

DEEP HYDRODESULFURIZATION OF GASOILS - MECHANISM OF ALKYLDIBENZOTHIOPHENES TRANSFORMATION ON BIFUNCTIONAL CATALYSTS

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INTRODUCTION

In order to decrease the pollution by diesel engines, the authorized maximum sulfur content in fuels has been severely lowered in certain countries. However, total hydrodesulfurization of gasoils is very difficult to reach with the catalysts used at present in the industrial units, probably because of the presence of hydrodesulfurization resistant molecules, such as 4,6-dimethyldibenzothiophene (1,2). Indeed, while dibenzothiophene is easy to decompose, this is not the case for 4,6-dimethyldibenzothiophene. Most of the other dialkyldibenzothiophenes are as reactive as dibenzothiophene, some of them being even more reactive (3-5). Consequently, one possibility of improving the reactivity of 4,6-dimethyldibenzothiophene is to transform it into a more reactive molecule, for example through isomerization (6,7). This reaction can be performed using acid catalysts (8,9).

In the present work we compare the transformation of dibenzothiophene and of 4,6-dimethyldibenzothiophene on catalysts such as a sulfided commercial NiMo on alumina catalyst, a physical mixture of this catalyst with silica-alumina, and on a NiMo on alumina catalyst containing Y-zeolite.

EXPERIMENTAL

The hydrodesulfurization of dibenzothiophene (DBT) and of 4,6-dimethyldibenzothiophene (46DMDBT) was carried out in a flow reactor at 340°C under a 4 MPa total pressure. Decalin was used as a solvent to which dimethyldisulfide was added to generate H₂S. The partial pressures were: DBT or 46DMDBT = 0.01 MPa, decalin = 0.89 MPa, H₂ = 3.0 MPa, H₂S = 0.05 MPa.

The reference hydrotreating catalyst was a commercial NiMo/alumina containing 3 wt.% NiO and 14 wt.% MoO₃. The silica-alumina was a Ketjen K14 sample, containing 14 wt.% alumina. The NiMo-Y zeolite catalyst was supplied by the « Institut Français du Pétrole » (Rueil-Malmaison, France). It contained 5 wt.% Y zeolite mixed with NiMo on alumina (NiO + MoO₃ = 16.8%). All the catalysts were first sulfided *in situ* by a mixture of 5 vol.% dimethyldisulfide in n-heptane, under the same hydrogen partial pressure and total pressure as those used for the reaction. The H₂S partial pressure was 0.125 MPa and that of n-heptane 0.75 MPa. The sulfiding feed was injected at a starting temperature of 150°C, raised to 350°C at a 5°C.min⁻¹ rate. After 14 hours, the temperature was lowered to 340°C, and the reaction mixture was substituted for the sulfiding feed.

The reactor effluents were condensed, and liquid samples were periodically collected and analyzed by gas-liquid chromatography (Varian 3400) on a 50-m DB17 capillary column (J&W Scientific). Unknown products were identified by GC-MS (Finnigan INCOS 500). The HDS conversions of the reactants were determined by using an external standard (1-methylnaphthalene).

4,6-Dimethyldibenzothiophene was synthesized (10) - and kindly supplied - by the « Institut de Recherche sur la Catalyse » (Villeurbanne, France). The other products were purchased from Aldrich.

RESULTS AND DISCUSSION

Transformation of dibenzothiophene and 4,6-dimethyldibenzothiophene over the sulfided NiMo on alumina catalyst.

The sulfided NiMo on alumina catalyst has a very stable activity for the conversion of DBT and of 46DMDBT. Figure 1 shows the total activity of the NiMo catalyst for the conversion of the two molecules. We can see that DBT, under our experimental conditions, is almost 5 times more reactive than 46DMDBT.

The DBT reaction products are biphenyl, tetrahydrodibenzothiophene, cyclohexylbenzene, and dicyclohexyl. If one considers the distribution of these products as a function of contact time, it is clear that biphenyl and tetrahydrodibenzothiophene are the only primary reaction products. In agreement with previous work (11,12), further experiments showed that, under our experimental conditions, biphenyl did not transform into cyclohexylbenzene, which means that cyclohexylbenzene is produced only from tetrahydrodibenzothiophene. Consequently, it can be concluded that the

transformation of DBT occurs through two parallel reactions : direct desulfurization (DDS) yielding biphenyl, and desulfurization after hydrogenation (HYD), yielding first tetrahydrodibenzothiophene, then cyclohexylbenzene. We can estimate that the DDS reaction occurs faster than the HYD reaction (by a factor of 4 in this case), in agreement with the literature (13-15).

The 46DMDBT reaction products are similar to the DBT products, except for the methyl groups. The reaction scheme is the same as in the case of DBT, but the product distribution differs significantly from the one observed in the case of DBT. Figure 1 shows that the HYD reaction (yielding 4,6-dimethyltetrahydrodibenzothiophene and 3-(3'-methylcyclohexyl)-toluene) is 5 times faster than the DDS reaction (yielding 3,3'-dimethylbiphenyl), which is the contrary of what was observed with DBT. The HYD reaction occurs at similar rates for both molecules, whereas the DDS reaction of DBT is faster by a factor of 25 than the DDS reaction of 46DMDBT. Consequently, we can conclude that it is owing to a very slow DDS reaction that 46DMDBT, when compared to DBT, transforms with difficulty (5, 16).

Transformation of dibenzothiophene and 4,6-dimethyldibenzothiophene on silica-alumina.

Long contact times were needed to observe the transformation of DBT and 46DMDBT on pure silica-alumina. In both cases, a very high conversion was obtained initially, but this conversion decreased very rapidly during the first 4 hours, then slower to reach approximately a zero value after 15 hours. Surprisingly, even at high conversion, none of the reaction products obtained with the NiMo on alumina catalyst was detectable by chromatographic analysis. In fact, the reactant transforms into products impossible to distinguish from those resulting from the decalin isomerization and cracking which also occur under the operating conditions.

Transformation of dibenzothiophene and 4,6-dimethyldibenzothiophene on bifunctional (acid + sulfide) catalysts.

The transformations of DBT and 46DMDBT were carried out either on a (1:5) physical mixture of NiMo on alumina with silica-alumina, or on the NiMo-Y zeolite catalyst. Both catalysts exhibited a slow 2-hour-deactivation period with 46DMDBT (the activity decreased by a factor 1.5), and were fairly stable with DBT.

Figure 2 compares the activities of all the catalysts calculated per kg of the sulfide component alone. The presence of an acid component had no effect in the case of DBT conversion, but increased the 46DMDBT reactivity by a factor of 2-2.5, which has already been observed by other authors (6,7). Moreover, two new products were formed from 46DMDBT : the first one was identified by GC-MS as an isomer of 46DMDBT, we suppose it to be 3,6-dimethyldibenzothiophene (36DMDBT) according to the chromatographic analyses reported in the literature (7); the second one, identified by GC-MS as an isomer of dimethylbiphenyl, is most likely 3,4'-dimethylbiphenyl (7). However, we observed that the amounts of DBT and 46DMDBT which were consumed were not balanced by the amounts of the hydrodesulfurization reaction products. In the case of DBT, smaller amounts of cyclohexylbenzene were detected with the bifunctional catalysts than with the pure sulfide catalyst. In the case of 46DMDBT, no 3-(3'-methylcyclohexyl)-toluene was detected. Because of the presence of the acid component, the missing compounds were converted into products which, owing to chromatographic interactions with the solvent reaction products, could not be detected.

To be able to observe the lacking reaction products, the transformations of DBT and of 46DMDBT were carried out on the NiMo-Y zeolite catalyst substituting cyclohexane for decalin as a solvent. Under these conditions, methylcyclohexane and toluene could be detected, and the amounts of consumed reactants were well-balanced by the amounts of the products formed. Figure 3 shows that 3,6-dimethyldibenzothiophene, 3,3'-dimethylbiphenyl and 4,6-dimethyltetrahydrodibenzothiophene are obviously primary reaction products, whereas 3,4'-dimethylbiphenyl, methylcyclohexane and toluene are secondary products. This allows us to propose a reaction scheme for the transformation of 46DMDBT on a bifunctional catalyst (scheme 1). In this scheme, the two reactions identified in the case of the pure sulfide catalyst can be found, the direct desulfurization (DDS) yielding 3,3'-dimethylbiphenyl, and the hydrogenation (HYD) yielding the methylcyclohexyltoluenes. The presence of an acid component induces the appearance of another reaction (ISOM). This acid-catalyzed reaction allows 46DMDBT to transform into 36DMDBT which in turn transforms, mainly through direct desulfurization, into 3,4'-dimethylbiphenyl (no 3,6-dimethyltetrahydrodibenzothiophene was found in the 4,6DMDBT reaction products). No methylcyclohexyltoluenes could be detected in the presence of an acid component, as reported by Landau et al. (6), but the presence of toluene and methylcyclohexane suggests that the methylcyclohexyltoluenes transformed through hydrocracking, as is commonly observed with bifunctional catalysts (18). Moreover, Figure 3 shows that there is more toluene than methylcyclohexane at high 46DMDBT conversions. We must suppose that 3,3'-dimethylbiphenyl or

3,4'-dimethylbiphenyl transform into toluene, as proposed by Lecrenay and Mochida (19). This reaction can occur through a mechanism which is derived from the reverse of the mechanism proposed by Gates, Katzer and Schuit (20) for the transformation of benzene into biphenyl. Owing to the existence of the ISOM reaction (scheme 1), the DDS reaction rate is higher than the HYD reaction rate, and thus produces an excess in toluene.

CONCLUSION

As expected, our results indicate that, owing to a very significant deactivation, the use of a purely acid catalyst is of no interest. However, a « bifunctional » catalyst, such as a sulfided NiMo on alumina plus an acidic function (silica-alumina or Y zeolite) is reasonably stable compared to the pure acid catalyst. The combination of an acid component with a hydrogenating component changes the deactivation process, which is well-known in hydrocracking reactions on bifunctional catalysts. However, the initial decrease in activity of these catalysts observed during 46DMDBT transformation suggests that part of the active sites deactivate. If this deactivation could be avoided, it is clear that the gain in activity resulting from the addition of the acid component could be even greater.

The reactivity of 46DMDBT is higher, at least by a factor 2, on the stabilized bifunctional catalysts than on the pure sulfided catalyst, whereas there is no effect of the acid component on the reactivity of DBT. The increase in 46DMDBT reactivity is linked to the formation of an isomer, most likely 36DMDBT. This is in agreement with the conclusion that alkyl groups in the 4 and 6 positions in DBT inhibit the DDS reaction more significantly than alkyl groups in other positions. In the case of DBT, the isomerization reaction is of course impossible, and it is quite normal to have no effect of an added acid component on the DBT transformation rate.

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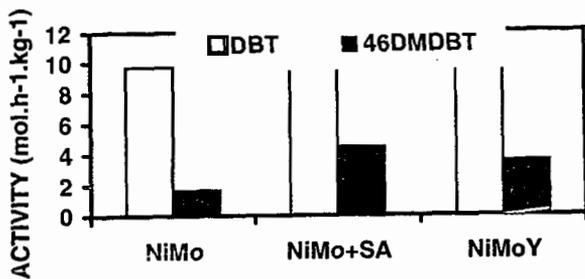


Figure 1. Activities of the sulfided NiMo on alumina catalyst for the transformation of dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (46DMDBT). DDS = direct desulfurization reaction, HYD = hydrogenation reaction.

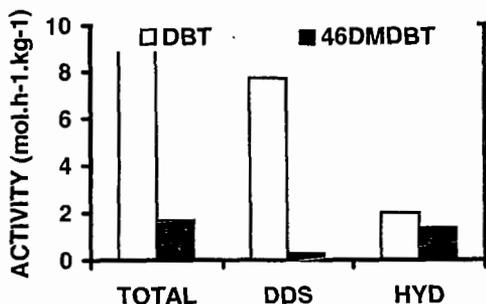


Figure 2. Activities of the sulfide functions of the catalysts for the transformation of dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (46DMDBT), NiMo = pure NiMo on alumina; NiMo + SA = NiMo on alumina mixed with silica-alumina; NiMoY = bifunctional NiMo - Y zeolite catalyst.

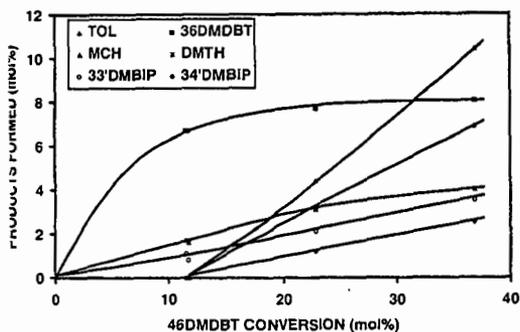
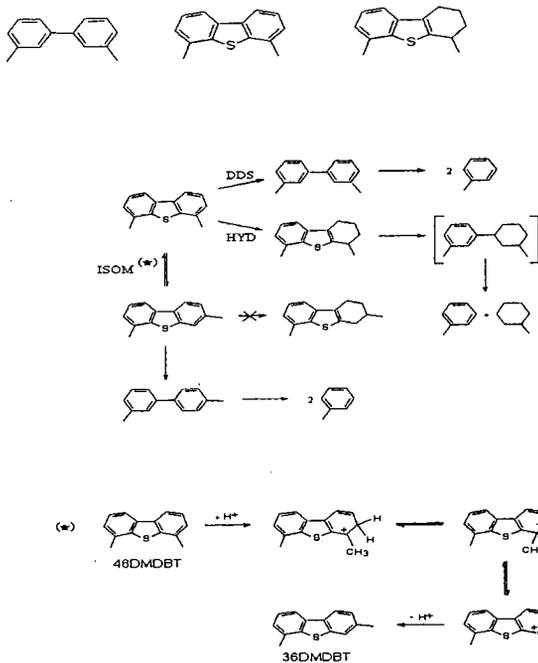


Figure 3. Hydrodesulfurization of 4,6-dimethyl dibenzothiophene on sulfided NiMo on alumina - Y zeolite catalyst. TOL = toluene, 36DMDBT = 3,6-dimethyl dibenzothiophene, MCH = methylcyclohexane, DMTH = 4,6-dimethyl tetrahydrodibenzothiophene, 33'DMBiP = 3,3'-

dimethylbiphenyl, 34'DMBiP = 3,4'-dimethylbiphenyl



Scheme 1. Transformation of 4,6-dimethylbenzothiophene on sulfided NiMo on alumina - Y zeolite catalyst.