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# Mutual influence of the HDS of dibenzothiophene and HDN of 2-methylpyridine

Marina Egorova and Roel Prins *

*Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology (ETH), 8093 Zurich, Switzerland*

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**Abstract**

The influence of 2-methylpyridine and 2-methylpiperidine on the hydrodesulfurization of dibenzothiophene (DBT) and the effect of DBT on the hydrodenitrogenation of 2-methylpyridine and 2-methylpiperidine were studied over a sulfided $NiMo/Al_2O_3$ catalyst at 5 MPa, 35 kPa $H_2S$, and 300 and 340 °C. Both N-containing molecules strongly suppressed the hydrogenation pathway of the hydrodesulfurization of DBT and inhibited the direct desulfurization route at both reaction temperatures. The inhibitory effect on the direct desulfurization was stronger for 2-methylpyridine than for 2-methylpiperidine. $H_2S$ promoted the hydrogenation of 2-methylpyridine up to 10 kPa and inhibited it at higher partial pressures. $H_2S$ had a positive influence on the hydrodenitrogenation conversions of 2-methylpiperidine and 2-methylpyridine. DBT had a negative effect on the hydrogenation of 2-methylpyridine, but did not influence the C–N bond cleavage of 2-methylpiperidine. Therefore, C–N and C–S bond breaking takes place at different active sites, whereas the hydrogenation sites for N- and S-containing molecules may be the same.


*Keywords:* Hydrotreating; Hydrodesulfurization; HDS; Dibenzothiophene; DBT; Hydrodenitrogenation; HDN; 2-Methylpyridine; 2-Methylpiperidine

## 1. Introduction

New environmental legislation has put the oil industry under increased pressure to limit the level of sulfur in gasoline and diesel fuel with a view to reducing exhaust emissions. A sulfur specification of 350 ppm is currently practiced in the EEC and a sulfur content as low as 50 or even 10 ppm is foreseen for the year 2005. Basic nitrogen compounds inhibit the hydrodesulfurization (HDS) of sulfur compounds through competitive adsorption, but in normal HDS this influence is negligible because the amount of N-containing molecules in gasoil is much smaller than that of S-containing molecules. Nitrogen compounds will be harmful in deep HDS, however, because then the amounts of N- and S-containing molecules are comparable.

The significance of competitive adsorption in hydrotreating reactions has been recognized for a long time [1] and several research groups investigated the effect of N-compounds on HDS [2–8] and of S-compounds on hydrodenitrogenation (HDN) [2,3,9,10]. Studies of the mutual influence of S- and N-containing molecules during hydrotreating showed that N-compounds have an inhibitory effect on HDS reactions, whereas the presence of S-containing molecules in some cases promotes HDN [10,11]. In the simulation of the kinetics, it is usually assumed that one active site is present on which HDS and HDN reactions take place [7,12], although the presence of two different sites (desulfurization and hydrogenation) was already reported in 1964 for the HDS of thiophene [13].

A systematic study of the interaction between catalytic hydrodesulfurization and hydrodenitrogenation was made by Satterfield et al. [2]. They studied the mutual influences of the HDS of thiophene and HDN of pyridine in the presence of sulfided $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, $NiW/Al_2O_3$, and $NiW/SiO_2–Al_2O_3$ catalysts. Over all four catalysts pyridine inhibited the HDS reaction, whereas thiophene had a dual effect on HDN. At low temperatures thiophene inhibited the HDN reaction by competing with pyridine for hydrogenation sites and at high temperatures the dominant effect was an improvement of C–N bond cleavage by $H_2S$, the product of the HDS reaction. The enhancement of the HDN by $H_2S$ was ascribed to the conservation of the catalyst in a completely sulfided state, in which it has a better HDN activity. The HDS sites were classified into two types: (i) active

* Corresponding author.
*E-mail address:* prins@tech.chem.ethz.ch (R. Prins).

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sites that are responsible for the majority of the HDS activity, but that are extremely sensitive to basic nitrogen compounds, and (ii) active sites that are less active in HDS, but also less susceptible to poisoning. Furthermore it was shown [3] that the first type of sites was responsible for the hydrogenation of S-containing molecules, because tetrahydrothiophene was not observed when pyridine was present in the feed.

Two reaction pathways were found for the HDS of dibenzothiophene (DBT), which take place on different sites. The first type of sites is responsible for the hydrogenation pathway, and the second type of sites is facilitating the direct sulfur removal or hydrogenolysis [4–6,14–18]. N-containing molecules were found to be strong inhibitors for the minor, hydrogenation pathway of the HDS of DBT. The overall conversion of DBT decreased only slightly, suggesting that the amount of product formed via the hydrogenolysis pathway increased. Some authors have even claimed an enhancement of this route in the presence of N-compounds [4–6].

We have studied the mutual influences of the HDS of DBT and the HDN of 2-methylpyridine and 2-methylpiperidine over a sulfided $NiMo/Al_2O_3$ catalyst. DBT was chosen because it allows the study of the removal of sulfur by the direct desulfurization pathway (hydrogenolysis) as well as by the hydrogenation pathway (hydrogenation followed by desulfurization). Pyridine is the smallest model molecule for studying HDN, but, although the reactions taking place in its HDN are now well understood, the study of its HDN kinetics proved to be extremely difficult. The reason for this difficulty is that two molecules of piperidine, the first intermediate in the HDN of pyridine, disproportionate to N-pentylpiperidine and ammonia [19]. However, the introduction of a methyl group on the $\alpha$ carbon atom of piperidine strongly suppresses the disproportionation, so that it hardly interferes with the other reactions taking place during the HDN of 2-methylpyridine and 2-methylpiperidine [20]. Therefore, we decided to use 2-methylpyridine and 2-methylpiperidine in our study of the influence of N-containing molecules on the HDS of DBT.

## 2. Experimental

The $NiMo/\gamma\text{-}Al_2O_3$ catalyst used in this work 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 $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Aldrich), followed by an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (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.

Reactions were carried out in a continuous mode in a fixed-bed inconel reactor (15 mm i.d., 320 mm long) that was heated by an oven. A sample of catalyst (0.05 g) 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 $H_2$ 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. The experiments were carried out at 300 and 340 °C. The composition of the gas-phase feed consisted of 130 kPa toluene (as solvent for the DBT and amine), 8 kPa dodecane (as reference for DBT and its derivatives in the GC analysis), 11 kPa heptane (as reference for the N-compounds in the GC analysis), 1 kPa dibenzothiophene, 2–10 kPa amine reactant, 35 kPa $H_2S$ (unless noted otherwise), and 4.8 MPa $H_2$. Toluene was chosen as the solvent due to its good ability to dissolve aromatic heterocycles like dibenzothiophene. We checked that in the presence of S- or N-containing molecules toluene did not undergo hydrogenation to methylcyclohexane. The partial pressure of $H_2S$ was kept sufficiently higher than that of DBT to avoid the influence of $H_2S$ formed during the HDS reaction.

The reaction products were analyzed by on- and off-line gas chromatography with a Varian 3800 GC instrument equipped with a CP-Sil 8 CB fused silica capillary column (50 m × 0.25 mm × 0.25 μm). Off-line analysis was used for the HDS of DBT because of the high boiling points of the reactant and reaction products. Detection was performed with a flame ionization detector as well as with a pulsed flame photometric detector, which is very useful for detecting small amounts of S- and N-containing compounds. 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 ($\tau$) 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, and during 2 weeks of operation almost no catalyst deactivation was observed.

## 3. Results

### 3.1. HDS of dibenzothiophene

The results of the experiments of the HDS of DBT carried out at 300 and 340 °C (Figs. 1 and 2) show that the reaction goes via two parallel pathways (Scheme 1): direct desulfurization (DDS), which yields biphenyl (BP), and hydrogenation (HYD) followed by desulfurization, which gives first tetrahydrodibenzothiophene (TH-DBT) and then cyclohexylbenzene (CHB). The two final products are biphenyl and cyclohexylbenzene. At 300 °C the selectivity of the biphenyl formation is about 85% at low and 80% at high weight time (Fig. 1b), whereas at the higher temperature of 340 °C those values are 90 and 70%, respectively (Fig. 2b). These results indicate that the DDS route is much easier than the HYD route, since the amount of biphenyl is six to nine times higher than the sum of tetrahydrodibenzothiophene and cyclohexylbenzene. Slow hydrogenation of biphenyl to

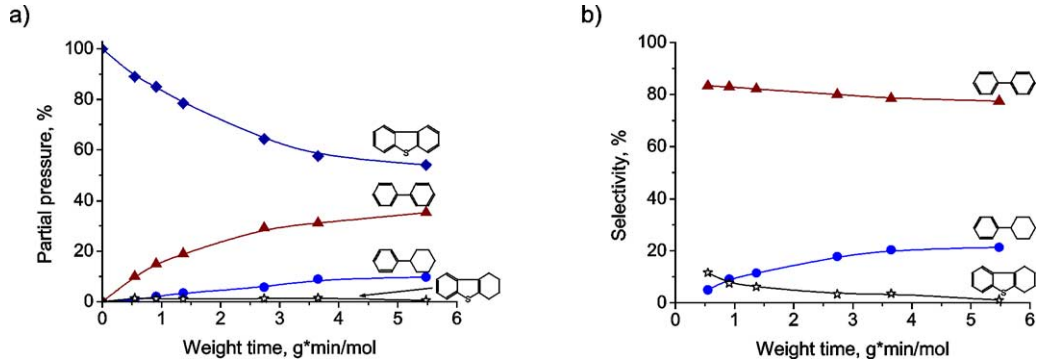



Fig. 1. Relative partial pressures (a) and selectivities (b) of the products of the HDS of dibenzothiophene at 300 °C as a function of weight time.

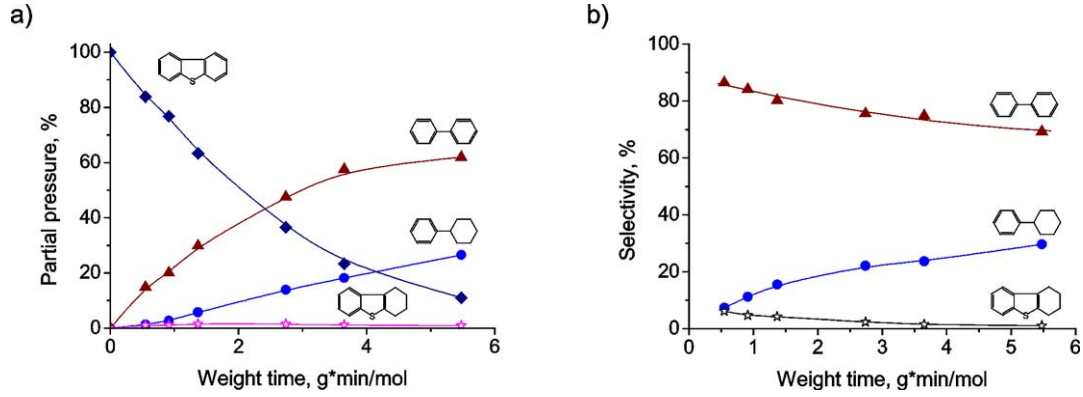
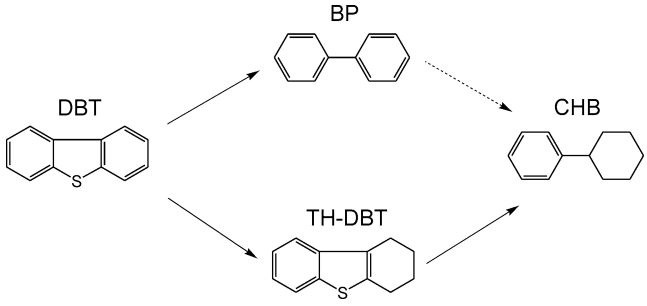



Fig. 2. Relative partial pressures (a) and selectivities (b) of the products of the HDS of dibenzothiophene at 340 °C as a function of weight time.




Scheme 1. Reaction network of the HDS of dibenzothiophene.

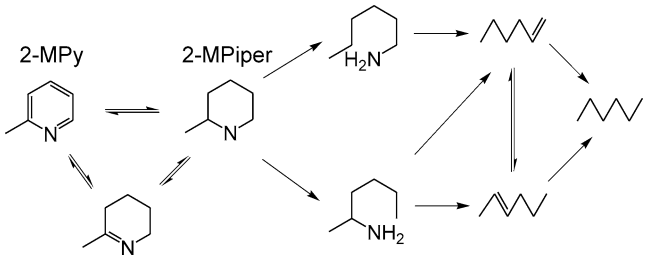
cyclohexylbenzene took place at both reaction temperatures, since the biphenyl selectivity decreased with weight time and the increase of the cyclohexylbenzene selectivity with weight time was higher than the decrease of the tetrahydrodibenzothiophene selectivity. The resulting overall mechanism of the HDS of DBT is represented in Scheme 1.

The DDS pathway is slightly enhanced at higher temperatures, since the selectivity toward biphenyl formation at low weight time is higher at 340 than at 300 °C. Thus, an increase of the temperature has a positive effect on the desulfurization reaction. At high weight time, the biphenyl selectivity was lower at 340 than at 300 °C, due to increased hydrogenation of biphenyl. At 340 °C and $\tau = 5.5$ g min/mol the DBT conversion was about 90%, but at 300 °C it was only 45%. As a consequence, the hydrogenation of biphenyl is not only intrinsically faster but also less inhibited by DBT at 340 °C.

The HDS of DBT is generally assumed to be a first-order reaction with respect to DBT [11]. Our DBT conversions at 300 °C confirm this, since we obtained a linear dependency when plotting $\ln[(C_{\mathrm{DBT}})/(C_{\mathrm{DBT}})^0]$ versus weight time and a high $R^2$ value. Also in the presence of the N-containing molecules the HDS of DBT could be approximated with first-order kinetics. Therefore, all the rate constants of the HDS of DBT with and without N-compounds at 300 °C were evaluated assuming the HDS of DBT to be a first-order reaction.

### 3.2. Inhibition of the HDS by N-containing molecules

The HDS of DBT was studied in the presence of 2-methylpyridine (2-MPy) and 2-methylpiperidine (2-MPiper) at 300 and 340 °C at different conversion levels of the N-compounds. The HDN network of 2-MPy and 2-MPiper was determined earlier [20] and is presented in Scheme 2. As expected, 2-MPiper is the only primary product in the HDN of 2-MPy, since the HDN of heterocyclic N-containing aromatic molecules can only occur after ring hydrogenation [21]. The HDN of 2-MPiper showed that four compounds, 1-aminohexane, 2-aminohexane, 2-methylpyridine, and 2-methyl-3,4,5,6-tetrahydropyridine, have nonzero selectivity at zero conversion of 2-MPiper and thus might be




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

considered to be primary products. Actually, aminoalkenes and aminoalkanethiols are expected to be primary products. Aminoalkenes, which are the primary products of the ring opening via elimination of alkylpiperidine, were not observed, probably because of their fast hydrogenation to the corresponding amines. Aminoalkanethiols can be formed by nucleophilic substitution of the alkylpiperidine by $H_2S$. They are probably not observed because of a fast $H_2S$ elimination or C–S hydrogenolysis. Comparison of the conversion of 2-aminohexane and 1-aminohexane showed that the reactivity of 2-aminohexane is higher than that of 1-aminohexane. Despite this higher reactivity, much more 2-aminohexane than 1-aminohexane was detected in the HDN of 2-MPiper [20]. Therefore, it can be concluded 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 actually has a negative rather than a positive influence on the C–N bond breaking. This suggests that the HDN of 2-MPiper occurs by nucleophilic substitution to 5-aminohexanethiol rather than via elimination to 5-aminohexene-1.

We first studied the HDS of 1 kPa DBT at 300 °C in the presence of 2, 6, and 10 kPa of 2-MPy and 2-MPiper. At this temperature 2-MPy only converts to 2-MPiper and, because of thermodynamics [22,23], this reaction is irreversible. In the presence of the N-containing molecules the HYD pathway of the HDS of DBT is strongly suppressed, since the selectivity toward biphenyl formation is increased from 85 to 96–98%. The conversion of DBT decreased with increasing partial pressure of the N-compounds, indicating that 2-MPy

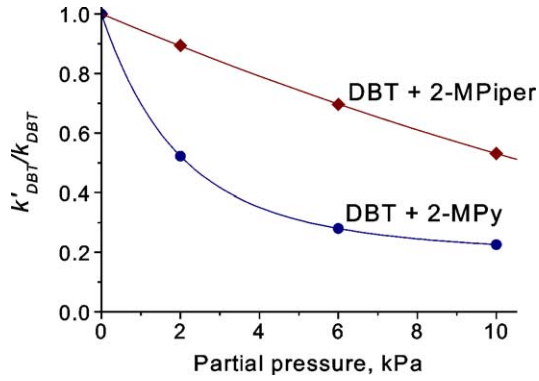



Fig. 3. Inhibition of the HDS of 1 kPa DBT in the presence of 2-methylpyridine (●) and 2-methylpiperidine (◆) at 300 °C.

and 2-MPiper not only suppress the hydrogenation route, but inhibit the hydrogenolysis (DDS) pathway as well. Since the transformation of DBT is still well described by first-order kinetics, we calculated $k'_{DBT}$ (the rate constant of the HDS of DBT in the presence of the N-compound) and plotted the ratio $k'_{DBT}/k_{DBT}$, where $k_{DBT}$ is the rate constant of the HDS of DBT alone, versus the partial pressure of the N-containing molecule in the gas phase (Fig. 3). One can see that the inhibition effect of 2-MPy is much stronger than that of 2-MPiper. While no conversion of 2-MPiper was observed in the competitive experiments, the conversion of 2-MPy varied from 50 to 20% when increasing its partial pressure in the feed.

At 340 °C, DBT could be fully converted and 2-MPy and 2-MPiper underwent hydrodenitrogenation in the simultaneous HDS and HDN reactions. Different partial pressures of 2-MPy and 2-MPiper (2, 6, and 10 kPa) were used. Again, just trace amounts of products formed via the HYD pathway of the HDS of DBT were observed; this route is strongly suppressed at 340 °C as well. The inhibition of the direct desulfurization pathway is clearly seen at high partial pressures of 2-MPy and 2-MPiper (Fig. 4). The decrease of the DBT conversion is almost the same in the presence of 10 kPa of both N-compounds. However, at 2 and 6 kPa the inhibitory influence of 2-MPy is stronger, as was observed at 300 °C. For the lowest concentration of 2-MPy and 2-MPiper studied (2 kPa) one can hardly see any influence on

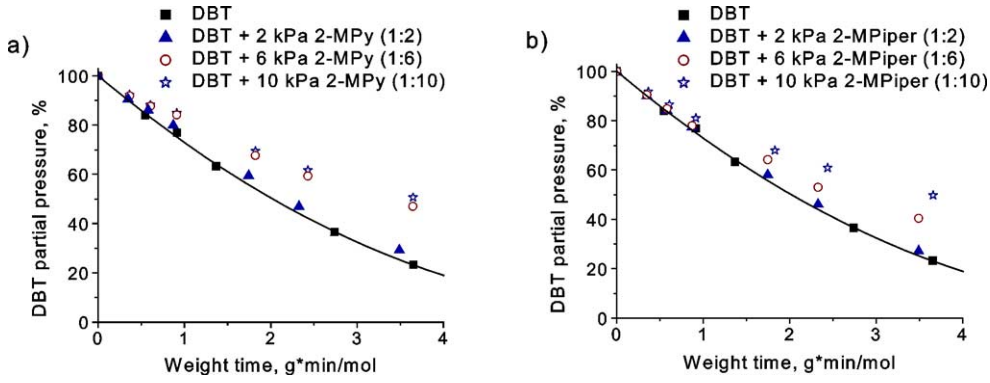



Fig. 4. Inhibition of the HDS of DBT in the presence of 2-methylpyridine (a) and 2-methylpiperidine (b) at 340 °C.

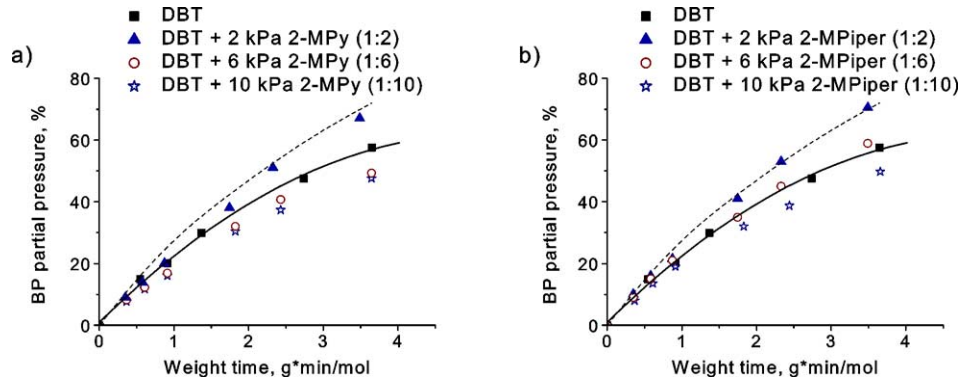



Fig. 5. Relative partial pressures of biphenyl in the HDS of DBT in the presence of 2-methylpyridine (a) and 2-methylpiperidine (b) at 340 °C.

the DBT conversion and in these experiments we observed an enhancement of the biphenyl formation (Fig. 5). This can be explained by the blocking of the HYD pathway, so that a higher amount of DBT is available for DDS. We verified this by kinetic calculations, assuming the DDS and HYD reactions of the DBT HDS to be first-order irreversible reactions running in parallel. The rate constants were obtained using the selectivity data (90% for DDS and 10% for HYD). Then excluding the HYD pathway from the HDS network of DBT we obtained 72% conversion toward biphenyl at $\tau = 3.5$ g min/mol. In Fig. 5 the theoretical conversion of DBT to biphenyl in the absence of the HYD pathway is presented by a dashed line. Therefore, we conclude that the enhancement of the biphenyl formation is due to the absence of the HYD route. At low concentrations of 2-MPy and 2-MPiper, the inhibition of the DDS pathway is minor and the DDS pathway profits fully from the blocking of the HYD pathway. At higher concentrations of 2-MPy and 2-MPiper, the DDS pathway is slowed down as well and the biphenyl curves lie under the curve obtained in the absence of the N-containing molecules (Fig. 5).

### 3.3. Effect of $H_2S$ on the HDN of 2-methylpyridine

Before studying the influence of DBT on the HDN of 2-MPy, we investigated the effect of $H_2S$ on the two reactions that take place in the HDN of 2-MPy: the hydrogenation of 2-MPy and the removal of nitrogen from 2-MPiper. Experiments on the hydrogenation of 2-MPy were performed at 300 °C, because at this temperature only hydrogenation to 2-MPiper occurred; 2-MPiper, in turn, did not react further. The removal of nitrogen from 2-MPy was studied at 340 °C.

The cleavage of the C($sp^3$)–N bond is known to be promoted by $H_2S$ [24–26]. In agreement with these results, our experiments of the HDN of 2-MPiper showed an enhancement of the HDN conversion with increasing $H_2S$ partial pressure from 30 to 160 kPa (Fig. 6).

The conversion of 2-MPy at a fixed weight time of 3 g min/mol and a temperature of 300 °C is presented in Fig. 7 as a function of the $H_2S$ pressure. The 2-MPy conversion increased up to 10 kPa $H_2S$ and decreased at higher $H_2S$ partial pressures. In the literature only inhibition of the

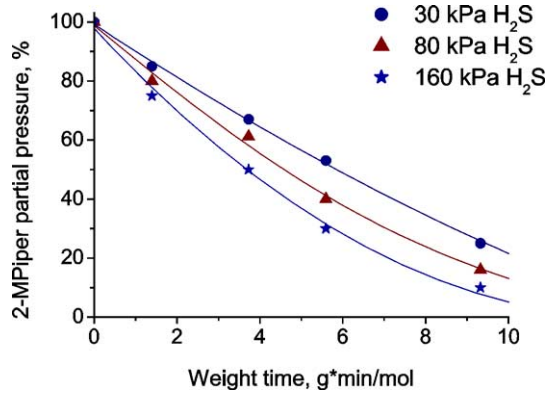



Fig. 6. HDN of 2-methylpiperidine at 340 °C and different $H_2S$ partial pressures.

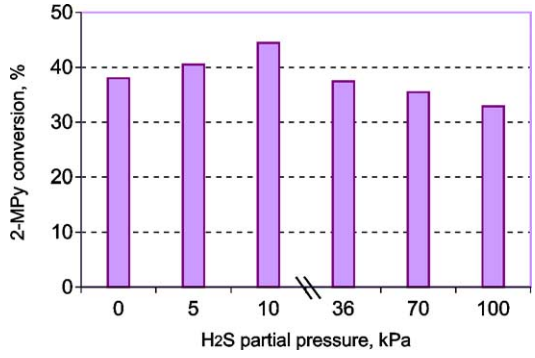



Fig. 7. Conversion of 2-methylpyridine at 300 °C and different $H_2S$ partial pressures and a weight time of 3 g min/mol.

hydrogenation of N-containing aromatic molecules by $H_2S$ has been reported [27,28]. The occurrence of an optimum $H_2S$ concentration may be caused by the fact that at high concentrations $H_2S$ adsorbs on the active sites and poisons the hydrogenation reaction, whereas at very low $H_2S$ concentrations the catalyst surface reconstructs and the number of hydrogenation sites decreases.

The hydrogenation of 2-MPy at 300 °C starts quite fast and levels off with weight time (Fig. 8). To determine if poisoning by the product was responsible for this leveling off, the reaction was repeated in the presence of 1 kPa 2-MPiper at a ratio of 2-MPy/2-MPiper = 6. The results show

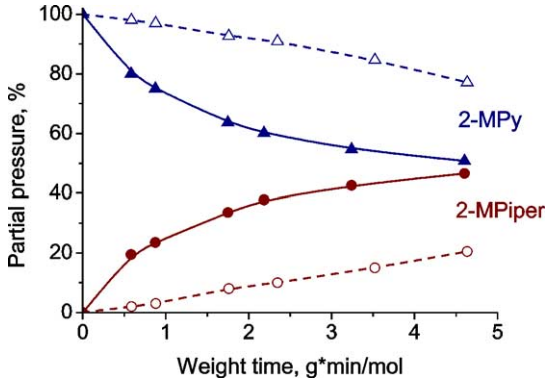



Fig. 8. Hydrogenation of 6 kPa 2-methylpyridine at 300 °C in the presence (- - -) and absence (—) of 1 kPa 2-methylpiperidine.

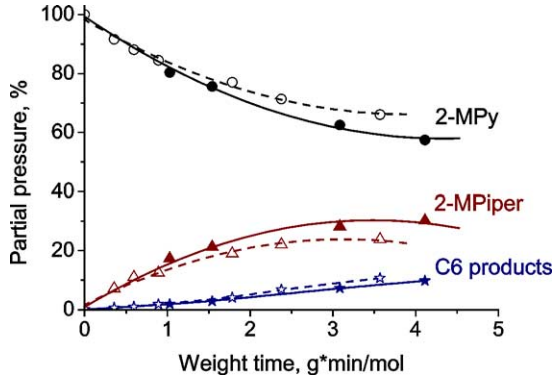



Fig. 10. HDN of 6 kPa 2-methylpyridine at 340 °C in the presence (- - -) and absence (—) of 1 kPa DBT.

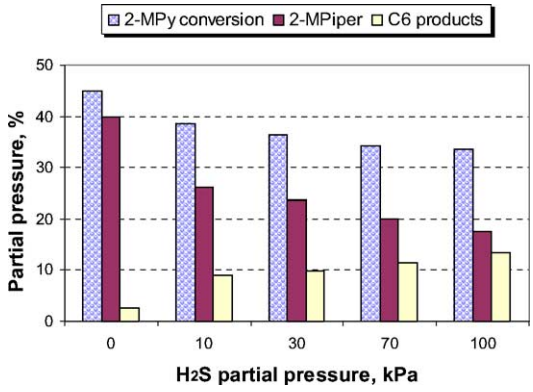



Fig. 9. Total conversion and product distribution in the HDN of 2-methylpyridine at 340 °C and different $H_2S$ partial pressures.

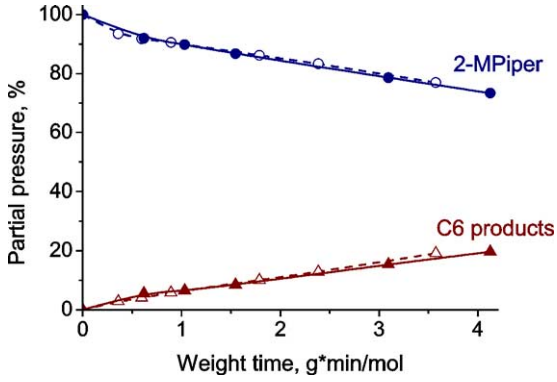



Fig. 11. HDN of 6 kPa 2-methylpiperidine at 340 °C in the presence (- - -) and absence (—) of 1 kPa DBT.

that such a small amount of 2-MPiper indeed strongly inhibits the hydrogenation reaction (Fig. 8). It indicates that 2-MPiper strongly adsorbs on the hydrogenation sites.

Studying the effect of $H_2S$ on the HDN of 2-MPy at 340 °C, we observed a decrease of 2-MPy conversion with an increase of $H_2S$ partial pressure from 0 to 10 kPa. The loss in the conversion was mainly due to the decrease of 2-MPiper formation, whereas the HDN conversion of 2-MPy to nitrogen-free $C_6$ products was enhanced almost by a factor of four (Fig. 9). Successive increases of the $H_2S$ partial pressure up to 100 kPa (30, 70, and 100) led to a further decrease of the 2-MPy conversion and 2-MPiper formation and to the increase of the HDN conversion of 2-MPy. However, these changes were not that significant as for the increase in $H_2S$ partial pressure from 0 to 10 kPa (Fig. 9). Therefore, we can conclude that at 340 °C $H_2S$ has a negative effect on the hydrogenation of 2-MPy and a positive influence on the HDN conversion of 2-MPy as well as 2-MPiper. These results are in good agreement with those reported in [24,25].

### *3.4. Influence of DBT on the HDN of N-compounds*

The N-containing molecules had a negative influence on both pathways of the HDS of DBT. They almost blocked the HYD pathway and inhibited the DDS pathway. In turn, DBT has a negative effect on the hydrogenation of 2-MPy at 300 °C. The conversion of 6 kPa 2-MPy to 2-MPiper decreased almost by a factor of two in the presence of 1 kPa DBT (not shown). This cannot be caused by the $H_2S$ released in the HDS reaction since the partial pressure of $H_2S$ in the feed was 35 kPa, 35 times higher than that of DBT. The observed inhibition effect must therefore be due to the presence of DBT.

The influence of DBT on the HDN of the N-containing molecules was also studied at 340 °C, when C–N bond cleavage took place as well. The results of the HDN of 2-MPy, carried out in parallel with the HDS of DBT, and of the HDN of 2-MPy alone are presented in Fig. 10. In the presence of DBT, the conversion of 2-MPy and the yield of 2-MPiper decreased, while the amount of C6 products (hexane, hexenes, and hexylamines) hardly changed. The conversion of 2-MPy was lower at 340 than at 300 °C, since the hydrogenation of 2-MPy to 2-MPiper becomes reversible. The inhibitory influence of DBT on the hydrogenation of 2-MPy was less strong at 340 than at 300 °C. The influence of DBT on the C–N bond cleavage of 2-MPiper to hexane, hexenes, and hexylamines [20] was studied at 340 °C. Fig. 11 shows that DBT does not have any influence on the HDN of 2-MPiper.

## 4. Discussion

As originally proposed by Houalla et al. [29], the reaction pathways for the HDS of DBT are (i) direct desulfurization to form biphenyl and (ii) hydrogenation to give 1,2,3,4-tetrahydrodibenzothiophene or 1,2,3,4,10,11-hexahydrodibenzothiophene, which are further desulfurized to cyclohexylbenzene. Our results show that over NiMo the desulfurization pathway is six times faster than the hydrogenation pathway at 300 °C and nine times faster at 340 °C (Figs. 1b and 2b). Desulfurization of the hydrogenated intermediate tetrahydrodibenzothiophene is also much faster than hydrogenation, since only amounts of tetrahydrodibenzothiophene as small as 1–2% were observed during the HDS reaction.

The biphenyl formed in the DDS pathway was slowly hydrogenated to cyclohexylbenzene at 300 °C and somewhat faster at 340 °C (Figs. 1b and 2b). The hydrogenation of biphenyl to cyclohexylbenzene during the HDS of DBT has also been observed in other studies [15,16,18]. It is more evident over NiMo catalysts than over CoMo catalysts [30], because NiMo is a better hydrogenation catalyst in comparison with CoMo. The higher activity of a nickel-containing catalyst has been ascribed to the structure of the catalyst. NiMo catalysts are more sensitive to the inhibiting effect of $H_2S$ than CoMo catalysts in HDS reactions [31–33]. This indicates that the state of sulfidation of a NiMo catalyst changes more strongly with the $H_2S$ partial pressure than that of a CoMo catalyst. At lower $H_2S$ partial pressure, the NiMo catalyst may be more easily depleted of sulfur and thus have a better hydrogenation activity. No further hydrogenation of cyclohexylbenzene to bicyclohexyl was observed under our reaction conditions. Therefore, Scheme 1 describes our results of the HDS of DBT best.

The hydrogenation of biphenyl, in the absence of S- or N-containing molecules, was about 10 times slower over our $NiMo/Al_2O_3$ catalyst than the hydrogenation of the biphenyl formed during the HDS reaction, however. Similarly low hydrogenation rates of biphenyl were obtained by Nagai et al. [5]. In their study of the HDS of DBT, they changed a feed, that contained 5 wt% DBT, to a feed containing 5 wt% DBT and 1 wt% biphenyl, and later switched back to the initial feed. No noticeable changes in the concentration of the cyclohexylbenzene formed were observed after the changes in the feed composition. We ascribe the difference between the hydrogenation of added biphenyl and of biphenyl formed in situ to hidden kinetics. When biphenyl is formed in situ, by the DDS of DBT, it is still adsorbed on the catalyst surface. In this flat, adsorbed state it can directly be hydrogenated, before desorbing from the catalytic site. When added to the gas phase, biphenyl has to diffuse to the catalytic sites and adsorb. In the gas phase, the two phenyl rings of biphenyl are not coplanar and some activation energy has must brought up to adsorb biphenyl in a flat conformation. This may explain the difference in the rate of hydrogenation between added and in situ formed biphenyl.

$H_2S$ inhibits the DDS pathway of the HDS of DBT strongly, but the HYD pathway only slightly [34]. This suggests that the hydrogenolysis and hydrogenation of DBT proceed on different catalytic sites. The sites active for the hydrogenation of DBT are very sensitive to poisoning by nitrogen bases, whereas the sites responsible for direct C–S bond cleavage are less susceptible to poisoning [4,5]. It was even reported that acridine has a promotion effect on the direct desulfurization of DBT over sulfided NiMo- and NiW-supported catalysts [35,36]. However, it has never been confirmed by systematic studies.

In the competitive HDS and HDN experiments at 300 °C, with feeds containing 1 kPa DBT and different partial pressures (2, 6, and 10 kPa) of 2-MPy or 2-MPiper, a decrease of the total conversion of DBT was observed in all reactions. The inhibition was stronger in the presence of 2-MPy than in 2-MPiper (Fig. 3). The HDS rate constant ($k'_{DBT}$) changed slightly in the presence of 2 kPa 2-MPiper, whereas in the presence of 2 kPa 2-MPy it decreased by 50%. The products of the HYD pathway of the HDS of DBT, such as tetrahydrodibenzothiophene and cyclohexylbenzene, were observed in very small amounts (2–4% of the total conversion). This shows that even small amounts of N-compounds significantly inhibit the hydrogenation of DBT and means that the slight inhibition of the HDS of DBT at 2 kPa of 2-MPiper is mainly due to the small contribution of the HYD route. At higher concentrations of 2-MPiper the inhibition of the DDS route becomes obvious. In the presence of 2-MPy, the DDS pathway is inhibited already at low 2-MPy partial pressures.

At the higher temperature of 340 °C, the DDS pathway was enhanced (Fig. 2b) and less sensitive to the low concentrations of N-compounds (Fig. 4). An amount of 2 kPa 2-MPy decreased the DBT conversion slightly, while 2 kPa 2-MPiper hardly changed the DBT conversion. The formation of biphenyl was enhanced (Fig. 5). Similar increases in one product, induced by inhibition of another product, were reported by others [4,5]. However, this increase in the concentration of biphenyl is not the result of a promoting effect of the N-containing molecules on the HDS of DBT, but the result of an increase of the DBT concentration, due to the absence of the HYD pathway. As a result, the ultimate yield of biphenyl can be 100 instead of 90% (dashed line in Fig. 5). Moreover, in the presence of N-containing molecules biphenyl is not further hydrogenated to cyclohexylbenzene. At higher 2-MPy and 2-MPiper concentrations, the inhibition of DDS became noticeable. Like at 300 °C, also at 340 °C the inhibitory effect of 2-MPy is larger than that of 2-MPiper. Hence, the N-containing molecules have a negative influence on both HYD and DDS pathways at both reaction temperatures, but, whereas the HYD route is strongly inhibited, the DDS route is less affected.

The less basic 2-MPy was found to be a stronger inhibitor than the more basic 2-MPiper for the DDS of DBT. This is in agreement with report that pyridine is a stronger poison than piperidine in the HDS of DBT [5]. Although

the aqueous basicity ($pK_a$) of aliphatic heterocyclic compounds is almost two times higher than that of heterocyclic aromatic compounds [5,37], their adsorption constants are lower [5,37]. Apparently, the aqueous basicity is a poor predictor of adsorption strength. A more appropriate parameter is the gas-phase proton affinity, which has a good correlation with the adsorption constant [7]. Indeed, the proton affinity and the adsorption constant of piperidine on sulfided NiMo catalyst are lower than those of pyridine [5]. This suggests that the stronger inhibitory effect of 2-MPy than of 2-MPiper is due to a higher adsorption constant on the catalyst surface. All observations are basically related to the major DDS pathway of the HDS of DBT. The picture for the HYD site can be different, because of the different nature of the site. Indeed, our results show that the more basic 2-MPiper inhibits the HYD pathway somewhat stronger than 2-MPy. This is in accordance with results reported by Zeuthen et al. [38], who showed that basic N-compounds influenced the HDS of diesel strongly. Since most sulfur compounds in their diesel were of the 4,6-dialkylDBT-type, these results are in good agreement with ours.

The adsorption constants of 2-MPy and 2-MPiper on the HDS sites were determined by analyzing our experimental results with the Langmuir-Hinshelwood model, by assuming that the HDS of DBT proceeds on a site that can be poisoned by 2-MPy and 2-MPiper:

$$\frac{\partial P_{\mathrm{DBT}}}{\partial \tau} = \frac{k K_{\mathrm{DBT}} P_{\mathrm{DBT}}}{1 + K_{\mathrm{DBT}} P_{\mathrm{DBT}} + K_{\mathrm{N}} P_{\mathrm{N}}}.$$

In the analysis we used the data of the HDS of DBT itself and of the HDS of DBT in the presence of 2, 6, and 10 kPa 2-MPy and 2-MPiper obtained at 300 °C. The adsorption constants of DBT, 2-MPy, and 2-MPiper on the HDS sites of the NiMo/$\gamma$-$Al_2O_3$ catalyst were found to be equal to 0.029, 0.53, and 0.076 $kPa^{-1}$, respectively. This shows that the adsorption constant of DBT is about 20 times smaller than that of 2-MPy and 2 times smaller than that of 2-MPiper and that the adsorption constant of 2-MPy is 7 times higher than that of 2-MPiper.

Two reactions take part in the HDN of 2-MPy (Scheme 2), hydrogenation–dehydrogenation and C–N bond cleavage. This suggests the presence of two active sites: sites responsible for the hydrogenation–dehydrogenation and sites promoting the C–N bond breaking. $H_2S$ has a dual effect on the HDN reactions of pyridine and quinoline [25,39,40]. It slightly inhibits the hydrogenation and dehydrogenation, but markedly accelerates the overall HDN rate because it promotes $C(sp^3)$–N bond cleavage. Our results show that there is an optimum $H_2S$ concentration for the hydrogenation of 2-MPy at 300 °C (Fig. 7). On the one hand, $H_2S$ creates acidic sites on the catalyst surface, thereby increasing the adsorption of a basic aromatic molecule. On the other hand, at higher concentrations $H_2S$ covers the vacancies on the catalyst surface and hinders the adsorption of N-containing molecules. 2-MPiper at 340 °C undergoes mainly HDN and $H_2S$ has a positive influence on the C–N bond cleavage (Fig. 6). Therefore, the effect of $H_2S$ on the overall conversion of 2-MPy could be promoting at lower and retarding at higher $H_2S$ partial pressures. However, our experiments showed that $H_2S$ has a small negative influence on the overall conversion of 2-MPy at 340 °C but a positive effect on the HDN conversion (Fig. 9). At first sight, it looks as if these results contradict the promotion effect of low amounts of $H_2S$ on both hydrogenation and C–N bond cleavage. However, at the higher temperature of 340 °C one more reaction takes part in the HDN of 2-MPy and that is the reverse reaction of dehydrogenation of 2-MPiper to 2-MPy. This reaction can be also promoted by a small amount of $H_2S$, just as the hydrogenation reaction, therefore, the overall conversion of 2-MPy would decrease with increase of $H_2S$ partial pressure. These results are in good agreement with those evidencing the dual effect of $H_2S$ on HDN [25,39,40].

A detailed study of the interaction between catalytic hydrodesulfurization and hydrodenitrogenation was first performed by Satterfield et al. [2,3] with thiophene and pyridine as model compounds. Thiophene had a dual effect on the HDN of pyridine. At low temperatures, the competitive adsorption of thiophene on hydrogenation sites retarded the hydrogenation of pyridine to piperidine, and thus reduced the overall reaction rate. At higher temperatures, $H_2S$ produced in the HDS of thiophene increased the rate of piperidine hydrogenolysis and enhanced the overall HDN reaction rate. Since these results were obtained in the absence of hydrogen sulfide, it is not clear if the inhibitory effect of the S-containing compound was due to $H_2S$ released in the HDS reaction or due to the S-containing molecule itself. Therefore, we performed our experiments at an $H_2S$ partial pressure, which was 35 times higher than that of DBT. The results show that DBT adsorbs much stronger on the hydrogenation sites than $H_2S$, since the conversion of 2-MPy to 2-MPiper in the presence of DBT decreased by a factor of two at 300 °C. At the higher temperature of 340 °C, the inhibitory effect of DBT on the hydrogenation of 2-MPy was less drastic as at 300 °C, but still obvious (Fig. 10).

Satterfield et al. showed that sulfur compounds as well as $H_2S$ promote the rupture of C–N bonds [2]. They also demonstrated that $H_2S$ released in the HDS of thiophene, and not thiophene itself, was responsible for the enhancement effect on HDN. This was confirmed by our results, which showed that, in the HDN of 2-MPy and of 2-MPiper, there was no change in the formation of $C_6$ products when DBT was added to the feed (Figs. 10 and 11). This proves that the active sites that facilitate C–N bond cleavage are different from those responsible for the HYD and DDS of S-containing molecules. At the same time, as noted above, N-containing compounds retard both DDS and HYD pathways, but to a different extent. The HYD pathway of the HDS of DBT was strongly suppressed in the presence of 2-MPy and 2-MPiper at 300 °C as well as at 340 °C, whereas the DDS pathway was inhibited to a smaller extent. At high temperatures and low partial pressures of 2-MPy and 2-MPiper it was almost not affected. Thus, while C–N bond

cleavage needs another site than the HYD and DDS of S-containing molecules (see above), the hydrogenation of S- and N-containing molecules may take place at the same active sites.

The enhancement of the C–N bond rupture and better HDN activity of the catalyst in the presence of higher amounts of $H_2S$ were previously associated with the maintenance of the catalyst in a completely sulfided state [3], since the active S-containing species will be unstable on the catalyst surface and will rapidly decompose in the absence of sufficient sulfur in the feed. However, we observed an increase in the HDN conversion of 2-methylpiperidine at much higher $H_2S$ partial pressures than needed to keep the catalyst in a completely sulfided state. 2-MPiper undergoes HDN via elimination or via nucleophilic substitution of the amine group by an SH group followed by hydrogenolysis of the C–S bond. In the latter case, $H_2S$ should be of importance in the HDN of 2-MPiper. It was recently shown that aliphatic amines undergo HDN mainly via nucleophilic substitution [41]. Therefore, the enhancement of the HDN of 2-MPiper with increasing $H_2S$ partial pressure may be ascribed to the reaction mechanism and not only to the sulfided state of the catalyst.

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