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Competitive hydrodesulfurization of 4,6-dimethyldibenzothiophene, hydrodenitrogenation of 2-methylpyridine, and hydrogenation of naphthalene over sulfided NiMo/γ-Al_2O_3

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Abstract

The hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene (4,6-DMDBT) was studied at 340 °C and 5 MPa in the presence of 2-methylpyridine and 2-methylpiperidine. Both N-containing molecules inhibited the HDS. The inhibitory effect of 2-methylpiperidine on the direct desulfurization and hydrogenation pathways of the HDS was slightly stronger than that of 2-methylpyridine. The desulfurization of 4,6-dimethyltetrahydrodibenzothiophene, an intermediate in the hydrogenation pathway, was extremely difficult in the presence of N-containing molecules. 4,6-DMDBT, in turn, inhibited the hydrogenation of 2-methylpyridine to 2-methylpiperidine but did not affect the C–N bond cleavage in the hydrodenitrogenation of 2-methylpiperidine. The use of toluene as an aromatic solvent had no effect on the HDS of dibenzothiophene and 4,6-DMDBT at 340 °C. Naphthalene inhibited the HDS of dibenzothiophene and 4,6-DMDBT without changing the product distributions. Both S-containing molecules suppressed the hydrogenation of naphthalene to the same extent.

Keywords: Hydrotreating; Hydrodesulfurization; HDS; Dibenzothiophene; DBT; 4,6-Dimethyldibenzothiophene; 4,6-DMDBT; Hydrodenitrogenation; HDN; 2-Methylpyridine; 2-Methylpiperidine; Hydrogenation; Aromatics; Naphthalene

1. Introduction

Research on the purification of fuels, including desulfurization, denitrogenation, and dearomatization, has become an important subject of environmental catalysis studies worldwide. The three major types of transportation fuels, gasoline, jet, and diesel fuel, differ in composition and properties [1]. Diesel fuel contains the most refractory sulfur compounds, alkylated benzothiophenes and alkylated and nonalkylated dibenzothiophenes. The sulfur content in diesel fuel is of environmental concern because, upon combustion, sulfur-containing molecules are converted to hydrocarbons and SO_x; the latter compounds not only contribute to acid rain but also poison the catalytic converter for the treatment of exhaust emission. Reducing the contents of aromatics as well as sulfur is generally desirable with respect to the quality of diesel fuel; the reduction of aromatics increases the cetane number and generally improves combustion characteristics [2,3]. Organic nitrogen compounds are constituents of liquid fuels that contribute to harmful NO_x emissions and poison acidic catalysts. They are among the strongest inhibitors of hydrodesulfurization (HDS) [4–10]. This inhibitory effect becomes more pronounced under conditions of deep HDS when the amounts of S and N compounds are comparable.

Dibenzothiophene (DBT) and its substituted derivatives undergo HDS via two parallel pathways: (i) direct desulfurization (DDS) or hydrogenolysis leading to the formation of biphenyls and (ii) hydrogenation (HYD) followed by desulfurization giving first tetrahydro- and hexahydrodibenzothiophenes, which are further desulfurized to cyclohexylbenzenes and bicyclohexyls [11–14]. DBT and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are used as model S compounds in our studies, because they represent the family of the most refractory S-containing molecules in oil distillates. It is well known that, over a NiMo/Al_2O_3 catalyst, DBT reacts preferentially via the DDS pathway, whereas 4,6-DMDBT converts mainly via the HYD pathway [15,16]. This is due to the strong steric hindrance of the two methyl

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groups in the 4 and 6 positions adjacent to the sulfur atom of DBT. The methyl substituents hinder the perpendicular one-point adsorption of the molecule on the catalyst surface that is needed for the DDS pathway of the HDS. The overall reactivity of DBT over Ni- or Co-promoted Mo/Al_2O_3 catalysts is one order of magnitude higher than that of 4,6-DMDBT [13,17,18].

The first systematic studies on simultaneous catalytic HDS and hydrodenitrogenation (HDN) were performed by Satterfield et al. [19,20]. They investigated the interaction in the HDS of thiophene and HDN of pyridine. However, when using thiophene as S-containing molecules, one cannot distinguish the DDS and HYD pathways in the HDS. In our previous work on the mutual influence of HDS and HDN we used DBT as a model S compound and 2-methylpyridine (2-MPy) and 2-methylpiperidine (2-MPiper) as N-containing molecules [16]. Both N compounds had a strong inhibitory effect on the HYD pathway of the HDS of DBT, with 2-MPiper having a somewhat stronger effect than 2-MPy. Both N-containing molecules also inhibited the DDS pathway of the HDS of DBT, 2-MPy being a stronger inhibitor than 2-MPiper. In the work reported here we studied the influence of 2-MPy and 2-MPiper on the HDS of 4,6-DMDBT, which undergoes HDS predominantly via the HYD route, and compared the results with those obtained for the HDS of DBT. We investigated the effect of the solvent and of naphthalene on the HDS of DBT and 4,6-DMDBT. The reverse influence of S-containing molecules on the HDN of 2-MPy and 2-MPiper and on the HYD of naphthalene was investigated as well.

2. Experimental

The $NiMo/\gamma\text{-}Al_2O_3$ catalyst contained 8 wt% Mo and 3 wt% Ni and was prepared by successive incipient wetness impregnation of $\gamma\text{-}Al_2O_3$ (Condea, pore volume 0.5 $cm^3\,g^{-1}$, specific surface area 230 $m^2\,g^{-1}$ with an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ followed by an aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$ (both Aldrich). After each impregnation step the catalyst was dried in air at ambient temperature for 4 h, then dried in an oven at 120 °C for 15 h, and finally calcined at 500 °C for 4 h.

A sample of 0.05 g of catalyst was diluted with 8 g SiC to achieve plug-flow conditions in the continuous flow fixed-bed reactor. The catalyst was sulfided in situ with a mixture of 10% H_2S in H_2 (25 ml min^{-1}) at 400 °C and 1.0 MPa for 4 h. After sulfidation, the pressure was increased to 5.0 MPa, the temperature was decreased to reaction temperature, and the liquid reactant was fed to the reactor by means of a Gilson 307 piston pump.

Reactions were carried out in continuous mode in a fixed-bed inconel reactor as described previously [16]. The experiments were carried out at 300 and 340 °C. The composition of the gas-phase feed consisted of 130 kPa toluene or decane (as solvent for the DBTs and amine), 8 kPa dodecane (as reference for DBT, 4,6-DMDBT, and their derivatives in the GC analysis), 11 kPa heptane (as reference for the N compounds in the GC analysis), 1 kPa DBT, or 4,6-DMDBT, 2–10 kPa 2-MPy or 2-MPiper, 1–10 kPa naphthalene, 35 kPa H_2S, and 4.8 MPa H_2. The partial pressure of H_2S in all the experiments was 35 times higher than that of DBT or 4,6-DMDBT to avoid an effect of the H_2S formed during the HDS reaction.

The reaction products were analyzed by on- and off-line gas chromatography as described earlier [16]. Weight time was defined as $\tau = w_{cat}/n_{feed}$, where w_{cat} denotes the catalyst weight and n_{feed} the total molar flow to the reactor. The weight time (τ) was changed by varying the flow rates of the liquid and the gaseous reactants while keeping their ratio constant. The reaction was stable after 3 to 4 h; during 2 weeks of operation almost no deactivation of the catalyst was observed. A single experiment lasted 36–48 h. The competitive experiments with different amounts of N-containing molecules were always carried out on the same sample of a catalyst.

3. Results

3.1. HDS of 4,6-dimethyldibenzothiophene

The rate of the HDS of 4,6-DMDBT and the resulting product distribution were investigated at 300 and 340 °C. 4,6-DMDBT undergoes HDS via the same reaction pathways as DBT: direct desulfurization and hydrogenation followed by desulfurization. The HYD pathway predominates at both reaction temperatures, since the amount of products obtained via this route is four to six times higher than that of 3,3′-dimethylbiphenyl formed via the DDS route (Figs. 1a and 2a). The selectivity toward 3,3′-dimethylbiphenyl formation or the DDS selectivity is 15% at 300 °C and 25% at 340 °C; the selectivity toward the HYD pathway is 85 and 75%, respectively (Figs. 1b and 2b). The selectivity toward the formation of 3,3′-dimethylbiphenyl remains constant during the course of the reaction, showing that this product is not hydrogenated further. 4,6-Dimethyltetrahydrodibenzothiophene formed via hydrogenation of 4,6-DMDBT is desulfurized to methylcyclohexyltoluene. We consider that 3,3′-dimethylbicyclohexyl is the product of further hydrogenation of the tetrahydro-intermediate to the perhydro-intermediate and subsequent desulfurization and not the product of the hydrogenation of methylcyclohexyltoluene. This is because the hydrogenation of the second ring in the biphenyl-like structures should be much more difficult than that of the first ring, since the partially hydrogenated molecule is not flat any more and it is more difficult to adsorb such a molecule on the catalyst surface as compared to biphenyl. Moreover, we know that the hydrogenation of the first ring of 3,3′-dimethylbiphenyl does not occur during the HDS of 4,6-DMDBT. The perhydro-intermediate was not observed in the product, probably because of its fast conversion and

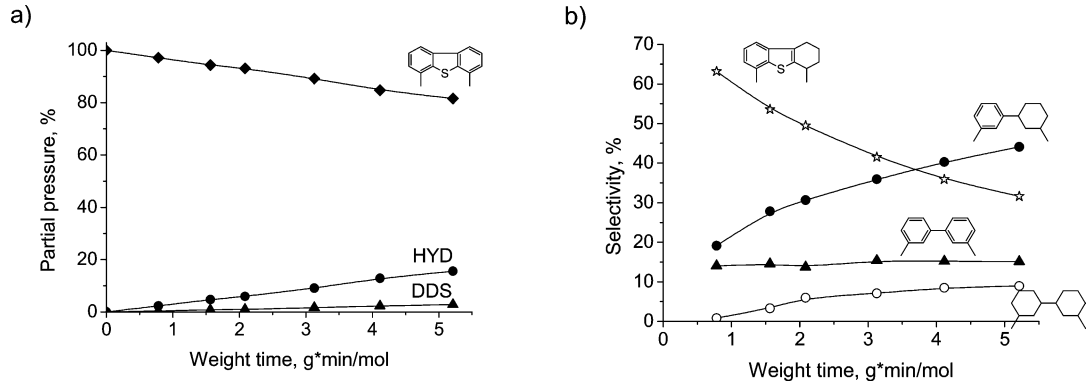


Fig. 1. Relative partial pressures (a) and selectivities (b) of the products of the HDS of 4,6-dimethyldibenzothiophene at 300 °C as a function of weight time.

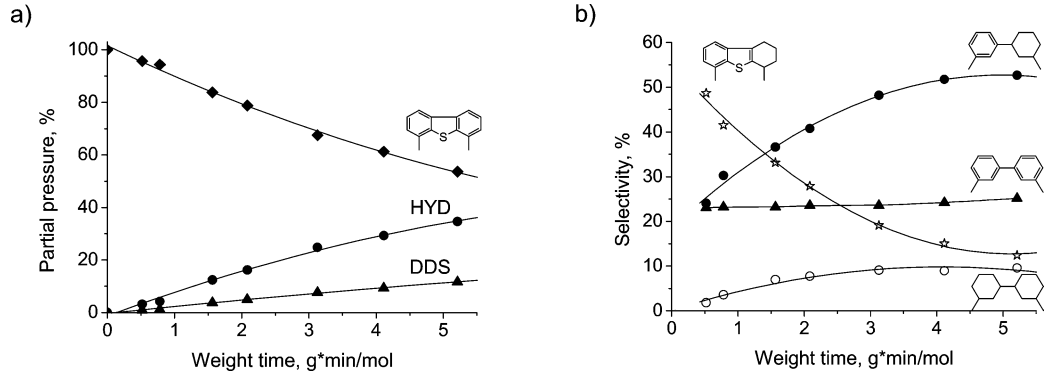
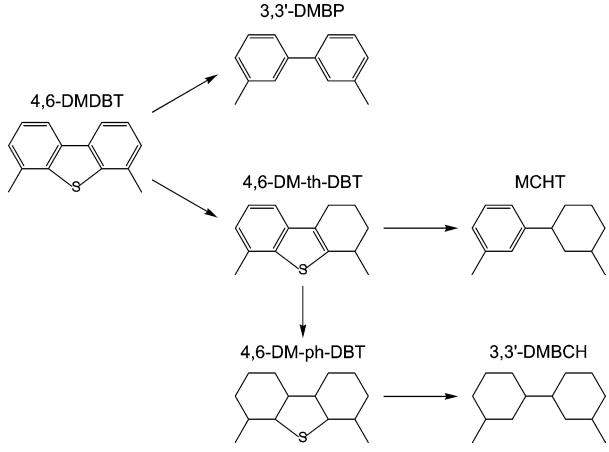


Fig. 2. Relative partial pressures (a) and selectivities (b) of the products of the HDS of 4,6-dimethyldibenzothiophene at 340 °C as a function of weight time.



Scheme 1. Reaction network of the HDS of 4,6-dimethyldibenzothiophene.

thus low concentration. Therefore, the overall reaction network of the HDS of 4,6-DMDBT is as shown in Scheme 1.

3.2. Influence of N-containing molecules on HDS

The effect of the N compounds on the HDS of 4,6-DMDBT was studied at 340 °C, where the conversion of 4,6-DMDBT was high enough to observe inhibitory effects. 2-MPy and 2-MPiper were used as model N-containing molecules since it was shown previously that the presence of the methyl group on the α-carbon atom of pyridine strongly suppresses the unwanted side reaction of disproportionation, which usually takes place in the HDN of pyridine and piperidine [21].

The results of competitive experiments performed at 2 and 6 kPa 2-MPy and 2-MPiper are shown in Figs. 3a and 3b. Both N-containing molecules strongly inhibit the overall HDS of 4,6-DMDBT. Already at 2 kPa 2-MPy or 2-MPiper, the conversion of 4,6-DMDBT decreased by a factor of 5 to 6, and at 6 kPa 2-MPy or 2-MPiper, the conversion of 4,6-DMDBT hardly reached 4% at $\tau = 5$ g min mol^{-1}. The inhibitory effects of 2-MPy and 2-MPiper are almost the same (Figs. 3a and 3b). Also the product distribution was almost identical; therefore, only the results of 2-MPiper are presented in Figs. 4a and 4b. The selectivity of the DDS pathway in the HDS of 4,6-DMDBT increased in the presence of the N-containing molecules from 25 to 35% at 2 kPa 2-MPy or 2-MPiper and to 45% at 6 kPa 2-MPy or 2-MPiper, but the HYD route still remained the major pathway. However, at 6 kPa 2-MPy and 2-MPiper, the only product of the HYD route is the partially hydrogenated 4,6-dimethyltetrahydrodibenzothiophene. At 2 kPa of 2-MPy or 2-MPiper, this compound is the main HYD product. The character of the selectivity curve of 4,6-dimethyltetrahydrodibenzothiophene (Fig. 4a) shows that when the N compounds are converted this intermediate can react further. Sulfur removal is, thus, strongly suppressed in the presence of N-containing molecules.

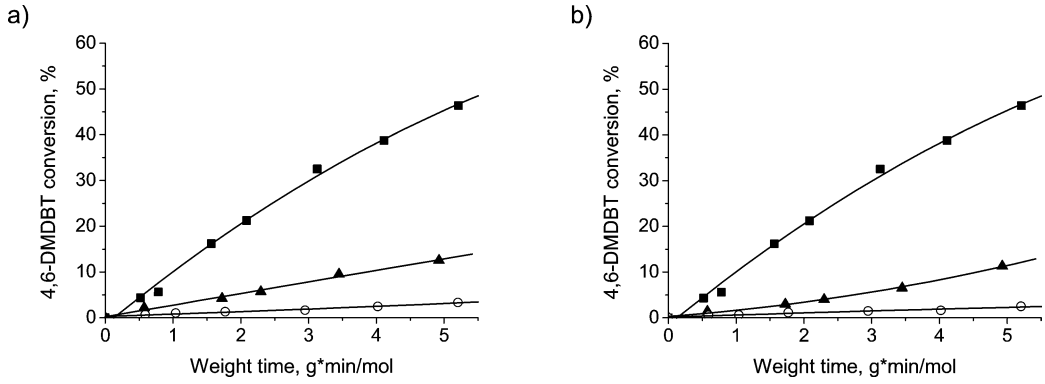


Fig. 3. Inhibition of the HDS of 4,6-DMDBT in the presence of 2-methylpyridine (a) and 2-methylpiperidine (b) at 340 °C. HDS of 4,6-DMDBT alone (■), in the presence of 2 kPa (▲) and 6 kPa (○) N-compounds.

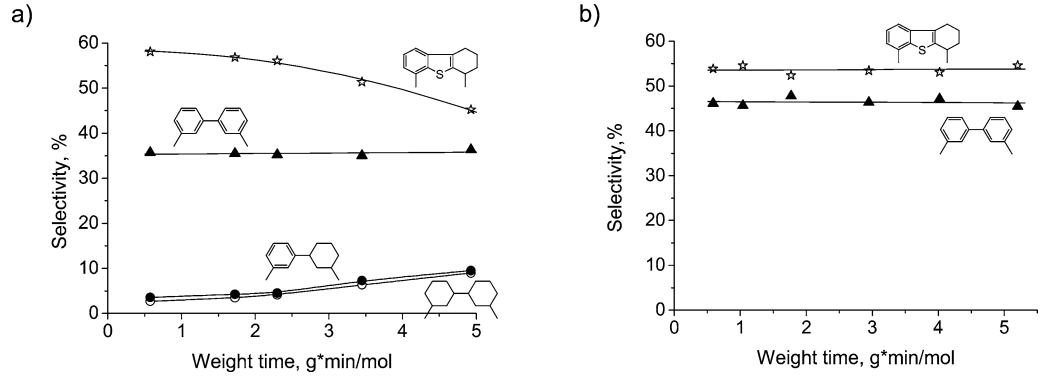
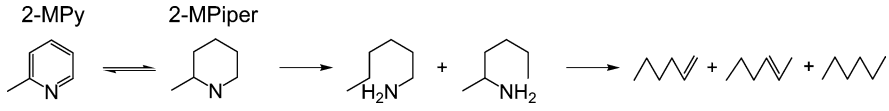


Fig. 4. Product distribution in the HDS of 4,6-DMDBT at 340 °C in the presence of 2 kPa (a) and 6 kPa (b) of 2-MPiper.



Scheme 2. Reaction network of the HDN of 2-methylpyridine and 2-methylpiperidine.

3.3. *Influence of S-containing molecules on HDN*

The influence of DBT and 4,6-DMDBT on the HDN of 2-MPy and 2-MPiper was studied at 340 °C. The HDN network of 2-MPy and 2-MPiper was determined earlier [21] (Scheme 2). 2-MPiper is the primary product in the HDN of 2-MPy, since the cleavage of the C–N bond in heterocyclic N-containing aromatic molecules can only occur after ring hydrogenation [22]. We found previously that the first C–N bond breaking in 2-MPiper occurs predominantly between the nitrogen atom and the carbon atom of the methylene group and that the methyl group has a negative rather than a positive influence on the C–N bond breaking [21].

In the presence of 1 kPa 4,6-DMDBT, the conversion of 6 kPa 2-MPy and the yield of 2-MPiper decreased, while the amount of C_6 products (hexane, hexenes, and hexylamines) increased slightly (Fig. 5). No changes were observed in the HDN of 2-MPiper in the presence of 4,6-DMDBT, neither in the conversion of 2-MPiper, nor in the formation of

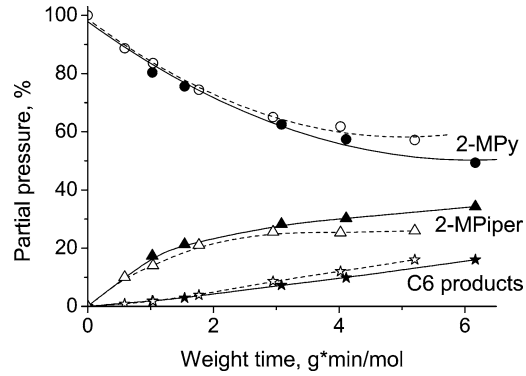


Fig. 5. HDN of 6 kPa 2-MPy at 340 °C in the presence (– – –) and absence (—) of 1 kPa 4,6-DMDBT.

C_6 products (not shown). The effect of 4,6-DMDBT on the HDN of 2-MPy and 2-MPiper was, thus, identical to that of DBT [16]. Hence, both S-containing molecules have an inhibitory effect on the hydrogenation of 2-MPy and no effect on the C–N bond cleavage in 2-MPiper.

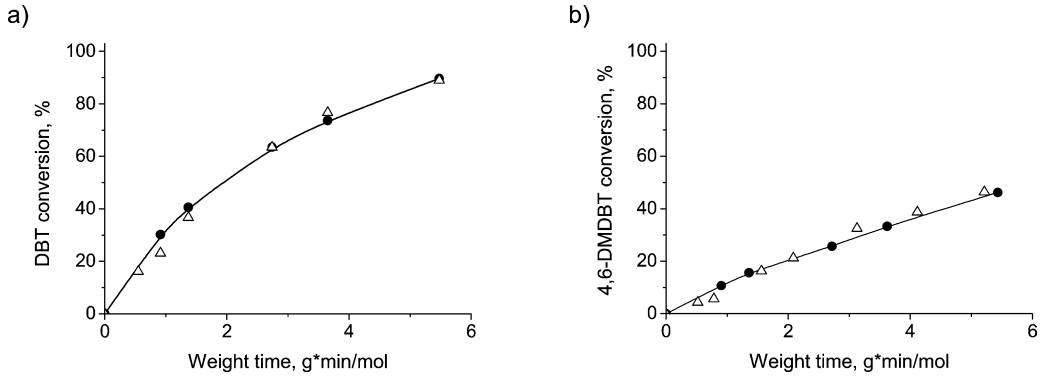


Fig. 6. Effect of the solvent on the HDS of DBT (a) and 4,6-DMDBT (b) at 340 °C in decane (●) and toluene (△).

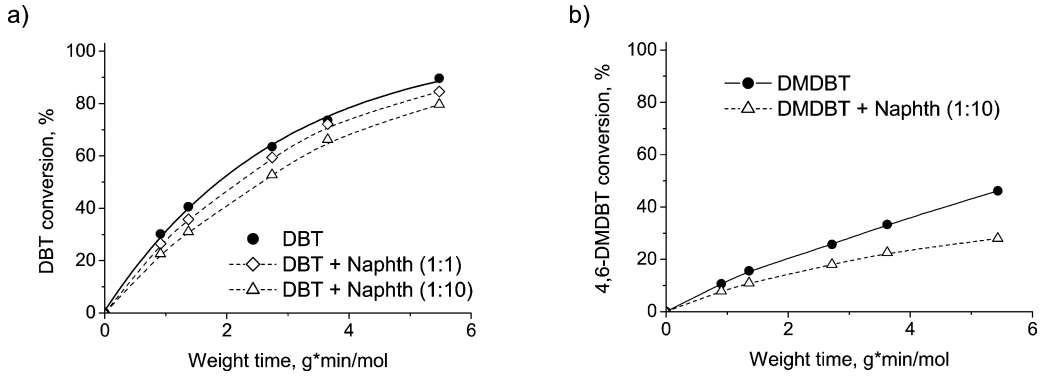


Fig. 7. Inhibition of the HDS of DBT (a) and 4,6-DMDBT (b) in the presence of naphthalene at 340 °C.

3.4. Effect of solvent on HDS

Toluene was the solvent in most of our HDS reactions, since the solubility of DBT and 4,6-DMDBT is much better in an aromatic solvent. However, aromatic molecules may compete with the S-containing reactant for the active sites on the catalyst surface. In order to determine whether the solvent had any effect on the HDS conversion we also performed HDS experiments of DBT and 4,6-DMDBT in decane. The results show that the conversions of both DBT (Fig. 6a) and 4,6-DMDBT (Fig. 6b) are the same in toluene and decane at 340 °C. The product distribution was also the same. Therefore, we conclude that the use of toluene as a solvent does not influence the HDS reactions of DBT and 4,6-DMDBT at 340 °C. Toluene itself did not undergo hydrogenation when S- or N-containing molecules were present in the feed.

3.5. Effect of naphthalene on HDS

The effect of naphthalene on the HDS of DBT and 4,6-DMDBT was studied at 340 °C. Naphthalene was used to study the effect of condensed aromatics on HDS. Already at 1 kPa naphthalene the conversion of DBT decreased slightly and at 10 kPa naphthalene by 10% (Fig. 7a); the product distribution remained the same however. The inhibitory effect of 10 kPa naphthalene was stronger in the HDS of 4,6-DMDBT than in the HDS of DBT. The initial rate of the

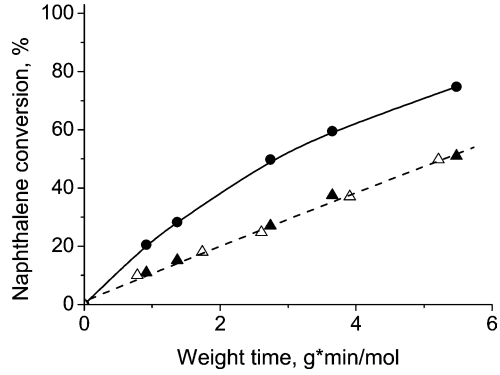


Fig. 8. Hydrogenation of 10 kPa naphthalene to tetralin in the presence (– – –) and absence (—) of 1 kPa DBT (▲) or 4,6-DMDBT (△).

HDS of 4,6-DMDBT decreased by a factor of 1.8, whereas that of DBT was affected by a factor of 1.34 at 10 kPa naphthalene (cf. Figs. 7a and 7b). The selectivities in the HDS of 4,6-DMDBT were not influenced by the presence of naphthalene. Thus, naphthalene affected the DDS and the HYD pathways of the HDS of both S-containing molecules to the same extent. The inhibitory effect of naphthalene was much weaker than that of the N-containing molecules.

3.6. Influence of S-containing molecules on HYD

The effects of the S-containing molecules on the hydrogenation of naphthalene are presented in Fig. 8. At a partial

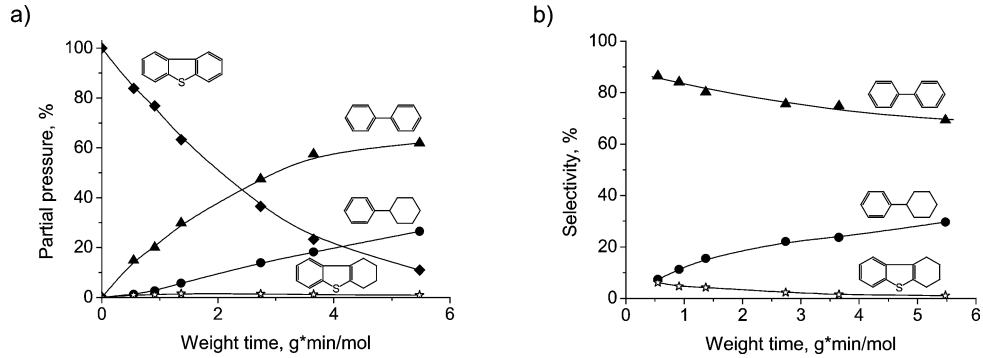
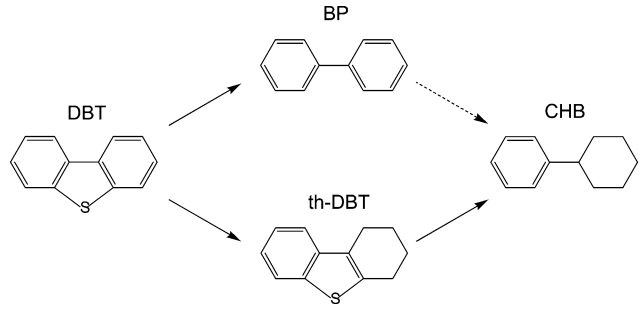


Fig. 9. Relative partial pressures (a) and selectivities (b) of the products of the HDS of dibenzothiophene at 340 °C as a function of weight time.

pressure of 1 kPa, DBT and 4,6-DMDBT inhibited the hydrogenation of 10 kPa naphthalene equally strongly. The partial pressure of hydrogen sulfide in these experiments was kept high to avoid an effect of H_2S formed during the HDS reaction. Under the conditions of our study (5 MPa total pressure and 340 °C) naphthalene is mainly converted to tetralin over $NiMo/Al_2O_3$. Further hydrogenation took place extremely slowly, as demonstrated by the negligible amounts of decalin: at 75% conversion of naphthalene the sum of *cis*-decalin and *trans*-decalin was only 1%.



Scheme 3. Reaction network of the HDS of dibenzothiophene.

4. Discussion

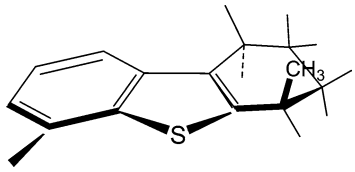
The aim of the present study was to compare the influence of N-containing molecules and aromatics on the HDS of DBT and 4,6-DMDBT in order to gain insight into the nature of the DDS and HYD active sites. The main difference between the HDS of DBT and 4,6-DMDBT is that DBT reacts predominantly via the DDS pathway and 4,6-DMDBT mainly via the HYD route. Thus, the selectivities for the DDS and HYD pathways in the HDS of DBT were 85 and 15% at 300 °C and 90 and 10% at 340 °C, respectively [16]. The product distribution showed that slow hydrogenation of biphenyl to cyclohexylbenzene took place, since the selectivity toward biphenyl formation decreased with weight time and the increase in the cyclohexylbenzene selectivity with weight time was higher than the decrease in the tetrahydrodibenzothiophene selectivity (Fig. 9). Therefore, the overall HDS network of DBT is as shown in Scheme 3.

In the HDS of 4,6-DMDBT, the selectivities toward the DDS and HYD are 15 and 85% at 300 °C and 25 and 75% at 340 °C, respectively (Figs. 1b and 2b). Thus, the product distribution is the reverse as in the HDS of DBT, where the DDS prevails. The selectivity toward the formation of 3,3′-dimethylbiphenyl remained constant during the reaction. This means that the ratio of the products obtained via two parallel pathways, DDS and HYD, did not change. Therefore, we conclude that the further hydrogenation of 3,3′-dimethylbiphenyl to methylcyclohexyltoluene in the HDS of 4,6-DMDBT does not take place. Temperature has a stronger promotional effect on the direct sulfur removal from both DBT and 4,6-DMDBT, since the DDS pathway is enhanced at 340 °C compared to 300 °C. Furthermore, the removal of sulfur from the partially hydrogenated intermediate improved, because the amount of 4,6-dimethyltetrahydrodibenzothiophene decreased and the amount of methylcyclohexyltoluene increased more strongly in the course of the reaction at higher temperature.

Table 1
Rate constants of the DDS and HYD pathways in the HDS of DBT and 4,6-DMDBT at 300 and 340 °C

	300 °C		340 °C	
	k_{DDS}	k_{HYD}	k_{DDS}	k_{HYD}
DBT	0.102	0.018	0.35	0.04
4,6-DMDBT	0.006	0.033	0.03	0.09

The HDS of DBT and 4,6-DMDBT can be well described as pseudo-first-order reactions with respect to the reactant, in good agreement with the literature [23–26]. The rate constants of the DDS and HYD pathways, k_{DDS} and k_{HYD}, can be obtained from the selectivity data. The kinetic results at 300 and 340 °C show that the overall HDS ($k_{DDS} + k_{HYD}$) of DBT is about three times faster than that of 4,6-DMDBT (Table 1). This value is somewhat smaller than the values of 5 to 6 [17,27,28] and 10 [13] reported in the literature. This can be explained by the high partial pressure of H_2S in our experiments to avoid the influence of H_2S released during HDS. Because hydrogen sulfide inhibits the HYD pathway to a lesser extent than the DDS pathway [18] and since HYD is the main route for the transformation of 4,6-DMDBT, the HDS of this molecule is less affected in the



Scheme 4. Conformation structure of 4,6-dimethyltetrahydrodibenzothiophene.

presence of H_2S. We also conclude from the data in Table 1 that the DDS of 4,6-DMDBT is 12 to 17 times slower than that of DBT. However, the HYD pathway of 4,6-DMDBT is two times faster than that of DBT. This must be due to the positive influence of the two methyl groups on the hydrogenation of an aromatic ring. Meille et al. observed a higher reactivity in the HDS of 2,8-DMDBT than in the HDS of DBT [17] and proposed an analogy with the hydrogenation of aromatics: toluene is more easily hydrogenated than benzene [29] and 3-methylbiphenyl more easily than biphenyl over metal sulfide catalysts [30]. In agreement with this explanation, we found that the hydrogenation of 3,3′-dimethylbiphenyl at 340 °C was two times faster than that of biphenyl over the $NiMo/Al_2O_3$ catalyst.

Although the HYD pathway is faster in the HDS of 4,6-DMDBT, the removal of sulfur from 4,6-dimethyltetrahydrodibenzothiophene takes place much slower than from tetrahydrodibenzothiophene, since the selectivity toward the formation of this intermediate is much higher in the HDS of 4,6-DMDBT than in that of DBT (cf. Figs. 2b and 9b). This means that the two methyl groups in the 4 and 6 positions not only sterically hinder the sulfur removal in the DDS but also in the HYD pathway. 4,6-DMDBT has a flat structure like DBT. The methyl groups adjacent to the sulfur atom are more spacious than the σ orbitals on the sulfur atom and hinder the molecule to approach the catalyst surface via the sulfur atom. Therefore, the adsorption of 4,6-DMDBT in the σ mode is weaker than that of DBT. When two double bonds of one benzene ring are hydrogenated, the hydrogenated part of the molecule is not flat any more (Scheme 4). The methyl group of the hydrogenated ring does not have to affect the adsorption because it can be turned away from the catalyst surface. However, the partially hydrogenated ring is puckered and one methylene group is under and one above the plane of the molecule. As a consequence, one of the hydrogen atom, at the carbon atom below the plane, hinders the adsorption. When a methyl group is present in the partially hydrogenated ring the structure is more rigid and the hydrogen of the methylene group extends further toward the catalyst suface. Therefore, the molecule is tilted on the surface and the adsorption of 4,6-dimethyltetrahydrodibenzothiophene is weaker than that of tetrahydrodibenzothiophene. Because of the resulting longer lifetime of 4,6-dimethyltetrahydrodibenzothiophene than of tetrahydrodibenzothiophene, the hydrogenation of the second benzene ring attains importance and 3,3′-dimethylbicyclohexyl is formed.

Fig. 10 shows that k_{HYD}, the rate constant for the HYD pathway in the HDS of DBT, strongly decreases in the presence of 2-MPy and 2-MPiper [16]; 2-MPiper retards k_{HYD} to a somewhat greater extent than 2-MPy. The major product of the HYD pathway is tetrahydrodibenzothiophene, but even at the highest partial pressure of 6 kPa 2-MPy and 2-MPiper the reaction of tetrahydrodibenzothiophene to cyclohexylbenzene was not totally inhibited. The DDS pathway was much less affected by 2-MPy and 2-MPiper; k_{DDS} was hardly affected at 2 kPa 2-MPiper and only slightly at 2 kPa 2-MPy. Since the HYD pathway was strongly inhibited already at low partial pressures of the N compounds and the total conversion changed slightly, the formation of biphenyl was enhanced. This enhancement resulted from the larger amount of DBT available for DDS, because HYD hardly occurred. This was proven by calculations in which it was assumed that the rate constant of the DDS pathway did not change in the presence of small amounts of 2-MPy and 2-MPiper and that the HYD pathway was completely blocked. At higher partial pressure of the N-containing molecules (6 kPa), the DDS pathway was more inhibited and 2-MPy had a stronger inhibitory effect than 2-MPiper (Fig. 10).

In the HDS of 4,6-DMDBT the difference between the effect of 2-MPy and 2-MPiper (Fig. 3) is less pronounced than in the case of DBT, as shown too by the rate constants of the DDS and HYD pathways (Fig. 11). For the HYD pathway the HDS of DBT and 4,6-DMDBT are similar: N-contain-

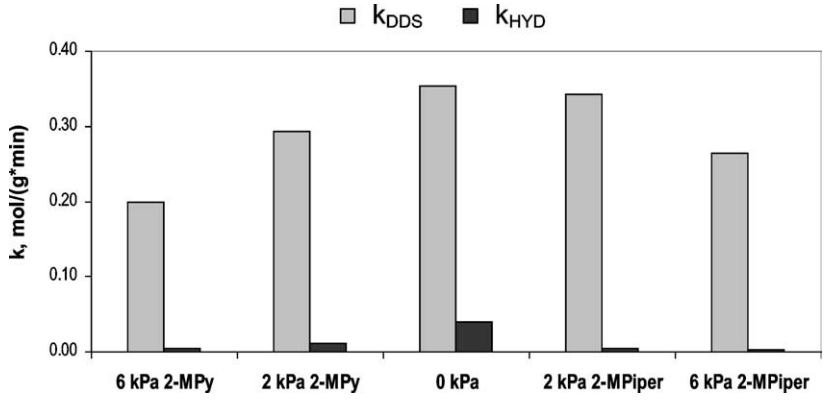


Fig. 10. Rate constants of the DDS and HYD pathways in the HDS of DBT in the presence of 2-MPy and 2-MPiper.

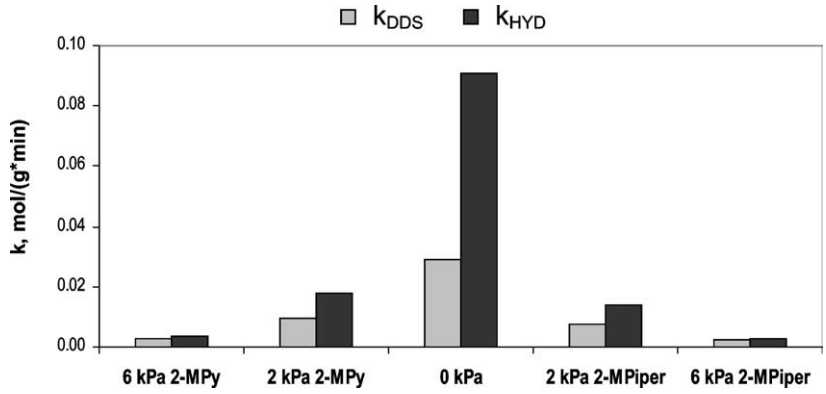


Fig. 11. Rate constants of the DDS and HYD pathways in the HDS of 4,6-DMDBT in the presence of 2-MPy and 2-MPiper.

ing molecules have a strong inhibitory influence and the effect of 2-MPiper is slightly stronger than that of 2-MPy (cf. Figs. 10 and 11). The inhibition can be indicated by the factor $k_{\mathrm{HYD}}/k'_{\mathrm{HYD}}$, where k_{HYD} is the rate constant of the HYD pathway in a single HDS reaction and k'_{HYD} is the HYD rate constant in a competitive experiment. The inhibition factors for the HYD route in the presence of 2-MPy and 2-MPiper were very similar in the HDS of DBT and 4,6-DMDBT. However, in the HDS of DBT the final product of the HYD pathway, cyclohexylbenzene, was observed at all partial pressures of N-containing molecules, whereas in the HDS of 4,6-DMDBT, at 6 kPa 2-MPy and 2-MPiper, the only product of the HYD route was 4,6-dimethyltetrahydrodibenzothiophene (Fig. 4b). Therefore, the real desulfurization of 4,6-DMDBT in the presence of N-compounds occurs predominantly via the DDS pathway. This indicates again the greater difficulty in the removal of sulfur from 4,6-dimethyltetrahydrodibenzothiophene than from tetrahydrodibenzothiophene. As indicated above, this difficulty may be due to the weaker adsorption of the tetrahydro-intermediate of 4,6-DMDBT than of DBT. Thus, this intermediate can hardly compete with the N-containing molecules for the active site. The DDS of 4,6-DMDBT was suppressed to a greater extent by the N compounds than that of DBT (cf. Figs. 10 and 11), which results from the weaker σ adsorption of 4,6-DMDBT than of DBT. Another difference in the HDS of DBT and 4,6-DMDBT is that the product of the DDS pathway is hydrogenated further in the case of DBT and does not react in the case of 4,6-DMDBT, despite the faster hydrogenation of 3,3′-dimethylbiphenyl as compared to biphenyl.

To better understand the nature of the inhibitory influence we studied the effect of 4,6-DMDBT on the HDN reactions. 4,6-DMDBT decreases slightly the hydrogenation of 2-MPy to 2-MPiper but has no influence on the C–N bond scission, since the conversion of 2-MPiper did not change in the presence of 4,6-DMDBT. The same results were obtained in the simultaneous HDN of 2-MPy and the HDS of DBT [16]. Previously, we had concluded that C–N and C–S bond cleavage take place at different sites, since the DDS of DBT and, correspondingly, the overall HDS was more strongly affected by 2-MPy, and DBT had an inhibitory effect on the hydrogenation of 2-MPy but not on the HDN of 2-MPiper. In the case of 4,6-DMDBT, however, 2-MPiper has a stronger retarding effect than 2-MPy on both DDS and HYD routes (Fig. 11). 4,6-DMDBT, in turn, had no influence on the C–N bond cleavage. DBT and 4,6-DMDBT can adsorb in the π mode and thus hinder the hydrogenation of 2-MPy. In the σ mode, however, the S-containing molecules adsorb apparently much weaker than 2-MPiper and therefore do not hinder the transformation of 2-MPiper.

A special case is the influence of 2-MPiper on the DDS of DBT [31]. Up to 1 kPa 2-MPiper promotes the DDS of DBT, but does not promote the DDS of 4,6-DMDBT. This enhancement was suggested to be the result of a structural or electronic modification of the catalyst surface through the adsorption of 2-MPiper in the σ mode. Because 2-MPiper promotes the DDS of DBT at low concentrations, the overall HDS is affected only slightly [31]. The DDS of 4,6-DMDBT is inhibited more strongly in the presence of 2 kPa 2-MPiper than that of DBT. This may be the result of the small adsorption constant of 4,6-DMDBT in the σ mode $K_{\text{2-MPiper}} \gg K^{\sigma}_{\mathrm{DBT}} \gg K^{\sigma}_{\text{4,6-DMDBT}}$ because of the hindrance of the methyl groups. This is why the DDS of 4,6-DMDBT is not improved at low partial pressures of 2-MPiper, in contrast to the DDS of DBT. Because the adsorption of 2-MPiper is much stronger than that of the S-containing molecules, the HDN of 2-MPiper is not affected by DBT and 4,6-DMDBT.

The composition of the hydrocarbons in the feed may affect the catalytic activity and selectivity under deep HDS conditions. Aromatic hydrocarbons in fuels have a detrimental effect on the catalyst activity [32]. In a series of papers Kabe and Ishihara and co-workers discussed the influence of solvents on the activity and selectivity of a sulfided $CoMo/Al_2O_3$ catalyst in the HDS of benzothiophene (BT) and DBT [33–35]. They found that the catalytic activity decreased in the order toluene > decalin > *n*-pentadecane > 1-methylnaphthalene in the HDS of BT and in the order *n*-heptane > xylene > decalin > tetralin in the HDS of DBT. The activation energies were unaffected by the solvents, but the heats of adsorption of BT and DBT on the $CoMo/Al_2O_3$

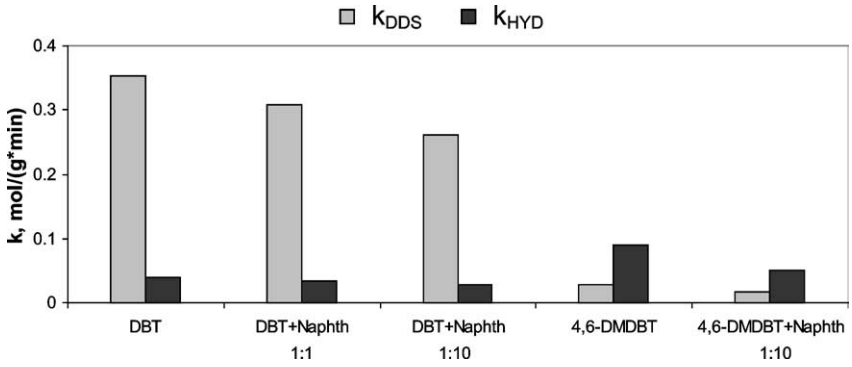


Fig. 12. Rate constants of the DDS and HYD pathways in the HDS of DBT and 4,6-DMDBT in the presence of naphthalene.

catalyst depended on the solvent and correlated well with the catalytic activity. Solvents with the largest retarding effects decreased the heats of adsorption of BT and DBT to a greater extent. Furthermore, in the HDS of DBT the solvent mainly affected the conversion to biphenyl, whereas it hardly affected the formation of cyclohexylbenzene [35]. According to a Langmuir–Hinshelwood model, with reactant and solvent molecules in the gas phase, the heat of adsorption of a reactant should not be affected by the presence of another molecule. However, if we assume that a solvent layer is present on the catalyst surface, then there will be an interaction between reactant and solvent molecules and the interaction energy will influence the apparent heat of adsorption. Ishihara et al. worked at rather low temperatures of 150 to 250 °C, which favors the formation of a liquid layer on the catalyst surface.

We found no difference between decane and toluene in the HDS rates of DBT and 4,6-DMDBT (Fig. 6); the product distribution was also unaffected. Toluene did not undergo hydrogenation to methylcyclohexane when DBT or 4,6-DMDBT were present in the feed. This indicates that the adsorption of toluene is much weaker than that of the S-containing molecules. The results reported by Kabe et al. [33] indicate that the effects of the solvent are more pronounced below 300 °C. At 300 °C, there was hardly any difference between *n*-heptane and xylene, which are very similar to the solvents used in our study. Moreover, the effects of the solvent were more pronounced at 0.1 than at 1 wt% DBT in the feed [34]. Our experiments were performed at 340 °C with 1.4 wt% DBT and 1.6 wt% 4,6-DMDBT. Therefore, our results do not contradict the results of Ishihara et al. At 340 °C, toluene, as an aromatic molecule, does not compete with the S compounds for the active sites, although there is a large excess amount of it in the feed.

Only limited information is available about the inhibition of the HDS of thiophene [5], DBT [36] and 4,6-DMDBT [9,37–40] by polycyclic aromatic compounds. Most studies indicate that the influence of aromatics on HDS is not negligible but that it is much weaker than that of basic organonitrogen compounds. Our results show that the rate constant of the HDS of DBT decreased by a factor of 1.34 and that of 4,6-DMDBT by a factor of 1.8 in the presence of 10 kPa naphthalene (Figs. 7a and 7b). Because naphthalene did not change the selectivities, the rate constants of the DDS and HYD pathways are affected to the same extent (Fig. 12). Farag et al. reported that a 100-fold excess of naphthalene relative to 4,6-DMDBT resulted in only slight decrease in the HYD selectivity [40]. They also noted, however, that the HYD/DDS ratio varied with the conversion of 4,6-DMDBT. These changes in the HYD/DDS ratios might be due to the fact that their study was carried out in an autoclave. In that case, the quantitative analysis can easily have an error of 10 to 15%. We believe that the HYD/DDS ratio stays constant within a single experiment on the HDS of 4,6-DMDBT, since the selectivity toward 3,3′-dimethylbiphenyl formation is constant in the course of the reaction (Figs. 1b and 2b). The HYD/DDS ratio is also unaffected by the presence of naphthalene. In the case of the HDS of DBT, biphenyl is hydrogenated further to cyclohexylbenzene. The presence of naphthalene does not change the product distribution in the HDS of DBT (Fig. 12).

Under our reaction conditions naphthalene converts predominantly to tetralin; only small amounts of decalin were observed, in good agreement with results obtained by Isoda et al. [38,39]. The effect of S-containing molecules on the hydrogenation reaction has been studied mainly in terms of the influence of H_2S [41–43]. We investigated the effect of DBT and 4,6-DMDBT on the hydrogenation of naphthalene at a reasonably high partial pressure of H_2S in order to avoid the influence of the H_2S released during the HDS reaction. Our data indicate that hydrogenation is inhibited in the presence of S compounds and that DBT and 4,6-DMDBT have the same effect (Fig. 8). Both DDS and HYD pathways of the HDS of DBT and 4,6-DMDBT are affected to the same extent in the presence of naphthalene, and the hydrogenation of naphthalene is equally suppressed by DBT and 4,6-DMDBT. Thus, we conclude that the hydrogenation of naphthalene takes place at both the DDS and the HYD sites. Moreover, we assume that the DDS and the HYD sites are the same and that the only factor, which determines the HDS pathway, is the adsorption conformation of the S-containing molecule. Kogan et al. also suggested that the HYD pathway of the HDS of thiophene takes place at the same catalytic sites as the DDS pathway [44].

5. Conclusion

In studying the mutual influence of the HDS of 4,6-DMDBT and HDN of 2-MPy and 2-MPiper, we found that both N-containing molecules are strong inhibitors of HDS. Moreover, the inhibitory effect of 2-MPiper was somewhat stronger than that of 2-MPy for the DDS and HYD pathways of the HDS of 4,6-DMDBT. 4,6-DMDBT and DBT suppressed the hydrogenation of 2-MPy but did not affect the C–N bond cleavage in the HDN of 2-MPiper. Therefore, we assume that adsorption of 2-MPiper on both DDS and HYD sites is much stronger than that of 4,6-DMDBT or DBT.

When toluene is used as a solvent, neither the rates of the HDS of DBT and 4,6-DMDBT nor the product distributions are affected. Toluene itself does not undergo hydrogenation in the presence of S or N compounds. Thus, the molecules of the solvent do not compete with reactant for the active sites.

Naphthalene inhibited the DDS and HYD pathways in the HDS of DBT and 4,6-DMDBT to the same extent. Thus, the hydrogenation of naphthalene takes place at both the DDS and the HYD sites. DBT and 4,6-DMDBT suppressed the hydrogenation of naphthalene to the same extent. We assume that the adsorption of naphthalene is much weaker than that of S-containing molecules.

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