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Hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene over sulfided NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3 catalysts

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Abstract

The hydrodesulfurization (HDS) of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) was studied over sulfided NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3 catalysts. The Ni and Co promoters strongly enhanced the activity of the Mo catalyst in the direct desulfurization pathway of the HDS of DBT and 4,6-DMDBT and in the final sulfur-removal step in the hydrogenation pathway, while the hydrogenation was moderately promoted. H_2S had a negative effect on the HDS of DBT and 4,6-DMDBT, which was strongest for the NiMo catalyst and stronger for the direct desulfurization pathway than for the hydrogenation pathway. Because the direct desulfurization pathway is less important for the HDS of 4,6-DMDBT than the hydrogenation pathway, the conversion of 4,6-DMDBT was less affected by H_2S than the conversion of DBT. The sulfur removal via the direct desulfurization pathway and the ultimate sulfur removal in the hydrogenation pathway were affected by H_2S to the same extent over all the catalysts. This suggests that the removal of sulfur from tetrahydrodibenzothiophenes takes place by hydrogenolysis, like the direct desulfurization of DBT to biphenyl. The CoMo catalyst performed better than the NiMo catalyst in the final desulfurization via the hydrogenation pathway in the HDS of 4,6-DMDBT at all partial pressures of H_2S.

Keywords: Hydrotreating; Hydrodesulfurization; HDS; Dibenzothiophene; DBT; 4,6-Dimethyldibenzothiophene; 4,6-DMDBT; Transition metal sulfide catalysts; Mo catalysts; CoMo catalyst; NiMo catalyst

1. Introduction

To improve the hydrodesulfurization (HDS) process, it is necessary to gain a better understanding of the conversion mechanisms of various sulfur compounds. Dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophenes (4,6-DMDBT) belong to the most refractory sulfur-containing molecules present in gas oil [1–12]. They are, therefore, often used as model sulfur compounds. DBT and alkyl-substituted DBT undergo HDS via two reaction pathways: (i) direct desulfurization (DDS), which leads to the formation of biphenyls; (ii) hydrogenation (HYD) yielding tetrahydro- and hexahydro-intermediates followed by desulfurization to cyclohexylbenzenes and bicyclohexyls. DBT is converted predominantly via the DDS pathway, whereas 4,6-DMDBT reacts mainly via the HYD pathway [5,8,12–16]. The reactivity of 4,6-DMDBT over Co- or Ni-promoted catalysts is 5 to 10 times smaller than that of DBT [10,12,17]. The difficulty in converting alkyl-substituted DBTs is due to the steric hindrance of alkyl groups, which are close to the sulfur atom and prevent the interaction of the sulfur atom with the active site. Kabe et al. reported that the adsorption constant of 4,6-DMDBT on the CoMo/Al_2O_3 catalyst was twice as high as that of DBT and suggested that DBTs adsorb by means of π bonding to the catalyst [6]. In this adsorption mode, the methyl groups do not hinder the adsorption of the molecule on the catalyst surface. Thus, they suggested that C–S bond scission occurs when DBT is adsorbed via the sulfur atom in the σ mode. In this case, the methyl groups hinder C–S bond scission [6]. They also reported that 4-methyltetrahydrodibenzothiophene, the hydrogenated intermediate in the HYD pathway, is easier to desulfurize than 4-methyldibenzothiophene. In our previous work we observed that 4,6-DMDBT converts somewhat faster via the

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HYD route than DBT over NiMo/Al_2O_3 but that the desulfurization of 4,6-dimethyltetrahydrodibenzothiophene occurs much slower than that of tetrahydrodibenzothiophene [16]. Thus, the two methyl substituents have a negative influence on the transformation of the partially hydrogenated intermediate. Further research is required to determine why the reactivity of 4,6-DMDBT is low.

A better knowledge of the catalytic sites involved in the transformation of sulfur-containing molecules may help us gain insight into the process of sulfur removal. Therefore, we studied the HDS of DBT and 4,6-DMDBT over different catalysts: sulfided NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3. Some researchers described the HDS of hindered sulfur-containing compounds over the CoMo or the NiMo catalysts [8,10,18,19], while others compared the catalysts [12,20–25]. Landau et al. found that a Co-promoted catalyst is more active in the HDS of substituted DBTs [22]. Mochida's group, on the other hand, reported that NiMo performs better than CoMo in the HDS of a gas oil [20] but is affected more strongly by aromatic compounds and H_2S [23]. Knudsen et al. studied catalysts for ultradeep HDS of diesel fuel and found that a NiMo catalyst performed well only when most of the heterocyclic compounds had been removed [25]. Thereafter, the NiMo catalyst was more active than the CoMo catalyst. At low H_2 pressures and high temperatures, a CoMo catalyst performs better than a NiMo catalyst [25]. To clarify the effect of the promoter, we carried out a detailed analysis of the HDS mechanisms of DBT and 4,6-DMDBT over sulfided CoMo, NiMo, and Mo catalysts supported on alumina. The effect of H_2S was studied to gain a better understanding of the nature of the DDS and HYD sites that take part in the HDS.

2. Experimental

The Mo/γ-Al_2O_3, NiMo/γ-Al_2O_3, and CoMo/γ-Al_2O_3 catalysts used in this work contained 8 wt% Mo and 0 or 3 wt% promoter (Ni or Co). They were prepared by successive incipient wetness impregnation of γ-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 (for the promoted catalysts) by an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ (all Aldrich). After each impregnation step the catalysts were dried in air at ambient temperature for 4 h and then in an oven at 120 °C for 15 h and finally calcined at 500 °C for 4 h.

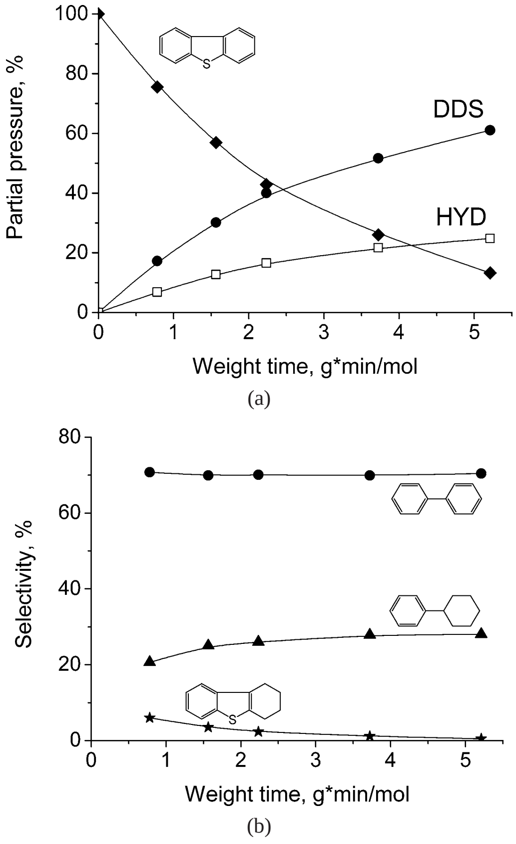
Reactions were carried out in a continuous mode in a fixed-bed inconel reactor, as described elsewhere [15]. All the experiments were performed at 340 °C. The gas-phase feed consisted of 130 kPa toluene (the solvent for the DBTs), 8 kPa dodecane (the reference for DBTs and their derivatives in the GC analysis), 1 kPa DBT or 4,6-DMDBT, 0–100 kPa H_2S and 4.8 MPa H_2.

The reaction products were analyzed by off-line gas chromatography, as described elsewhere [15]. Weight time was defined as $\tau = w_{\mathrm{cat}}/n_{\mathrm{feed}}$, where w_{cat} denotes the catalyst weight and n_{feed} the total molar flow to the reactor ($1\ \mathrm{g\,min/mol} = 1.8 \times 10^{-2}\ \mathrm{g\,h/L}$). 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; during the 2 weeks of operation there was almost no deactivation of the catalyst.

3. Results

3.1. HDS of DBT over CoMo/γ-Al_2O_3

The HDS of DBT was studied at 340 °C and 35 kPa H_2S over the CoMo/γ-Al_2O_3 catalyst. Fig. 1 shows the relative partial pressures of DBT and its products as well as the product selectivities. Four reaction products were observed: Biphenyl and cyclohexylbenzene were the final products of the DDS and HYD pathways, respectively, and tetrahydrodibenzothiophene and hexahydrodibenzothiophene were intermediates in the HYD pathway of the HDS. The HYD curve in Fig. 1a represents the sum of all the hydrogenation products (tetrahydrodibenzothiophene, hexahydrodibenzothiophene, and cyclohexylbenzene). GC-MS showed that the tetrahydro-intermediate was 1,2,3,4-tetrahydrodibenzothiophene, with the double bond at the bridge between the par-



(a)

(b)

Fig. 1. Relative partial pressures (a) and selectivities (b) of the products in the HDS of dibenzothiophene at 340 °C and 35 kPa H_2S over CoMo/γ-Al_2O_3 as a function of weight time.

tially hydrogenated 6-ring and the thiophene ring. Only trace amounts of hexahydrodibenzothiophene were detected; its relative partial pressure did not exceed 0.5% and its selectivity was 1.5% at the lowest weight time, decreasing to 0.14% at the highest weight time (values not plotted in Fig. 1).

The product distribution (Fig. 1b) shows that the selectivity of biphenyl formation, that is, the selectivity for the DDS pathway, is 70% and remains constant during the reaction. The selectivity toward the formation of tetrahydrodibenzothiophene was rather low, 6% at the lowest and 0.45% at the highest weight time. This shows that this intermediate is quickly converted.

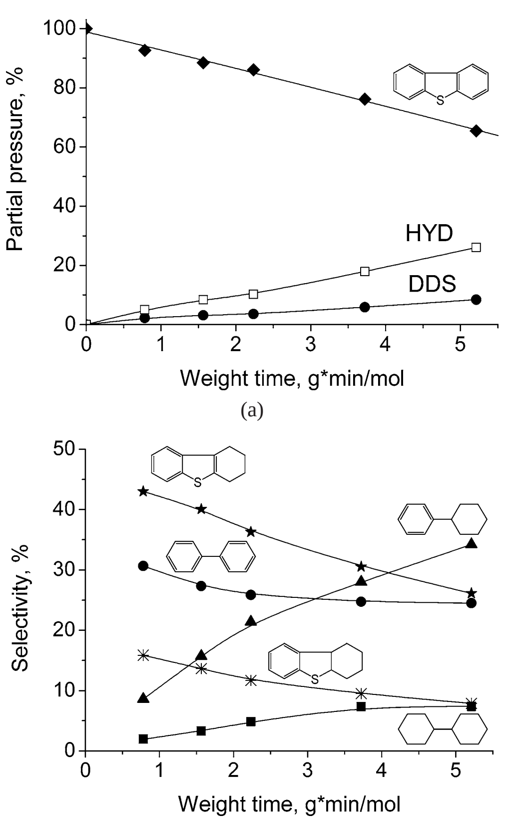
3.2. HDS of DBT over Mo/γ-Al_2O_3

Fig. 2 shows the relative partial pressures and product selectivities in the HDS of DBT over Mo/γ-Al_2O_3 at 340 °C and 35 kPa H_2S. The overall conversion was much lower over Mo than over CoMo and, although the same products were observed, the product distribution was completely different. In contrast to the CoMo (Fig. 1a) and NiMo catalysts [15], Mo/γ-Al_2O_3 mainly catalyzed the HYD pathway (Fig. 2a). Biphenyl, the product of the DDS pathway, was detected in much smaller amounts over the Mo catalyst than over the CoMo and NiMo catalysts. The presence of bicyclohexyl is typical of Mo/γ-Al_2O_3 (Fig. 2b). This product was not observed at all over the NiMo and CoMo catalysts.

The DDS selectivity approached 35% at low weight time and decreased to 25% at higher weight time (Fig. 2b). Up to a weight time of 4 g min/mol, the main reaction product is tetrahydrodibenzothiophene, the intermediate in the HYD pathway (Fig. 2b). The yield of hexahydrodibenzothiophene was about 3 to 22 times higher in the presence of the Mo catalyst than in the presence of the CoMo catalyst.

3.3. HDS of 4,6-DMDBT over CoMo/γ-Al_2O_3

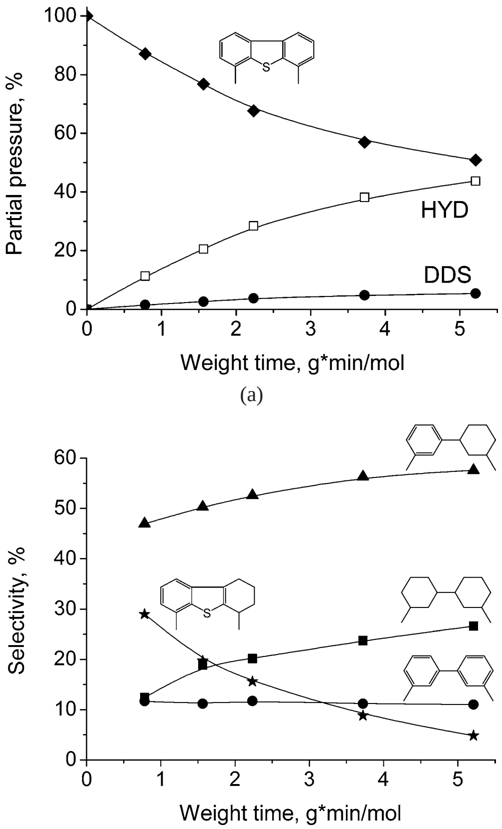
Fig. 3 shows the results of the HDS of 4,6-DMDBT over the CoMo/γ-Al_2O_3 catalyst at 340 °C and 35 kPa H_2S. 3,3-Dimethylbiphenyl was the product of the DDS route and 4,6-dimethyltetrahydrodibenzothiophene, 1-methyl-3-(2-methylphenyl)cyclohexane (which we will refer to as methylcyclohexyltoluene) and 3,3′-dimethylbicyclohexyl were the products of the HYD pathway. The results of the GC-MS analysis showed that the tetrahydro-intermediate was 4,6-dimethyl-1,2,3,4-tetrahydrodibenzothiophene. The conversion via the HYD route was much higher than that via the DDS pathway (Fig. 3a), and the total conversion was much smaller than that of DBT (cf. Figs. 1a and 3a).



(a)

(b)

Fig. 2. Relative partial pressures (a) and selectivities (b) of the products in the HDS of dibenzothiophene at 340 °C and 35 kPa H_2S over Mo/γ-Al_2O_3 as a function of weight time.



(a)

(b)

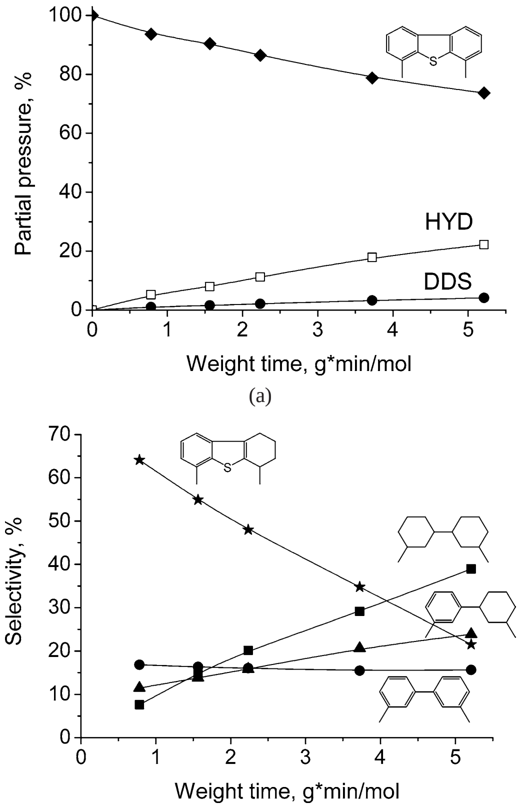
Fig. 3. Relative partial pressures (a) and selectivities (b) of the products in the HDS of 4,6-dimethyldibenzothiophene at 340 °C and 35 kPa H_2S over CoMo/γ-Al_2O_3 as a function of weight time.

The selectivity toward the formation of 3,3′-dimethylbiphenyl (DDS selectivity) was only 12% and remained constant during the reaction (Fig. 3b). The main reaction product is methylcyclohexyltoluene even at the lowest weight time, and 3,3′-dimethylbicyclohexyl is the second most abundant product at $\tau \geqslant 1.7$ g min/mol (Fig. 3b). The yield of the partially hydrogenated intermediate, 4,6-dimethyltetrahydrodibenzothiophene, is higher than that of tetrahydrodibenzothiophene in the HDS of DBT.

3.4. HDS of 4,6-DMDBT over Mo/γ-Al_2O_3

The Mo/γ-Al_2O_3 catalyst was only slightly less active in the HDS of 4,6-DMDBT than in the HDS of DBT under the same reaction conditions (340 °C and 35 kPa H_2S) (cf. Figs. 2a and 4a). The same products were observed as over the CoMo catalyst. On the Mo catalyst the HYD conversions of DBT and 4,6-DMDBT were almost the same, while the DDS conversion of 4,6-DMDBT was lower than that of DBT (cf. Figs. 2a and 4a).

The DDS selectivity (3,3′-dimethylbiphenyl formation) is 16% during the whole reaction (Fig. 4b), somewhat higher than over the CoMo catalyst (12%). However, the yield of 3,3′-dimethylbiphenyl was higher over the CoMo catalyst because of the higher conversion of the reactant. 4,6-Dimethyltetrahydrodibenzothiophene is the main reaction product up to $\tau = 4$ g min/mol (Fig. 4b). The main desulfurized product of the HDS of 4,6-DMDBT over the Mo catalyst was 3,3′-dimethylbicyclohexyl.



(a)

(b)

Fig. 4. Relative partial pressures (a) and selectivities (b) of the products in the HDS of 4,6-dimethyldibenzothiophene at 340 °C and 35 kPa H_2S over Mo/γ-Al_2O_3 as a function of weight time.

3.5. Effect of H_2S on the HDS of DBT and 4,6-DMDBT

The effect of different initial partial pressures (0, 10, 35, and 100 kPa) of hydrogen sulfide on the HDS of DBT and 4,6-DMDBT was studied over all three catalysts: NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3. Over NiMo/γ-Al_2O_3 the HDS of DBT was extremely fast in the absence of H_2S and reached 100% conversion already at $\tau = 1.5$ g min/mol. Over CoMo/γ-Al_2O_3 the same conversion was reached at $\tau = 2.3$ g min/mol and over the Mo/γ-Al_2O_3 catalyst the conversion of DBT was only 55% at $\tau = 3.7$ g min/mol. Since the feed contained only 1 kPa of DBT or 4,6-DMDBT, its influence on the H_2S partial pressure during reaction was small at $P_{H_2S}(\text{init}) = 10$ kPa and negligible at $P_{H_2S}(\text{init}) = 35$ and 100 kPa. For the experiments at $P_{H_2S}(\text{init}) = 0$ kPa, however, the amount of H_2S present during reaction was equal to the amount formed in the HDS reaction. The results obtained in the absence of added H_2S therefore do not really correspond to $P_{H_2S} = 0$ kPa, but correspond to P_{H_2S} due to the desulfurization conversion.

H_2S strongly inhibited the conversion of DBT over all three catalysts. At 100 kPa H_2S and $\tau = 3.7$ min/mol the conversion of DBT reached 60% over NiMo, 53% over CoMo, and 24% over the Mo catalyst. The conversion of DBT and 4,6-DMDBT was well described by pseudo-first-order kinetics. The plots of $\ln(C/C_0)$ versus weight time were always linear with high R^2 values (0.97–0.99). In Fig. 5 we present the plot for the HDS of DBT at 35 kPa H_2S over the NiMo catalyst, where the DBT conversion at the highest weight time was 90%. To prove that we also deal with pseudo-first-order reactions when the catalyst activity is lower (and thus lower conversions are obtained), we performed experiments on the HDS of DBT at two initial partial pressures of the reactant (0.5 and 2 kPa) over the Mo catalyst. It was found that the conversion of DBT did not depend on its initial concentration, showing that also

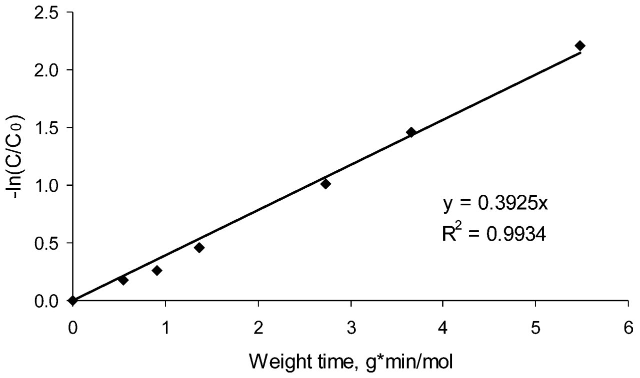


Fig. 5. Plot of $\ln(C/C_0)$ versus weight time for the HDS of DBT at 35 kPa H_2S and 340 °C over NiMo/γ-Al_2O_3.

over Mo/γ-Al_2O_3 the HDS reaction follows first-order behavior. The observed first-order behavior seems to contradict the general belief that HDS is strongly inhibited by reactant molecules. It should be realized, however, that most studies have been executed at a lower temperature than ours. In accordance with the literature [3,26], we observed a decreasing conversion when increasing the partial pressure of DBT from 0.1 to 3 kPa at the lower temperature of 300 °C and calculated an adsorption constant of 2 kPa^{-1}. This means that at 340 °C and with $P_{H_2S} \gg P_{DBT}$ and $K_{H_2S} > K_{DBT}$ [3,26] the equation

$$r = kK_{DBT}P_{DBT}/(1 + K_{DBT}P_{DBT} + K_{H_2S}P_{H_2S})$$

can be replaced by $r = k'P_{DBT}$. The constant k' is a pseudo rate constant which contains the influence of P_{H_2} and P_{H_2S}.

Table 1 gives the pseudo rate constants of the total conversion of DBT (k_{tot}) for the three catalysts at different partial pressures of H_2S. At $P_{H_2S}(\text{init}) = 0$ kPa, the rate of total DBT conversion was almost 10 times higher over the NiMo catalyst and 6 times higher over the CoMo catalyst than over the Mo catalyst. This is in good agreement with published results [10,17]. These k_{tot} ratios hardly changed in the presence of 10 kPa H_2S. At higher P_{H_2S}, the positive influence of the promoters was less outspoken. This is clearly shown in Fig. 6 in which the pseudo rate constants k_{tot} are plotted as a logarithmic function of P_{H_2S}. This figure indicates that H_2S inhibits the HDS of DBT more strongly over the NiMo and CoMo catalysts than over Mo.

To analyze the product distributions at different partial pressures of H_2S, the pseudo rate constants of the DDS pathway (k_{DDS}) and of the HYD pathway (k_{HYD}) in the HDS of DBT were determined from k_{tot} and the selectivities at low weight time. The resulting k_{DDS} and k_{HYD} values are presented in Table 1. In the absence of H_2S, all three catalysts performed better via the DDS than via the HYD pathway. The Ni and Co promoters improved the DDS activity of the Mo catalyst greatly and the HYD activity moderately. In the presence of H_2S the activity of all three catalysts decreased strongly. At higher partial pressures of H_2S, however, the CoMo catalyst was less affected than the NiMo catalyst, and the activity of the Mo catalyst hardly changed. Over all the catalysts, the DDS pathway was suppressed to a greater extent than the HYD pathway. The rate constant of the HYD pathway, k_{HYD}, was almost the same at 0 and 100 kPa H_2S over the Mo catalyst. As a consequence, at 35 and 100 kPa H_2S the contribution of the HYD pathway was larger than that of the DDS pathway (Table 1).

Table 1
Rate constants of the total, DDS, and HYD (desulfurization) conversions of DBT and of the desulfurization of tetrahydrodibenzothiophene over NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3 catalysts at different initial partial pressures of H_2S

Catalyst	Rate constant, mol/(g min)	P_{H_2S}(init), kPa			
		0	10	35	100
NiMo	k_{tot}	2.33	1.06	0.39	0.25
	k_{DDS}	2.05	0.90	0.32	0.17
	k_{HYD}	0.28	0.16	0.07	0.08
	k_{DESULF}^{HYD}	36	15	5.3	2.7
CoMo	k_{tot}	1.42	0.42	0.36	0.20
	k_{DDS}	1.31	0.34	0.28	0.14
	k_{HYD}	0.11	0.08	0.08	0.06
	k_{DESULF}^{HYD}	29	9.1	5.1	3.3
Mo	k_{tot}	0.25	0.09	0.08	0.08
	k_{DDS}	0.19	0.05	0.03	0.03
	k_{HYD}	0.06	0.04	0.05	0.05
	k_{DESULF}^{HYD}	4.7	1.3	0.70	0.50

The yields of the partially hydrogenated sulfur-containing intermediates were much lower over the NiMo and CoMo catalysts than over the Mo catalyst. Therefore, the desulfurization (the total sulfur removal) of DBT via the HYD pathway is also improved by the promoters. The selectivities of the partially hydrogenated intermediates increased with increasing partial pressure of H_2S. We estimated the rate constant k_{DESULF}^{HYD} of the final desulfurization step in the HYD pathway by analyzing this pathway as a series of first-order reactions A → B → C with rate constants k_{HYD} and k_{DESULF}^{HYD}. The concentration of the intermediate B is given by the expression [27]:

$$C_B = C_{A_0}\frac{k_{HYD}}{k_{DESULF}^{HYD} - k_{HYD}} \times \left[\exp(-k_{HYD}\tau) - \exp\left(-k_{DESULF}^{HYD}\tau\right)\right].$$

The rate constant of the HYD pathway (k_{HYD}) is already known; thus, we can calculate k_{DESULF}^{HYD} from the concentration of the intermediate B, tetrahydrodibenzothiophene, at weight time τ. The rate constants k_{DESULF}^{HYD} for the different catalysts and at different H_2S partial pressures are given in Table 1. The activity of the CoMo and NiMo catalysts for the final sulfur removal via HYD is much higher than that of the Mo catalyst. H_2S suppresses k_{DESULF}^{HYD} much more strongly than k_{HYD}, the rate constant of the hydrogenation of DBT to tetrahydrodibenzothiophene. The ratio of the rate constants of sulfur removal via the DDS and HYD pathways (k_{DDS}/k_{DESULF}^{HYD}) remained constant at different partial pres-

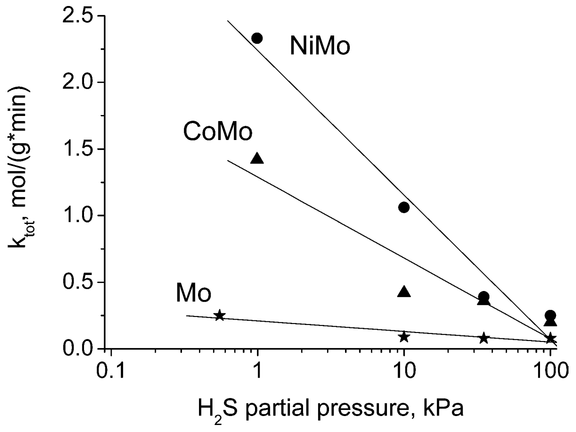


Fig. 6. Rate constants of the total conversion of DBT over NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3 catalysts at different partial pressures of H_2S.

Table 2
Rate constants of the total, DDS, and HYD (desulfurization) conversions of 4,6-DMDBT and of the desulfurization of 4,6-dimethyltetrahydrodibenzothiophene over NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3 catalysts at different initial partial pressures of H_2S

Catalyst	Rate constant, mol/(g min)	P_{H_2S}(init), kPa			
		0	10	35	100
NiMo	k_{tot}	0.20	0.13	0.11	0.08
	k_{DDS}	0.08	0.04	0.03	0.02
	k_{HYD}	0.12	0.09	0.08	0.06
	$k_{\mathrm{DESULF}}^{\mathrm{HYD}}$	3.6	1.9	1.2	0.91
CoMo	k_{tot}	0.16	0.12	0.12	0.09
	k_{DDS}	0.06	0.03	0.02	0.01
	k_{HYD}	0.10	0.09	0.10	0.08
	$k_{\mathrm{DESULF}}^{\mathrm{HYD}}$	4.2	3.0	2.0	1.8
Mo	k_{tot}	0.09	0.08	0.07	0.07
	k_{DDS}	0.02	0.01	0.01	0.01
	k_{HYD}	0.07	0.07	0.06	0.06
	$k_{\mathrm{DESULF}}^{\mathrm{HYD}}$	0.88	0.52	0.50	0.36

sures of H_2S over all three catalysts. It was equal to 0.06 for NiMo, 0.045 for CoMo, and 0.04 for Mo. This means that the desulfurizations of DBT to biphenyl and of tetrahydrodibenzothiophene to cyclohexylbenzene are inhibited to the same extent by H_2S. The $k_{\mathrm{DDS}}/k_{\mathrm{DESULF}}^{\mathrm{HYD}}$ values show that the desulfurization via the DDS pathway is 16 to 25 times slower than the desulfurization of the hydrogenated intermediate.

The rate constants of the hydrogenation, k_{HYD}, and the rate constants of the desulfurizations via the DDS and HYD pathways, k_{DDS} and $k_{\mathrm{DESULF}}^{\mathrm{HYD}}$, for the HDS of 4,6-DMDBT in the presence of different catalysts and at different partial pressures of H_2S were calculated in the same way as for the HDS of DBT. The results are presented in Table 2. The differences in the performance of the Co- or Ni-promoted catalyst and the Mo catalyst were smaller in the HDS of 4,6-DMDBT than in the HDS of DBT (cf. Tables 1 and 2). Thus, the pseudo rate constant k_{tot} of the overall conversion of 4,6-DMDBT was only 2.2 times higher over the NiMo catalyst than over the Mo catalyst and 1.9 times higher over the CoMo catalyst in the absence of added H_2S. Increasing the partial pressure of H_2S led to a decrease of k_{tot} for all catalysts, but most strongly for NiMo (Fig. 7). As a consequence, at 35 and 100 kPa H_2S, the CoMo catalyst was more active in the HDS of 4,6-DMDBT than the NiMo catalyst. This indicates that CoMo is a better catalyst under HDS conditions (at least when only S compounds are present).

The HYD pathway of the HDS of 4,6-DMDBT was less strongly suppressed by H_2S than the DDS pathway over all three catalysts (Table 2). However, the fraction of the partially hydrogenated intermediates in the HYD pathway increased at increasing H_2S partial pressures. The pseudo rate constant $k_{\mathrm{DESULF}}^{\mathrm{HYD}}$ of the Mo catalyst in the removal of sulfur via HYD is enhanced by the Ni and Co promoters but to a lesser extent than in the HDS of DBT (cf. Tables 1 and 2). The ratio $k_{\mathrm{DDS}}/k_{\mathrm{DESULF}}^{\mathrm{HYD}}$ was constant at all partial pressures of H_2S and over all catalysts (0.02 for NiMo and Mo, and 0.01 for CoMo). This indicates that the DDS desulfurization of 4,6-DMDBT is inhibited to the same extent by H_2S as the HYD desulfurization of 4,6-dimethyltetrahydrodibenzothiophene. The $k_{\mathrm{DESULF}}^{\mathrm{HYD}}$ values for the HDS of DBT and 4,6-DMDBT show that the methyl groups have a strong inhibitory effect not only on the DDS pathway but also on the desulfurization via the HYD pathway. The final desulfurization of 4,6-DMDBT via HYD is always faster over the CoMo than over the NiMo catalyst (Table 2).

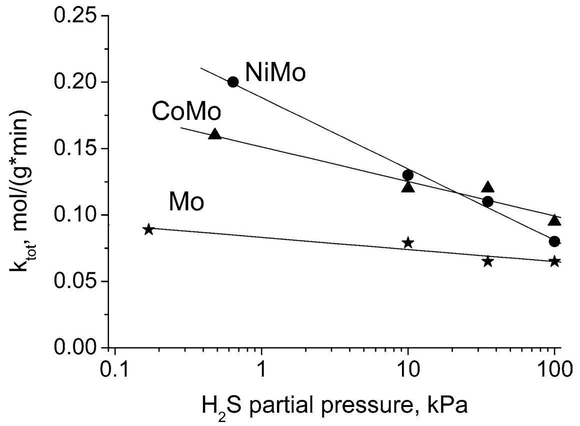


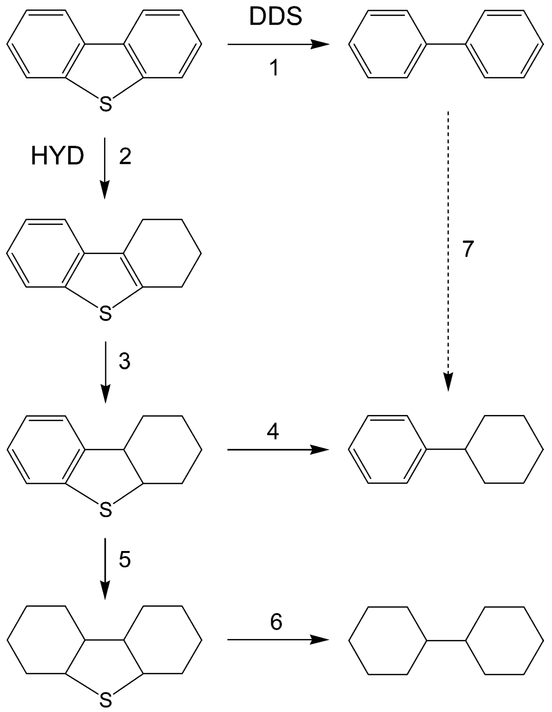
Fig. 7. Rate constants of the total conversion of 4,6-DMDBT over NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3 catalysts at different partial pressures of H_2S.

4. Discussion

4.1. DBT

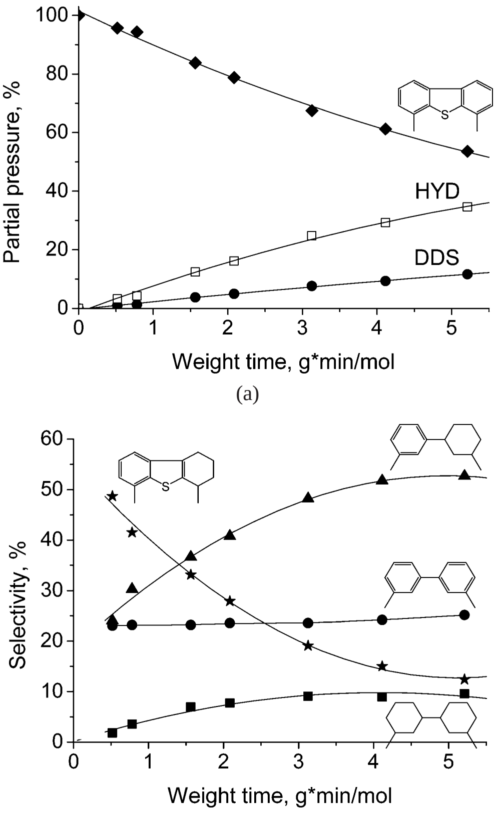
To enable a comparison of the CoMo and Mo catalysts with the NiMo/γ-Al_2O_3 catalyst in the HDS of DBT and 4,6-DMDBT at 340 °C and 35 kPa H_2S, we call to mind the results obtained for the NiMo catalyst [15,16]. They are very similar to those of the CoMo catalyst. The HDS of DBT was slightly faster over the Ni-promoted catalyst than over the CoMo catalyst, and both catalysts were much more active than the Mo catalyst (Table 1).

At all partial pressures of H_2S the DDS pathway of the HDS of DBT is about an order of magnitude faster over the CoMo and NiMo catalysts than over the Mo catalyst (Table 1). The rate of the HYD pathway is just slightly higher for the CoMo and NiMo catalysts than for the Mo catalyst but the product distribution is different. In the presence of NiMo and CoMo the main HYD product is cyclohexylbenzene (Fig. 1b), whereas over Mo cyclohexylbenzene constitutes only 45% of the HYD products at $\tau = 5$ g min/mol (Fig. 2b). Another 45% comes from the tetrahydro- and hexahydrodibenzothiophenes. Therefore, the promotion of the Mo catalyst by Ni or Co is due not only to the better performance of the DDS pathway but also to faster desulfurization via the HYD pathway. This was confirmed by the $k_{\mathrm{DESULF}}^{\mathrm{HYD}}$ values (Table 1).



Scheme 1. Reaction network of the HDS of dibenzothiophene in the presence of transition metal sulfide catalysts.

A detailed network of the HDS of dibenzothiophene was proposed by Houalla et al. in 1978 [28]. Their data indicate that the conversion of dibenzothiophene occurs preferentially via the path with the least hydrogen consumption (DDS pathway) and that hydrogenation of biphenyl and cyclohexylbenzene is comparatively slow. A similar network, desulfurization to biphenyl and hydrogenation to tetrahydro- and hexahydrodibenzothiophene followed by desulfurization to cyclohexylbenzene, was proposed by other groups [29–31]. Our data suggest that the overall network of the HDS of DBT is as represented in Scheme 1. Over the CoMo and NiMo catalysts the HDS of DBT most probably occurs via reactions 1, 2, 3, and 4. The tetrahydro-intermediate was observed over CoMo and NiMo. Trace amounts of the hexahydro-intermediate were observed over CoMo but not over NiMo. Over the Mo catalyst, hexahydrodibenzothiophene was detected in higher concentrations and bicyclohexyl was observed as well. We assume that bicyclohexyl is formed by hydrogenation of the partially hydrogenated intermediates to perhydrodibenzothiophene and subsequent desulfurization. The hydrogenation of cyclohexylbenzene to bicyclohexyl is unlikely since the hydrogenation of the second phenyl ring of biphenyl ought to be more difficult than that of the first ring. Our results show that the latter does not occur over CoMo and occurs only slowly over NiMo and Mo. Therefore, the HDS of DBT over the Mo catalyst occurs via reactions 1, 2, 3, 4, 5, and 6. Over the NiMo and CoMo catalysts, the hydrogenation of the first phenyl ring is the rate-limiting step in the HYD pathway, and the desulfurization of the partially hydrogenated intermediates is rather fast, since the yields of these intermediates are very low (Fig. 1b). Therefore, further hydrogenation of hexahydrodibenzothiophene to perhydrodibenzothiophene does not occur. Over the Mo catalyst, however, the lifetime of the partially hydrogenated molecules is longer. Thus, the hydrogenation to perhydrodibenzothiophene, followed by desulfurization to bicyclohexyl, becomes possible. Reaction 7, the hydrogenation of biphenyl to cyclohexylbenzene, was observed over the NiMo and Mo catalysts but not over the CoMo catalyst. This suggests that the active sites facilitating HDS over the NiMo and Mo catalysts are different from those over the CoMo catalyst. One reason for this difference may be that, according to DFT theory, the active sites of the NiMo and Mo catalysts are at the molybdenum edge, whereas the Co atoms are at the sulfur edge of the MoS_2 slab [32,33].



(a)

(b)

Fig. 8. Relative partial pressures (a) and selectivities (b) of the products of the HDS of 4,6-dimethyldibenzothiophene at 340 °C and 35 kPa H_2S over NiMo/γ-Al_2O_3 as a function of weight time.

4.2. 4,6-DMDBT

The HDS of 4,6-DMDBT over the NiMo and CoMo catalysts was much slower than the HDS of DBT (cf. Tables 1 and 2). At 35 kPa H_2S, the total conversion of 4,6-DMDBT was slightly higher over the CoMo than over the NiMo catalyst due to a somewhat smaller DDS conversion but higher HYD conversion (cf. Figs. 3a and 8a). Thus, the first reaction, the hydrogenation, was faster over CoMo. Table 2 shows that the subsequent desulfurization via the HYD pathway is also easier over the CoMo catalyst. Since HYD is the main pathway in the transformation of 4,6-DMDBT, both its overall conversion and its desulfurization are faster over the CoMo catalyst. The pseudo rate constants of the total 4,6-DMDBT conversion (k_{tot}) over the three catalysts are plotted as a logarithmic function of P_{H_2S} in Fig. 7. The NiMo catalyst was more active than the CoMo catalyst up to 29 kPa H_2S, but at higher P_{H_2S} the CoMo catalyst performed better. Therefore, it is assumed that NiMo performs better than CoMo under deep HDS conditions (at low partial pressures of H_2S), without however considering the influence of impurities such as nitrogen-containing compounds.

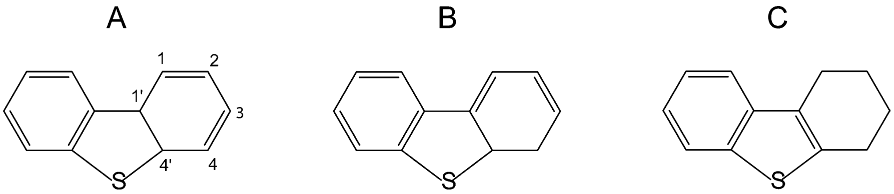
The activity of the Mo catalyst is somewhat lower in the HDS of 4,6-DMDBT than the activity of the Ni- and Co-promoted catalysts (Fig. 7), but for all three catalysts HYD prevails over DDS. Furthermore, the hydrogenation rate constants of the three catalysts are similar. However, the amount of hydrogenated, but not desulfurized, products was higher over the Mo catalyst than over the promoted catalysts. The lowest selectivity for 4,6-dimethyltetrahydrodibenzothiophene was observed for the CoMo catalyst. We assume that the mechanism of the HDS of 4,6-DMDBT is similar to that of DBT (Scheme 1). Hexahydro- and perhydro-intermediates were not observed for 4,6-DMDBT in our experiments, probably because of their fast desulfurization. The hydrogenation of 3,3′-dimethylbiphenyl to methylcyclohexyltoluene (reaction 7 in Scheme 1) clearly did not occur, as shown by the fact that the DDS selectivity to 3,3′-dimethylbiphenyl remained constant for all three catalysts. The hydrogenation of methylcyclohexyltoluene to 3,3′-dimethylbicyclohexyl will probably be even more difficult to achieve. Therefore, we assume that it does not occur either. Thus, 3,3′-dimethylbicyclohexyl can only be the product of further hydrogenation of 4,6-dimethyltetrahydrodibenzothiophene to 4,6-dimethylperhydrodibenzothiophene (reactions 3 and 5 in Scheme 1) followed by desulfurization. In the HDS of 4,6-DMDBT the lifetime of the partially hydrogenated intermediate (4,6-dimethyltetrahydrodibenzothiophene) is quite long, as is also the case for tetrahydrodibenzothiophene in the HDS of DBT over the Mo catalyst. Therefore, further hydrogenation to 4,6-dimethylperhydrodibenzothiophene followed by desulfurization can take place. The larger amount of 3,3′-dimethylbicyclohexyl than that of methylcyclohexyltoluene in the reaction products over the Mo catalyst indicates that hydrogenation of 4,6-dimethylhexahydrodibenzothiophene occurs faster than its desulfurization to methylcyclohexyltoluene.

The desulfurization of 4,6-DMDBT in the presence of the NiMo, CoMo, and Mo catalysts proceeds mainly via reactions 2, 3, 4, 5, and 6. Over the Mo catalyst reactions 2, 3, 5, and 6 are the most important, since 3,3′-dimethylbicyclohexyl was observed as the main product. Over the Co- and Ni-promoted catalysts the most important reactions are reactions 2, 3, and 4. The NiMo and CoMo catalysts have a higher activity than the Mo catalyst in the DDS pathway, but the difference is not as large as in the HDS of DBT. This shows the strong steric hindrance of the two methyl groups on the DDS reactivity of the DBT molecule.

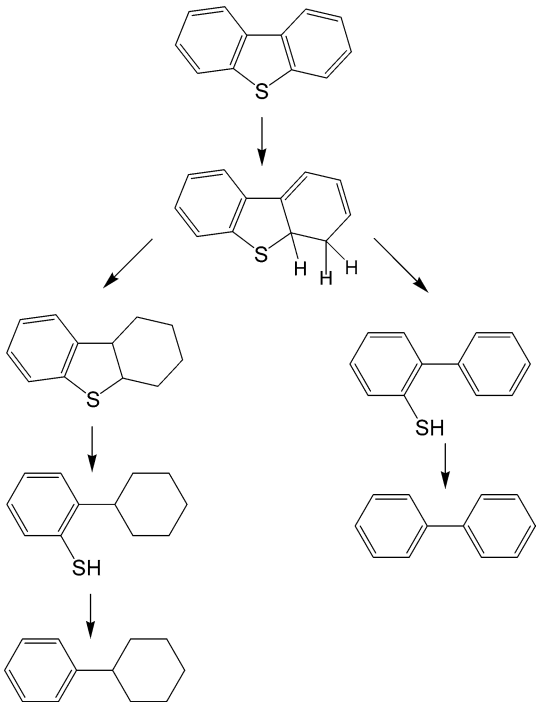
4.3. Reaction mechanisms and catalytic sites

The cause of the inhibitory effect of the methyl groups on the reactivity of the DBT molecule is still not completely understood. Some researchers attributed the lower reactivity of 4,6-DMDBT to its lower adsorption strength on the catalyst surface [2,8,20], whereas others explained it by steric hindrance of the methyl groups on the C–S bond scission reaction [6,10,12]. Meille et al. reported that the adsorption equilibrium constants of DBT, 4-methyldibenzothiophene, 4,6-DMDBT, and 2,8-DMDBT were almost the same on a sulfided NiMo catalyst [10]. Kabe et al. reported that the adsorption equilibrium constants of 4-methyldibenzothiophene and 4,6-DMDBT were even higher than that of DBT on a $CoMo/Al_2O_3$ catalyst [6]. The adsorption constants of the different sulfur-containing molecules were estimated by taking into account the total conversion of the reactant and assuming that the DDS and HYD pathways take place at the same active sites. This approach is the right one when the DDS and HYD reaction routes go through a common intermediate.

The presence of a common intermediate for the DDS and HYD reaction pathways in the HDS of DBT was first suggested by Singhal et al. [34]. As a common intermediate they suggested 1′,4′-dihydrodibenzothiophene, in which the hydrogenated bond is between the 6-ring and 5-ring (Scheme 2A). This proposal was supported by other researchers, who suggested that elimination is the main reaction through which sulfur is removed [10,12,35]. They assumed that 4,4′-dihydrodibenzothiophene (Scheme 2B) is the common intermediate and that biphenyl is the product of four consecutive reactions, two hydrogenations, each followed by elimination (Scheme 3). In essence, they rule out the possibility that thiophenol can be hydrodesulfurized by hydrogenolysis. The HYD pathway also consists of hydrogenation and elimination reactions, but there are



Scheme 2. The structures of proposed intermediates in the HDS of DBT [12,35].



Scheme 3. Reaction network of the HDS of dibenzothiophene suggested by Bataille et al. [12].

two additional hydrogenation steps at the beginning. It is known, however, that the hydrogenation of a carbon–carbon double bond with three substituents (RXC=CHR′) is more difficult than that of a double bond with two substituents (RHC=CHR′) [36]. Furthermore, the stability of the 4,4′-dihydro-intermediate (Scheme 2B) is extremely low from an energetical point of view. This intermediate B still seems to have a conjugation between the π electrons of the phenyl group and of the partially hydrogenated ring. In reality, because of the presence of the two sp^3-hybridized carbon atoms, the phenyl and hexadiene rings are not coplanar. Intermediate A (Scheme 2) has the *cis* conformation and, thus, the plane of the diene fragment (1,2,3,4) is oriented at an angle of 54.7° to the plane of the remaining benzothiophene fragment. The conjugation in this dihydrodibenzothiophene molecule is interrupted. Finally, in all the published studies on the HDS of DBTs the only partially hydrogenated intermediate observed was 1,2,3,4-tetrahydrodibenzothiophene, with the double bond in the bridge position (Scheme 2C). This suggests that this double bond is the most difficult to hydrogenate and that such an intermediate is the most stable. The proposal for a common intermediate for the DDS and HYD pathways is also based on the assumption that elimination is the only reaction responsible for C–S bond breaking [12]. This assumption is much too restrictive, however, because methanethiol and neopentanethiol can be easily hydrodesulfurized to H_2S and methane and neopentane, respectively. This shows that hydrogenolysis is a clear alternative to elimination whenever no β-H atoms are available. This suggests that the HDS of DBT might occur by hydrogenolysis of the two C–S bonds. Therefore, the assumption of a common dihydro-intermediate for both DDS and HYD reaction pathways seems to be unfounded.

For these reasons and in conformity with other authors [37–39], we assume that the two HDS pathways do not have a common intermediate and are determined by the conformation of the adsorbed DBT molecule. DDS occurs through σ adsorption of the DBT molecule via the sulfur atom, and HYD proceeds through π adsorption of the reactant via the aromatic system. This would require two adsorption constants for the DDS and HYD pathways and these constants may be different.

A vibrational study of organometallic complexes with thiophene ligands was used to model the adsorption of thiophene on a hydrodesulfurization catalyst [40]. It was found that in the η^1(S) bonding mode of thiophene (σ adsorption) the C–C bonds in the C_4 hydrocarbon backbone are slightly stronger, while the C–S bonds are substantially weaker relative to free thiophene. Therefore, it was suggested that the cleavage of the C–S bond occurs when thiophene is adsorbed on a coordinately unsaturated Mo site via the sulfur atom in the σ mode. Vecchi et al. [41] described the effect of the methyl groups on σ coordination in Ru complexes of DBT, 4-methyldibenzothiophene, 4,6-DMDBT, and 2,8-DMDBT. They observed that the binding strength increased in the order 4,6-DMDBT $<$ 4-methyldibenzothiophene $<$ DBT $<$ 2,8-DMDBT, in good agreement with catalytic experiments [6,10].

A study of the C–S bond cleavage in methyl-substituted thiophenes and benzothiophenes in the presence of a binuclear Re complex [42] led to the conclusion that thiophenes and benzothiophenes reacted with $Re_2(CO)_{10}$ to different products. Therefore, it was suggested that the HDS of thiophenes and benzothiophenes may occur via different pathways. DFT calculations of different adsorption conformations of DBT derivatives indicated that the adsorption properties of the refractory DBT and 4,6-DMDBT molecules are very different from those of smaller model compounds such as thiophene and benzothiophene [43,44]. The main reason for this difference is the aromaticity of the DBT structure, making π adsorption more likely than σ adsorption. It was shown that the methyl groups do indeed hinder the perpendicular σ adsorption of DBT but hardly affect the flat adsorption via the aromatic π system.

The inhibitory effect of H_2S on the HDS activity of CoMo-, NiMo-, and Mo/Al_2O_3 catalysts was studied before by Kasahara et al. [45]. They found that H_2S decreased the conversions of benzothiophene and DBT on all the catalysts. Moreover, the inhibitory effect of H_2S on NiMo was stronger than on the CoMo and Mo catalysts. In agreement with their observations, our results show that the total activity in the HDS of DBT and 4,6-DMDBT is suppressed to a greater extent by H_2S over the NiMo catalyst. In our work, the Mo catalyst was least affected by H_2S in the HDS of DBT and of 4,6-DMDBT (Tables 1 and 2). Moreover, the inhibition by H_2S was larger in the HDS of DBT than of

4,6-DMDBT (Tables 1 and 2). This is due to the stronger inhibitory effect of H_2S on the DDS pathway than on the HYD pathway. Since the contribution of the DDS is larger in the case of the HDS of DBT, the overall HDS is affected more strongly in the case of DBT. These results are in agreement with those of Bataille et al. [12]. They also observed that the HDS of DBT was affected more strongly by H_2S than that of 4,6-DMDBT over a NiMo catalyst.

The equal inhibition by H_2S of the DDS pathway and the final sulfur removal via the HYD pathway, in the HDS of DBT as well as 4,6-DMDBT over all three catalysts, suggest that the desulfurization via the DDS and HYD pathways occurs over the same active sites and that a similar mechanism of sulfur removal is involved in the DDS pathway and in the final step of the HYD pathway. Thus, we suggest that the tetrahydro-intermediate can be desulfurized only via σ adsorption on the active site after having been desorbed from the catalyst surface. Whether the tetrahydro-intermediate is desulfurized by elimination or hydrogenolysis is unknown. Assuming that, as usual, elimination occurs only when the β-H atom is in *trans* position to the S atom on the α-carbon atom, then elimination is not possible for sulfur atoms in ring structures and hydrogenolysis would be responsible for breaking the first C–S bond in the thiophene ring. Hermann et al. also suggested that common steps are involved in both HDS pathways [46]. They found that the activities of the transition metal sulfides in the HDS of 4,6-DMDBT followed the same trends as in the HDS of DBT, although the DDS pathway was of major importance for DBT, while the HYD pathway was prevalent for 4,6-DMDBT.

The final desulfurization of the hindered 4,6-DMDBT via HYD is substantially slower than that of DBT (Tables 1 and 2). Therefore, the methyl groups suppress not only the σ adsorption of the reactant, but also of the partially hydrogenated intermediate. The DDS pathway is retarded to a greater extent by the presence of the methyl groups than is the sulfur removal via the HYD pathway, especially over the CoMo catalyst, as shown by the lower the $k_{\mathrm{DDS}}/k^{\mathrm{HYD}}_{\mathrm{DESULF}}$ values (Section 3.5). This may be due to the lower flexibility in DBT and 4,6-DMDBT than in their partly hydrogenated intermediates, making adsorption easier for the latter molecules.

It is generally assumed that the catalytically active sites in Mo/γ-Al_2O_3 hydrotreating catalysts are the molybdenum atoms at the edges and corners of the MoS_2 crystallites, which have at least one sulfur vacancy, which enables chemical adsorption of the reacting molecule on the molybdenum atom [9,47–49]. Upon the addition of nickel and cobalt, the HDS and HDN activities of a MoS_2/γ-Al_2O_3 catalyst increase substantially. Density-functional theory (DFT) calculations show that the most stable position for the promoter atom (Co or Ni) is at the edge; there it substitutes the molybdenum atom [50] and forms the so-called Co–Mo–S phase (Ni–Mo–S phase for Ni–Mo catalysts) [9]. DFT calculations suggest that the combined action of the promoter (Ni or Co) and the molybdenum atom is responsible for the catalysis [32,50,51]. It was shown that a sulfur atom between a nickel (or cobalt) and a molybdenum atom is less strongly bonded than a sulfur atom between two molybdenum atoms and can be more easily removed, thus creating a vacancy. Therefore, the promoter may enhance the intrinsic rate of the C–S bond cleavage by increasing the electron density on the active Mo sites, as well as by creating a larger number of sulfur vacancies on the Ni- and Co-promoted catalysts.

We suggest that the DDS active sites and the sites at which sulfur is removed from the partially hydrogenated intermediates are the same and constitute a sulfur vacancy on the catalyst surface. Therefore, H_2S has a strong inhibitory influence on the sulfur removal via both reaction pathways. The hydrogenation of DBT and 4,6-DMDBT, on the other hand, is hardly affected by H_2S (Tables 1 and 2). This suggests that vacancies are not required for the flat π adsorption of the S-containing molecules and that hydrogenation may even occur over the surface, which is completely covered with sulfur. Another possibility is that the DDS active sites are located at the edges of the MoS_2 slabs and that the HYD active sites are at the corners, which are less sensitive to the presence of H_2S and allow the π adsorption of the spacious molecules.

5. Conclusion

The data obtained in this study indicate that the HDS of DBT and 4,6-DMDBT occurs via the same reaction network over NiMo, CoMo, and Mo catalysts. Ni and Co promoters noticeably improve the DDS activity of the Mo catalyst in the HDS of DBT and, to a lesser extent, in the HDS of 4,6-DMDBT. Since the DDS is the main reaction pathway in the HDS of DBT, the overall activity of the Mo catalyst in the transformation of DBT is remarkably improved by promotion. We suggest that the DDS and HYD pathways of HDS are determined by the adsorption conformation of the reactant molecule on the catalyst surface. The DDS occurs via σ adsorption, and the HYD pathway requires π adsorption. The resilience of 4,6-DMDBT is the result of the hindered removal of sulfur in the DDS pathway as well as in the HYD pathway.

H_2S suppresses the transformation of DBT and 4,6-DMDBT over all three catalysts. The NiMo catalyst is affected most and the Mo catalyst is least affected by the presence of H_2S. The DDS pathway was inhibited more strongly by H_2S than was the HYD pathway in the HDS of DBT and 4,6-DMDBT over all three catalysts. The final desulfurization via the HYD pathway was affected to the same extent as the DDS pathway, as shown by the constant $k_{\mathrm{DDS}}/k^{\mathrm{HYD}}_{\mathrm{DESULF}}$ ratio at all H_2S partial pressures over all catalysts. This suggests that the same mechanism is active in the DDS and in the final HYD step. In the HDS of 4,6-DMDBT the desulfurization via the HYD pathway was inhibited less by H_2S over the CoMo than over the NiMo catalyst. Because the activity of the CoMo catalyst was lower at low $P_{\mathrm{H_2S}}$, there is a crossover point, at which the CoMo catalyst becomes better than the NiMo catalyst. As a consequence, at partial pressures of H_2S higher than 29 kPa, the CoMo catalyst performed better in the HDS of 4,6-DMDBT than the NiMo catalyst.

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