THE STUDIES OF HYDRODESULFURIZATION OF 4,6-DIMETHYLDIBENZOTHIOPHENE ON SULFIDED Mo/γ-Al_2O_3: THE EFFECTS OF REACTIVE TEMPERATURE AND PRESSURE

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Introduction

Deep hydrodesulfurization (HDS) of diesel oil has attracted much attention recently as the more and more strict environmental regulations. Among the sulfur compounds of diesel oil, dibenzothiophenes (DBTs, such as dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT)) are found the refractory compounds to HDS [1-4]. However, even now scientists have different ideas on the adsorption states of DBTs over the HDS catalysts and carriers [5-7], as a result, they proposed different HDS mechanism of DBTs. On the other hand, the reactive thermodynamics and kinetics of HDS of DBTs are still studied inadequately. Therefore, the studies of HDS of DBTs are the key subjects to the deep HDS of diesel oil.

In this paper, the HDS of 4,6-DMDBT on sulfided Mo/γ-Al_2O_3 catalyst was studied, moreover, the reaction network and mechanisms were advanced on the basis of GC, and GC-MS analyses of the reaction products.

Experimental

Material and Catalyst. DBT was synthesized by a modified procedure of the literature [8]. Its purity is 99.7%, and its melting point is 98.2-98.4°C. 4,6-DMDBT was synthesized according to an improved method of literature [9]. Its purity is 99.6%, and its melting point is 153.5-154.1°C.

Mo/γ-Al_2O_3 catalyst was prepared in the following way. γ-Al_2O_3(20-40 mesh) was impregnated with an aqueous solution of ammonium heptamolybdate, followed by drying at 120ºC for 5h, and calcinations in air at 500ºC for 5h. The Mo/γ-Al_2O_3 catalyst contained 16.7wt%MoO_3.

Reactor and Experimental Procedure. The HDS reaction was carried out in a fixed-bed flow microreactor, consisting of a 17mm i.d. stainless steel tube. 5ml Mo/γ-Al_2O_3 catalyst (20-40 mesh) was packed in the middle section of the tube, and the other sections were filled by quartz sand. The catalyst was presulfided before HDS reaction with 3wt%CS_2 in cyclohexane for 6h at 2.0MPa, 300°C, LHSV, $3h^{-1}$ and H_2/feed ratio (V/V), 200/1. After presulfidation, the reactant (2wt%4,6-DMDBT or 2wt%DBT in toluene) was pumped into the reactor. 6h later, sampling of products was started at intervals of 30 min. the samples were immediately analyzed by gas chromatograph. Reaction pressure and temperature were then changed for studying the effects of them on HDS of 4,6-DMDBT. The reaction pressures used were 2.0, 1.5, 1.0MPa, while the reaction temperatures used were 300ºC, 280ºC, 260ºC.

Analysis

The samples were analyzed by Varian 3800 Chromatograph. The products were identified by GC-MS (Finnigan SSQ710).

Results and Discussion

The Analysis of Products of HDS and The Reaction Network

The products from reactions of 4,6-DMDBT and their yield at 300ºC under 2.0MPa over sulfided Mo/γ-Al_2O_3 were shown in Table 1. The isomerization of 4,6-DMDBT to 3,6-DMDBT and the other C2-DBTs was found on sulfided Mo/γ-Al_2O_3 catalyst as well as HDS. From Table 1 it can propose that the HDS of 4,6-DMDBT may occur through two types of reaction routes: 1) direct desulfurization (DDS), the hydrogenolysis of C-S bond of the 4,6-DMDBT to form 3,3'-dimethylbiphenyl, which can be further hydrogenated into 3-(3'-methyl-cyclohexyl)-toluene; 2) desulfurization through hydrogenation (HYD), which first forms 4,6-dimethyltetrahydrodibenzothiophene(4,6-DMTHDBT) and 4,6-dimethylhexahydrodibenzothiophene(4,6-DMHHDBT), followed by their desulfurization to provide 3-(3'-methyl-cyclohexyl)-toluene. 3,3'-dimethyldicyclohexyl among the products of HDS of 4,6-DMDBT is yielded from the hydrogenation of 3-(3'-methyl-cyclohexyl)-toluene. The reaction network for HDS of 4,6-DMDBT is shown in Scheme 1.

Table 2 shows the products from HDS of DBT and their concentration at 300ºC under 2.0Mpa over sulfided Mo/γ-Al_2O_3. Comparing Table 2 with Table 1, it can be found that under the same reaction conditions, the conversion of 4,6-DMDBT is lower than that of DBT, and the molar ratio of the products of HYD route to DDS route in the products of HDS of 4,6-DMDBT is about 7.42. But to DBT, it is only 1.33, which means that the HDS of 4,6-DMDBT is essentially through the HYD routes, while to DBT, the contributions of both routes is comparable. The methyl groups in 4,6-DMDBT molecule spatially hinds the "end on adsorption" of sulfur atom on the active sites of the catalyst, which depresses the DDS route and leads to the reduction of conversion of 4,6-DMDBT.

On the other hand, although on the Mo/γ-Al_2O_3 catalyst, 4,6-DMDBT is less reactive than DBT, the difference between the two reactants is not as significant as that generally observed on the CoMo/γ-Al_2O_3 catalyst. The reason for that is on the Mo/γ-Al_2O_3 catalyst, the HYD route is important for both compounds. Co can increase remarkably the hydrodesulfurization activity of the sulfided Mo/γ-Al_2O_3 catalyst, especially for the DDS route. This tremendously enhances the rate of DDS route of the HDS of DBT, but for 4,6-DMDBT, the effect is limited for steric hindrance of methyl groups.

The Effect of Reaction Pressure And Reaction Temperature on HDS of 4,6-DMDBT

The concentration of products for HDS of 4,6-DMDBT under different reaction pressures at 300ºC is shown in Fig.1. Fig.1 illustrates that the reaction velocity of HYD routes in HDS of 4,6-DMDBT obviously decreases with the descending of reaction pressure. But the effect on DDS pathway is much smaller than that on HYD. It can also be found that the effect of reaction pressure on the transformation of 4,6-DMDBT is very obvious for the high selectivity of HYD route in the HDS reaction network of 4,6-DMDBT.

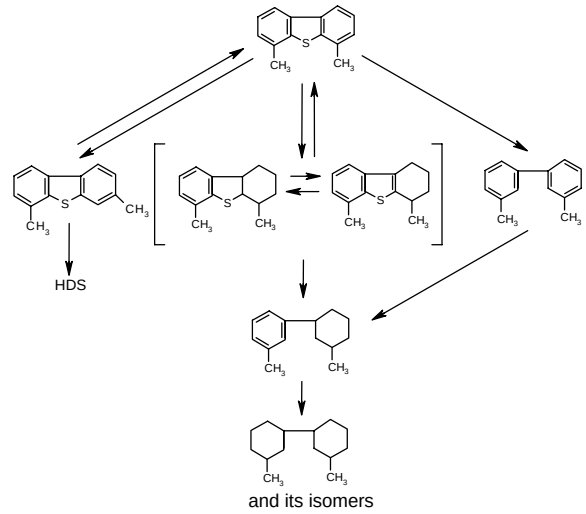
The concentration of products of HDS of 4,6-DMDBT at different reaction temperatures under 2.0MPa is shown in Fig.2. From Fig.2 it can be found that the reaction rates of desulfurization products among the HDS products of 4,6-DMDBT all decrease with the descending of reaction temperature, not only that through the DDS route but also that through the HYD route. However, the transformation of 4,6-DMDBT is not remarkably affected since under relatively low reaction temperature 4,6-DMDBT mainly converses into partly hydrogenated products (i.e. 4,6-DMTHDBT and 4,6-DMHHDBT). The electron donor induction of the methyl groups in 4,6-DMDBT can promote the hydrogenation of the adjacent phenyl, leading to the reduction of activation energy of that.

Conclusion

The isomerization of 4,6-DMDBT is found on sulfided Mo/γ-Al_2O_3 catalyst as well as HDS. Its HDS occurs through the DDS route and HYD route. But the contribution of the HYD route on the products exceeds greatly over the DDS route. Under the same experimental conditions, it was found the conversation of 4,6-DMDBT is lower than that of DBT, which indicates that the methyl groups in 4,6-DMDBT cause the spatial restraining for the "end up adsorption" of sulfur atom on the active site of the catalyst, and lead to the low HDS reactivity of 4,6-DMDBT. Effect of reaction pressure on the HYD route is higher than that on the DDS route for HDS of 4,6-DMDBT. Reaction temperature has obvious effect on desulfurization products yielded through both the DDS route and the HYD route. Under relatively low reaction temperature 4,6-DMDBT mainly transforms into partly hydrogenated products (i.e. 4,6-DMTHDBT and 4,6-DMHHDBT). The electron donor induction of the methyl groups in 4,6-DMDBT can promote the hydrogenation of the adjacent phenyl, leading to the reduction of activation energy of the HYD route.

Table1 Concentration of HDS products of 4,6-DMDBT

Product	Concentration, mol%
C2-DBT	0.58
3,6-DMDBT	2.24
4, 6-DMDBT	72.01
4,6-DMTHDBTand its isomers	10.46
4,6-DMHHDBT and its isomers	2.75
3,4'-dimethylbiphenyl	0.06
3,3'-dimethylbiphenyl	2.93
3-(3'-methyl-cyclohexyl)-toluene and its isomers	6.55
3,3'-dimethyldicyclohexyl and its isomer	2.42



Scheme1 Reaction network for HDS of 4,6-DMDBT on sulfided Mo/γ-Al_2O_3.

Table2. Concentration of HDS products of DBT

Product	Concentration, mol%
DBT	48.37
4H-DBT	5.25
6H-DBT	1.07
biphenyl	22.09
cyclohexylbenzene	21.36
Bicyclohexene and its isomer	1.87

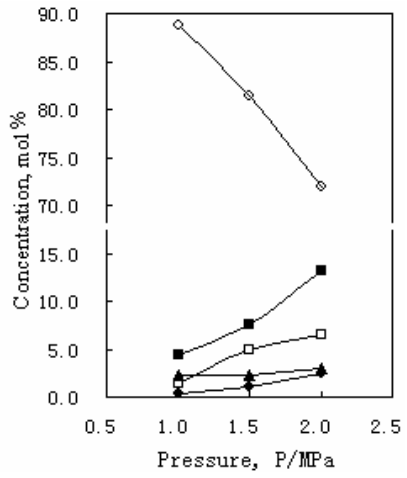


Fig.1 Concentration of hydrodesulfurization products of 4,6-DMDBT under different reaction pressure,
○4, 6-DMDBT, ■ 4,6-DMTHDBT+4,6-DMHHDBT,
□ 3,3'-dimethylcyclohexylbenzene, ▲ 3,3'-dimethylbiphenyl, ● 3,3'-dimethyldicyclohexyl

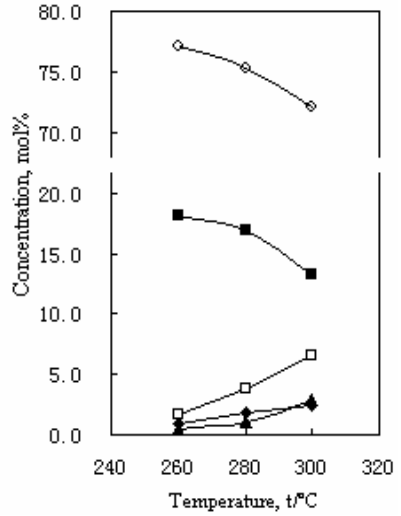


Fig.2 Concentration of HDS products of 4,6-DMDBT under different reaction temperatures,
○4, 6-DMDBT, ■4,6-DMTHDBT+4,6-DMHHDBT,
□ 3,3'-dimethylcyclohexylbenzene, ▲3,3'-dimethylbiphenyl, ●3,3'-dimethyldicyclohexyl

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