBT HDS.

Consequently, the performance of $CoMoS/Al_2O_3$ containing different amounts of acid, which have been adjusted by either acidic additives or nitrogen compounds, show a single trend in their HDS activity and product distributions depending on the catalyst acidity. The trend can be explained by considering the relative contributions of HYD, DDS, and particularly MIG to the overall HDS.

Combined Effects of Acidic and Basic Species

Figs. 2 and 3 show HDS results obtained using $NiMoS/Al_2O_3$ catalysts with different fluorine contents and under the condition that the reaction mixture contains different concentrations of nitrogen compounds [4]. The conversions decrease as a function of the amount of nitrogen compounds present, obviously because the active sites of the catalysts are poisoned by the basic species. Quinoline is more effective for this poisoning than carbazole because the former is more basic than the latter.

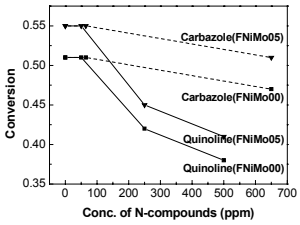

Fig. 2. The effect of nitrogen impurities on the performance of FNiMoX catalysts in DBT HDS. FNiMoX designates $NiMo/Al_2O_3$ catalyst containing X times 0.1 wt.% of fluorine.

In the HDS of DBT, the initial difference in activity between FNiMo05 and FNiMo00 is maintained regardless of the concentrations of the nitrogen compounds, indicating that the active sites of the catalysts are poisoned in proportion to the amounts of basic species present. This result is in contrast to the case of 4,6-DMDBT HDS, which shows that the activity difference is gradually reduced as the concentration of the nitrogen compounds becomes higher.

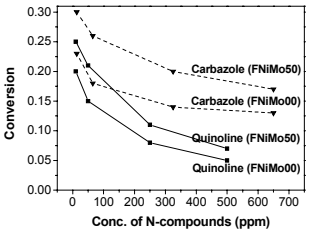

Fig. 3. The effect of nitrogen impurities on the performance of FNiMoX catalysts in 4,6-DMDBT HDS. FNiMoX designates $NiMo/Al_2O_3$ catalyst containing X times 0.1 wt.% of fluorine.

The rates of DBT HDS are largely determined by the amounts of edge and corner sites of MoS_2-like structures or cobalt atoms at the edges of the MoS_2, which are active for the DDS and HYD routes and can be measured by nitric oxide chemisorption. The number of active sites are enhanced by the acid treatment of the catalysts and likewise poisoned by the basic species. Accordingly, the activity of the catalysts for DBT HDS decreases in proportion to the amounts of basic compounds present.

In the case of 4,6-DMDBT HDS, however, the migration of methyl groups in the ring on the acidic sites of the catalysts should be considered as an additional factor, which particularly promotes the DDS rates. In the case of FNiMo00, which contains no fluorine, the acidic sites are present in relatively small amounts and therefore are easily poisoned by the nitrogen compounds. This is reflected by the initial rapid drop in the conversion for FNiMo00, when concentrations of N-compounds are lower than about 200 ppm, as observed in Fig. 3. In the case of FNiMo50, however, the amounts of acidic sites are large and therefore decrease even at high concentrations of nitrogen compounds. Such a difference in the residual amounts of the acidic sites between two catalysts is represented by the non-parallel change in the conversions, shown in Fig. 3.

Conclusion

The performance of Mo-based catalysts in the HDS of DBT compounds is significantly affected by the presence of acidic and basic species, which modify the dispersion of molybdenum on the catalysts, the incorporation of cobalt into molybdenum to produce a Co-Mo-O phase, and the migration of methyl groups in the aromatic ring. It is particularly noteworthy that the methyl-group migration is critical in the HDS of methyl-substituted DBT compounds, which are subject to steric hindrance by the methyl groups. The conversions and product distributions obtained in the HDS change characteristically depending on the types of DBT compounds, the acidic and basic species involved in the reaction, and promoter metals included in the catalysts.

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