

# Kinetics of the HDS of 4,6-dimethyldibenzothiophene and its hydrogenated intermediates over sulfided Mo and NiMo on $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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## Abstract

To study the hydrodesulfurization (HDS) reaction network of 4,6-dimethyldibenzothiophene (DMDBT), three hydrogenated intermediates—tetrahydro-, hexahydro-, and dodecahydro-DMDBT—were synthesized, and their HDS was investigated over sulfided Mo and NiMo on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts at 300 °C and 5 MPa. Tetrahydro-DMDBT reacted by hydrogenation to hexahydro-DMDBT, which in turn reacted to dodecahydro-DMDBT by hydrogenation and to 3,3'-dimethylcyclohexylbenzene by desulfurization. All four diastereoisomers of hexahydro-DMDBT were observed, all of which interconverted rapidly during HDS. Dodecahydro-DMDBT reacted by desulfurization to 3,3'-dimethylbicyclohexyl. The rate constants of all steps in the kinetic network of the HDS of DMDBT could be measured over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and those of some steps could be measured over NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The first step—hydrogenation of DMDBT to tetrahydro-DMDBT—is the slowest, rate-determining step, but the hydrogenation of and the sulfur removal from hexahydro-DMDBT are also slow. Opening of the sulfur-containing ring in DMDBT and its hydrogenated intermediates occurs by C–S hydrogenolysis rather than by elimination.

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**Keywords:** Hydrodesulfurization; HDS; Kinetics; 4,6-Dimethyldibenzothiophene; 4,6-DMDBT; Hydrogenated intermediates; Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

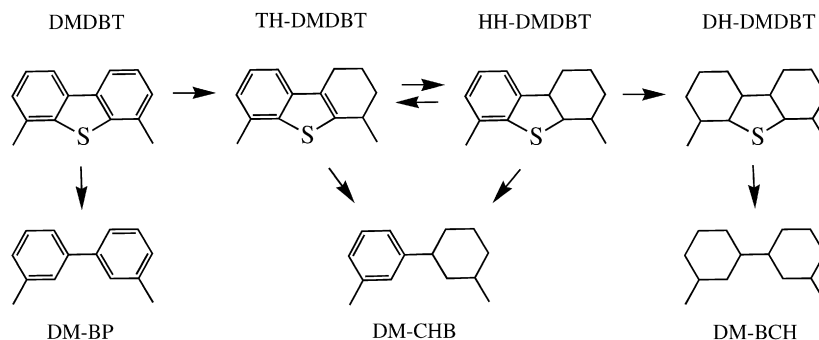
## 1. Introduction

By the year 2010, the maximum allowed amount of sulfur in gasoline and diesel fuel will be only about 10 ppm in many parts of the world. Deep hydrodesulfurization (HDS) technology must be implemented to attain this low sulfur level. This also means that 4,6-dialkyldibenzothiophene molecules, which are very difficult to desulfurize because of the alkyl groups adjacent to the sulfur atom, will have to undergo HDS [1–4]. Consequently, 4,6-dimethyldibenzothiophene (DMDBT) is often used as a model molecule in HDS studies. Extensive research over metal sulfide catalysts has shown that the HDS of dibenzothiophene (DBT) and DMDBT occurs through two reaction pathways. In the direct desulfurization (DDS) pathway, 3,3'-dimethylbiphenyl (DM-BP) is formed. Some authors believe that the DDS of DMDBT occurs via a partially hydrogenated

dihydro-intermediate, which loses H<sub>2</sub>S by elimination [5], whereas others have proposed that the C–S bonds of DMDBT are broken by hydrogenolysis [6–9]. In the hydrogenation (HYD) pathway, the reactant molecule is first hydrogenated to tetrahydro-, hexahydro-, and decahydro-intermediates of DMDBT (designated TH-DMDBT, HH-DMDBT, and DH-DMDBT, respectively), the C–S bonds of which are then broken to form 1-methyl-3-(3-methylcyclohexyl)benzene (designated 3,3'-dimethylcyclohexylbenzene [DM-CHB]) and 1-methyl-3-(3-methylcyclohexyl)cyclohexane (or 3,3'-dimethylbicyclohexyl [DM-BCH]). These are presented in Scheme 1, with all sulfur-containing compounds connected by (de)hydrogenation on the top horizontal line and the final hydrocarbon products on the bottom line. The HDS of DBT occurs mainly through the DDS pathway, but the HYD pathway dominates the HDS of DMDBT [1–4]. It is commonly assumed that this is because of the fact that in the DDS pathway, the reactant needs to adsorb in a  $\sigma$  mode, perpendicular to the catalyst surface. In this mode, the neighboring methyl groups hinder bonding with the catalytic sites because they extend further into space than the

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Scheme 1. Reaction network of the HDS of DMDBT.

lone pairs of the sulfur atom, which are responsible for the  $\sigma$  bonding [1–4,10,11].

The HDS of DMDBT occurs predominantly through the HYD pathway and thus is dependent on the hydrogenating ability of the catalyst. Nevertheless, in the HYD pathway C–S bonds also must be broken; this raises the question of whether this occurs through hydrogenolysis or through  $\text{H}_2\text{S}$  elimination. Up to now, information on the network of the HDS of DMDBT has been obtained only by studying DMDBT itself [1–5]. Sometimes the reaction network itself was discussed even though none of the TH-DMDBT, HH-DMDBT, and DH-DMDBT intermediates were observed [12]. But because this network is complex, studying only the reaction of DMDBT itself is not sufficient; the reactions of the intermediates should be studied as well. Consequently, we have synthesized the three key intermediates, TH-DMDBT, HH-DMDBT, and DH-DMDBT, and studied their HDS. The questions that we address are how fast or slow the different reaction steps in the HDS network occur, how DDS occurs, and how the last part of the HYD route (the final removal of sulfur from the hydrogenated DBT intermediates) occurs.

## 2. Experimental

### 2.1. Catalyst preparation and reaction procedure

$\text{Mo}/\gamma\text{-Al}_2\text{O}_3$  and  $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$  catalysts with 8 wt% Mo and 0 or 3 wt% Ni were prepared by incipient wetness impregnation of  $\gamma\text{-Al}_2\text{O}_3$  (Condea, pore volume  $0.5\text{ cm}^3\text{ g}^{-1}$ , specific surface area  $230\text{ m}^2/\text{g}$ ) with an aqueous solution of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ , followed by an aqueous solution of  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (all Aldrich) for the promoted catalyst. After each impregnation step, the catalysts were dried in air at ambient temperature for 4 h and then in an oven at  $120\text{ }^\circ\text{C}$  for 15 h, and finally calcined at  $500\text{ }^\circ\text{C}$  for 4 h. Before the reaction, the catalysts were activated by in situ sulfidation with a mixture of 10%  $\text{H}_2\text{S}$  in  $\text{H}_2$  (50 ml/min) at  $400\text{ }^\circ\text{C}$  and 1 MPa for 4 h. HDS reactions were carried out in a continuous mode in a fixed-bed Inconel reactor, as described elsewhere [13]. Most experiments were performed at  $300\text{ }^\circ\text{C}$ , because at higher temperatures, the reactions of TH-DMDBT and HH-DMDBT were too fast. This also allowed comparison with published results for the HDS of DMDBT over  $\text{Pd}/\text{Al}_2\text{O}_3$  [14]. A consequence of the choice of  $300\text{ }^\circ\text{C}$  was that the rate of the HDS reaction

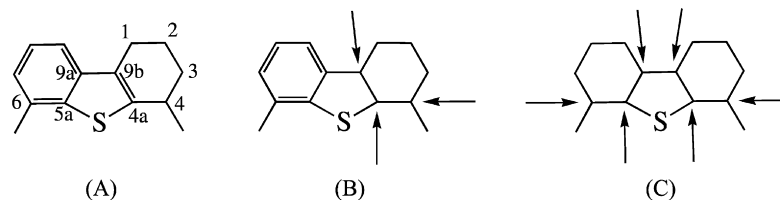
of DMDBT over the Mo catalyst became rather slow; therefore, some experiments were carried out at  $320$  and  $340\text{ }^\circ\text{C}$ .

The gas-phase feed consisted of 1 kPa of reactant (DMDBT, TH-DMDBT, HH-DMDBT, or DH-DMDBT), 130 kPa of toluene (solvent for the reactant), 8 kPa of dodecane (GC reference for the DMDBT derivatives), 35 kPa of  $\text{H}_2\text{S}$ , and 4.8 MPa of  $\text{H}_2$ . Previous tests verified that toluene does not influence the HDS of DMDBT [13]. For the experiments at different  $\text{H}_2\text{S}$  partial pressures (0–100 kPa), the partial pressure of  $\text{H}_2$  was varied to keep the total pressure constant at 5 MPa. The reaction products were analyzed by off-line gas chromatography, as described elsewhere [13]. Weight time was defined as  $\tau = w_{\text{cat}}/n_{\text{feed}}$ , where  $w_{\text{cat}}$  denotes the catalyst weight and  $n_{\text{feed}}$  denotes the total molar flow to the reactor ( $1\text{ g min/mol} = 0.15\text{ g h/l}$ ). The weight time was changed by varying the flow rates of the liquid and the gaseous reactants while keeping their ratio constant. The reaction was stable after 3–4 h; during the 2 weeks of operation, almost no deactivation of the catalyst occurred.

### 2.2. Preparation of DMDBT intermediates

TH-DMDBT was synthesized by hydrogenation of DMDBT over 40 mg of sulfided  $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$  catalyst at  $320\text{ }^\circ\text{C}$ , 5 MPa total pressure, and weight time  $\tau = 4.9\text{ g min/mol}$ . The reaction conditions were chosen to maximize the yield of TH-DMDBT and minimize the loss of sulfur-containing products to hydrocarbons. The gas-phase feed consisted of 130 kPa of toluene, 2.5 kPa of DMDBT (almost the limit of the solubility in toluene,  $45\text{ mg/ml}$ ), 20 kPa of  $\text{H}_2\text{S}$ , and 4.85 MPa of  $\text{H}_2$ . The selectivity to TH-DMDBT was 58% at 31% conversion of DMDBT. The product was separated and purified by crystallization, column chromatography, and vacuum distillation, as described previously [14,15]. MS and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy characterized the final TH-DMDBT product as 1,2,3,4-tetrahydro-4,6-DMDBT (Scheme 2A).

HH-DMDBT and DH-DMDBT were prepared by hydrogenation of DMDBT in a 300-ml stainless steel autoclave at the lower temperature of  $200\text{ }^\circ\text{C}$  and higher pressure of 15 MPa  $\text{H}_2$  for 5 h over 10 g of a 10 wt%  $\text{Pd}/\text{C}$  catalyst. The autoclave was loaded with 10 g of DMDBT, 10 g of catalyst, and 180 ml of glacial acetic acid. (This solvent is crucial for high conversion.) At 53% conversion, the selectivity to HH-DMDBT was 79%. Separation and purification were performed as described previ-



Scheme 2. (A) 1,2,3,4-Tetrahydro-4,6-dimethyldibenzothiophene (TH-DMDBT), (B) hexahydro-4,6-dimethyldibenzothiophene (HH-DMDBT), and (C) dodecahydro-4,6-dimethyldibenzothiophene (DH-DMDBT) with chiral carbon atoms indicated by arrows.

ously [15]. HH-DMDBT has three chiral centers (Scheme 2B). Thus, the hydrogen atoms on the carbon atoms in positions 4, 4a, and 9b can be in either *cis* or *trans* configuration relative to each other, leading to 4 different diastereomers. Three HH-DMDBT diastereomers could be isolated: 28% isomer A, 9% isomer B, and 63% isomer C.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, MS/MS experiments, and X-ray crystal structure determination [15] revealed that isomer A had a 4,4a-*trans*;4a,9b-*cis* configuration, isomer B had a 4,4a-*trans*;4a,9b-*trans* configuration, and isomer C had a 4,4a-*cis*;4a,9b-*cis* configuration. A small amount of the fourth diastereomer, D, which must have a 4,4a-*cis*;4a,9b-*trans* configuration, was observed, but it was insufficient to allow isolation for characterization.

The hydrogenation of DMDBT in the autoclave at 200 °C and 15 MPa over 15 g of a 10 wt% Pd/C catalyst (conversion, 71%; selectivity to DH-DMDBT, 32%) led almost exclusively to the production of one DH-DMDBT diastereomer with the 4,4a-*cis*;4a,9b-*cis*;5a,6-*trans*;5a,9a-*trans*;9a,9b-*cis* configuration of the six chiral centers of the molecule (Scheme 2C).

### 3. Results

#### 3.1. HDS of DMDBT

The sulfided  $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$  catalyst exhibited low HDS activity; only 18% of DMDBT was converted at 300 °C and  $\tau = 5.2$  g min/mol in the absence of  $\text{H}_2\text{S}$ . The same intermediates and products were observed as in the HDS of DMDBT over  $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$  [14,16]: DM-BP, the product of the DDS route, and TH-DMDBT, HH-DMDBT, DH-DMDBT, DM-CHB, and DM-BCH, the intermediate and final products of the HYD pathway (Scheme 1). Only trace amounts of DH-DMDBT were detected. The yields of the other five compounds increased with weight time. The selectivity to TH-DMDBT decreased with weight time (Fig. 1), but in all cases TH-DMDBT was the most abundant compound, with a selectivity >47% at  $\tau = 5.2$  g min/mol and 0 kPa  $\text{H}_2\text{S}$ . The selectivity to HH-DMDBT, the second most abundant product, first increased with weight time and then leveled off at  $\tau > 2.2$  g min/mol. As shown in Fig. 1a, these two partially hydrogenated sulfur compounds represented 89% of the reaction products at short weight time ( $\tau = 0.8$  g min/mol) and 73% at high weight time. This indicates that sulfur removal is difficult over  $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$  and that under our conditions, the HDS reaction was still in its initial stage. DM-CHB and DM-BCH, the final products of the HYD pathway, exhibited continuously increasing selectivity. The selectivity toward the formation of DM-BP, the DDS product, was

rather low; it decreased from 4.8 to 3.6% with weight time in the absence of  $\text{H}_2\text{S}$ .

$\text{H}_2\text{S}$  had only a slight influence on the conversion of DMDBT. The yields of TH-DMDBT, HH-DMDBT, and DM-BCH increased, whereas the yields of DM-BP and DM-CBH decreased slightly in the presence of 10 kPa  $\text{H}_2\text{S}$ . This led to a small increase in the selectivity to HH-DMDBT and decreases in the selectivity to DM-CHB and DM-BP (Fig. 1). Whereas DM-CHB was the main hydrocarbon product in the absence of  $\text{H}_2\text{S}$ , DM-BCH was the major HDS product in the presence of  $\text{H}_2\text{S}$ . Increasing the  $\text{H}_2\text{S}$  partial pressure to 100 kPa had little effect on the HDS of DMDBT over sulfided  $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ .

The sulfided  $\text{Ni-Mo}/\gamma\text{-Al}_2\text{O}_3$  catalyst exhibited a much higher HDS activity than the  $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$  catalyst in the absence of  $\text{H}_2\text{S}$ . At 300 °C, 0 kPa  $\text{H}_2\text{S}$ , and  $\tau = 5.2$  g min/mol, the conversion of DMDBT reached 51% (Fig. 2a). DM-CHB became the most abundant product at  $\tau > 0.8$  g min/mol, and its yield reached 32% at  $\tau = 5.2$  g min/mol (Fig. 2a), almost 12 times higher than over  $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ . Although conversion

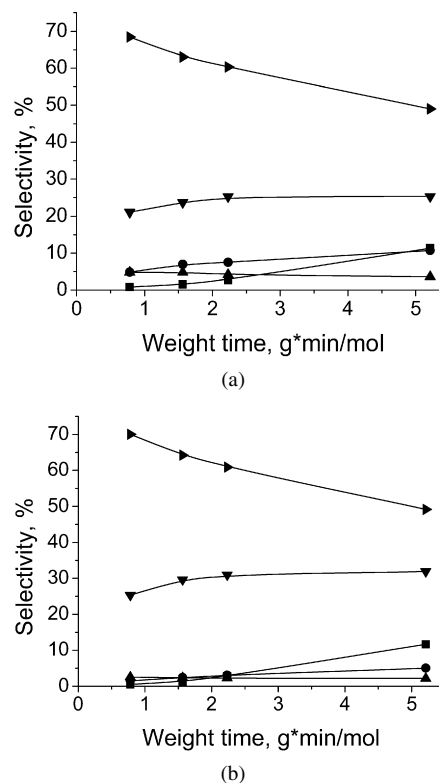


Fig. 1. Product selectivities in the HDS of DMDBT over  $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$  at 300 °C and 0 (a) and 10 (b) kPa  $\text{H}_2\text{S}$  as a function of weight time ( $\blacktriangleright$ ) TH-DMDBT; ( $\blacktriangledown$ ) HH-DMDBT; ( $\blacktriangle$ ) DM-BP; ( $\bullet$ ) DM-CHB; ( $\blacksquare$ ) DM-BCH.

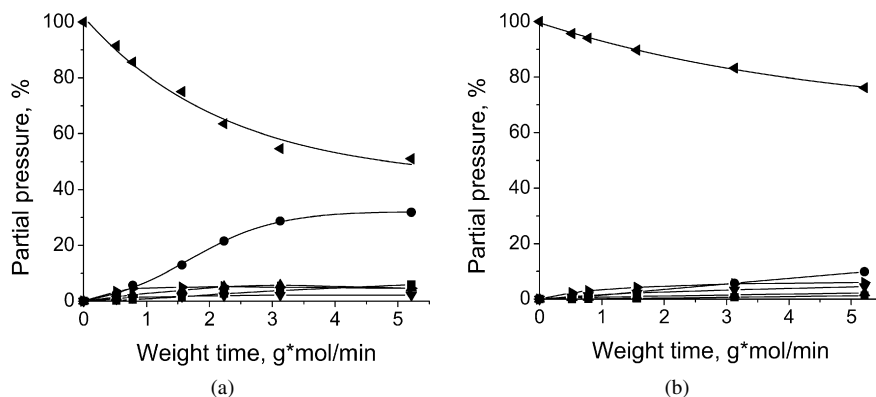


Fig. 2. Partial pressures of reactant and products in the HDS of DMDBT over Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C and 0 (a) and 10 (b) kPa H<sub>2</sub>S as a function of weight time ((◄) DMDBT; (►) TH-DMDBT; (▼) HH-DMDBT; (▲) DM-BP; (●) DM-CHB; (■) DM-BCH).

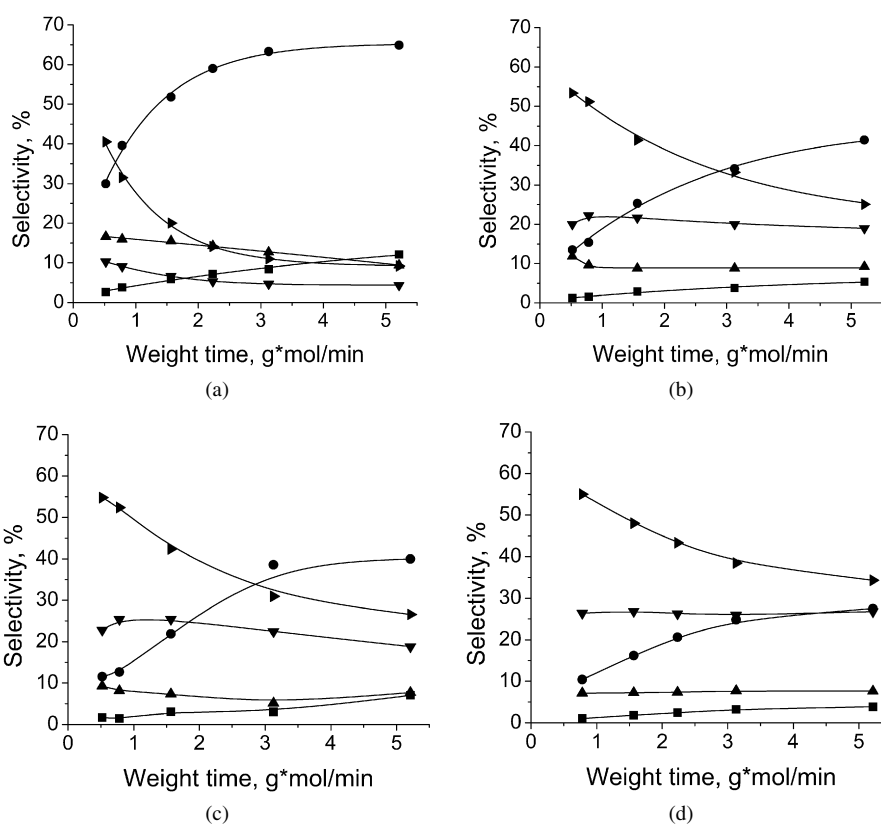


Fig. 3. Product selectivities in the HDS of DMDBT over Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C and 0 (a), 10 (b), 35 (c) and 100 (d) kPa H<sub>2</sub>S as a function of weight time ((►) TH-DMDBT; (▼) HH-DMDBT; (▲) DM-BP; (●) DM-CHB; (■) DM-BCH).

was higher over the Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst than over the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, the selectivity to DM-BP was higher over Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> than over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 16.6% at the lowest weight time and 9.4% at the highest weight time (Fig. 3a).

H<sub>2</sub>S strongly inhibited the conversion of DMDBT and the formation of DM-CHB over Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Fig. 2b). At  $\tau = 5.2$  g min/mol and 10 kPa H<sub>2</sub>S, the conversion of DMDBT and the yield of DM-CHB decreased drastically, to 24 and 10%, respectively. Similar to Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, a further increase in the partial pressure of H<sub>2</sub>S from 10 to 100 kPa had little influence on the total conversion of DMDBT. However, the selectivities to the three HDS products (DM-CHB, DM-BCH, and DM-BP)

decreased with H<sub>2</sub>S partial pressure, and TH-DMDBT became the most abundant product at all weight times at 100 kPa H<sub>2</sub>S (Fig. 3d). In contrast to the HDS of DMDBT over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, DM-CHB was always the major desulfurized hydrocarbon product over Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in both the presence and absence of H<sub>2</sub>S.

Assuming pseudo-first-order kinetics for the HDS of DMDBT, we calculated the rate constant of the overall conversion of DMDBT ( $k_{\text{DMDBT}}$ ) at short weight time. By taking the selectivities of the pathways into account, we could also calculate the rate constants of the two routes ( $k_{\text{HYD}}$  and  $k_{\text{DDS}}$ ). The results over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at different H<sub>2</sub>S

Table 1  
The pseudo-first-order rate constants for the HDS of DMDBT over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C and different H<sub>2</sub>S partial pressures

Catalyst	Rate constant (mol/(g min))	H <sub>2</sub> S partial pressure (kPa)			
		0	10	35	100
Mo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$k_{\text{DMDBT}}$	0.036	0.035	0.038	0.049
	$k_{\text{DDS}}$	0.002	0.001	0.001	0.001
	$k_{\text{HYD}}$	0.034	0.034	0.037	0.048
NiMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$k_{\text{DMDBT}}$	0.19	0.080	0.076	0.050
	$k_{\text{DDS}}$	0.03	0.009	0.006	0.004
	$k_{\text{HYD}}$	0.16	0.071	0.070	0.046

partial pressures are given in Table 1. In the absence of H<sub>2</sub>S, the pseudo-rate constant  $k_{\text{DMDBT}}$  of the overall conversion of DMDBT over the Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 5.3 times higher than that over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. However, when the H<sub>2</sub>S partial pressure was increased to 100 kPa, the values of  $k_{\text{DMDBT}}$  for the two catalysts became almost the same, indicating a strong inhibitory effect of H<sub>2</sub>S on the HDS activity of Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, as mentioned above.

### 3.2. HDS of TH-DMDBT

The partially hydrogenated TH-DMDBT converted rapidly to HH-DMDBT over the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 300 °C and

in the presence of 35 kPa H<sub>2</sub>S (Fig. 4a). HH-DMDBT was a primary product, and its selectivity decreased with increasing weight time; it was 82% at the lowest weight time (Fig. 4b). Based on its constant (low) selectivity, DM-CHB seemed to be a primary product as well. The HH-DMDBT intermediate was hydrogenated to DH-DMDBT, the yield of which was very low (only 0.7% at the highest weight time), and desulfurized to DM-BCH. For  $\tau > 1.6$  g min/mol, the major final reaction product was DM-BCH (Fig. 4).

The conversion of TH-DMDBT over NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C and in the presence of 35 kPa H<sub>2</sub>S was faster and the yield of HH-DMDBT was lower (Fig. 5a) than over the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (Fig. 4a). Only a trace of DH-DMDBT was detected at the highest weight time. However, the total amount of desulfurized products (DM-CHB and DM-BCH) at  $\tau = 5.3$  g min/mol was much higher over Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (87%) than over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (36%). The final product distribution was different over the NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The major reaction product was DM-CHB instead of DM-BCH (Figs. 5b and 4b, respectively), with a selectivity of 87% at the highest weight time. These results are in good agreement with our previous results on the HDS of DMDBT [17].

From the conversion of TH-DMDBT at low weight time and assuming pseudo-first-order kinetics, we calculated  $k_{\text{TH-DMDBT}}$

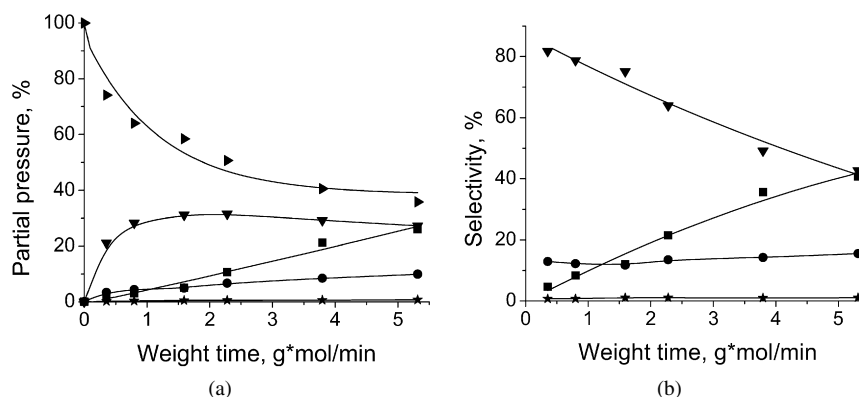


Fig. 4. Partial pressures of reactant and products (a) and product selectivities (b) in the HDS of TH-DMDBT over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C in the presence of 35 kPa H<sub>2</sub>S as a function of weight time (( $\blacktriangleright$ ) TH-DMDBT; ( $\blacktriangledown$ ) HH-DMDBT; ( $\blackstar$ ) DH-DMDBT; ( $\bullet$ ) DM-CHB; ( $\blacksquare$ ) DM-BCH).

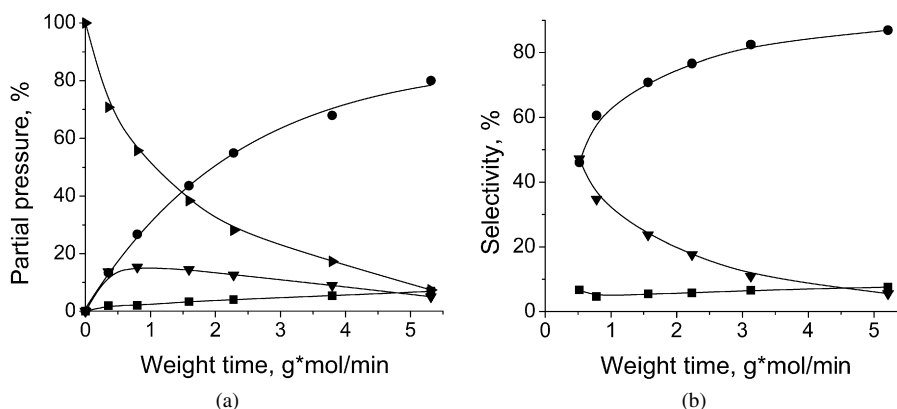


Fig. 5. Partial pressures of reactant and products (a) and product selectivities (b) in the HDS of TH-DMDBT over Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C in the presence of 35 kPa H<sub>2</sub>S as a function of weight time (( $\blacktriangleright$ ) TH-DMDBT; ( $\blacktriangledown$ ) HH-DMDBT; ( $\bullet$ ) DM-CHB; ( $\blacksquare$ ) DM-BCH).

$= 0.8 \pm 0.1$  and  $1.0 \pm 0.1$  mol/(g min) for Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively.

### 3.3. HDS of HH-DMDBT

Only two isomers of HH-DMDBT, the 4,4a-*trans*;4a,9b-*cis* isomer A and the 4,4a-*cis*;4a,9b-*cis* isomer C, were prepared in sufficient amounts to carry out HDS experiments. Their HDS was studied over the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 300 °C and two

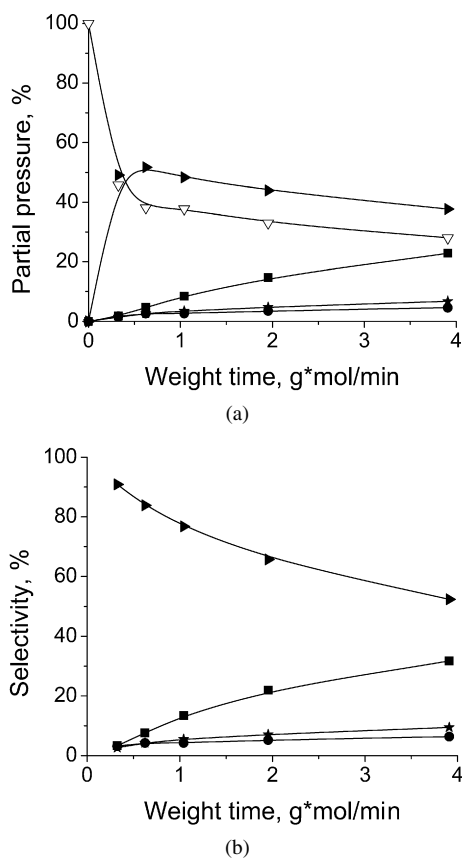


Fig. 6. Partial pressures of reactant and products (a) and product selectivities (b) in the HDS of HH-DMDBT isomer C over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C and 10 kPa H<sub>2</sub>S as a function of weight time ( $\nabla$ ) HH-DMDBT (C); ( $\blacktriangleright$ ) TH-DMDBT; ( $\blackstar$ ) DH-DMDBT; ( $\bullet$ ) DM-CHB; ( $\blacksquare$ ) DM-BCH.

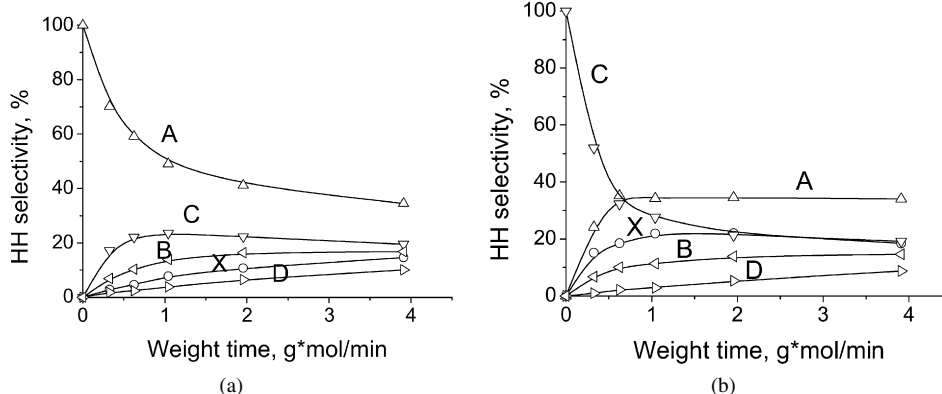


Fig. 7. Distribution of hexahydro-isomers in the HDS of HH-DMDBT isomer A (a) and isomer C (b) over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C and 10 kPa H<sub>2</sub>S as a function of weight time.

H<sub>2</sub>S partial pressures (10 and 35 kPa). Because of their similar HDS behavior, only the HDS results of isomer C are shown here (Fig. 6).

HH-DMDBT was very reactive in the presence of 10 kPa H<sub>2</sub>S (Fig. 6a). A conversion of 65% was already reached at  $\tau = 0.6$  g min/mol, due mainly to the interconversion of HH-DMDBT to TH-DMDBT (with a selectivity of almost 90%). The TH-DMDBT and HH-DMDBT partial pressures leveled off thereafter. TH-DMDBT, formed by dehydrogenation, was always the most abundant product, with 56% selectivity at high weight time ( $\tau = 3.9$  g min/mol and 10 kPa H<sub>2</sub>S). A trace of DMDBT was observed as the product of subsequent dehydrogenation. The selectivities of DH-DMDBT, DM-BCH, and DM-CHB all increased with weight time (Fig. 6b), with DM-BCH being much more abundant than DM-CHB. The conversion of the HH-DMDBT isomer C and the yield of TH-DMDBT were hardly affected by an increase in the H<sub>2</sub>S partial pressure from 10 to 35 kPa. However, the yield of DM-BCH at  $\tau = 2.0$  g min/mol decreased from 15% at 10 kPa H<sub>2</sub>S to 9% at 35 kPa H<sub>2</sub>S. At the same time, the yield of DH-DMDBT increased slightly.

During the HDS reaction, isomerization of the *trans*-*cis* and *cis*-*cis* isomers to the other isomers of HH-DMDBT occurred. GC-MS identified five isomers with mass 218. The MS patterns of four of these could be identified [15] as those of isomers A (*trans*-*cis*), B (*trans*-*trans*), C (*cis*-*cis*), and D (*cis*-*trans*). Another GC peak belonged to mass 218 as well, but the identity of this isomer X could not be determined. The selectivities of the isomers, normalized to the total amount of HH-DMDBT, demonstrate that the *trans*-*cis* isomer quickly converted to the *cis*-*cis* isomer, so that equilibrium was approached already at  $\tau = 1.0$  g min/mol and 10 kPa H<sub>2</sub>S (Fig. 7a). The *cis*-*cis* isomer also quickly converted to the *trans*-*cis* and *trans*-*trans* isomers at 10 kPa H<sub>2</sub>S (Fig. 7b). The distribution of the isomers in the HDS of the *trans*-*cis* and *cis*-*cis* isomers at high weight time did not change on an increase of the H<sub>2</sub>S partial pressure to 35 kPa; only the selectivity to X decreased.

HH-DMDBT can convert in three different ways over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: (1) by hydrogenation to DH-DMDBT and further desulfurization to DM-BCH, (2) by dehydrogenation to TH-DMDBT, and (3) by direct sulfur removal to DM-CHB. Thus,

Table 2

The pseudo-first-order rate constants for the HDS of HH-DMDBT isomer C over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C and different H<sub>2</sub>S partial pressures

Rate constant (mol/(g min))	H <sub>2</sub> S partial pressure (kPa)	
	10	35
$k_{\text{HH-DMDBT}}$	2.40 ± 0.10	2.56 ± 0.10
$k_{\text{hydrogenation}}$	0.04 ± 0.03	0.07 ± 0.03
$k_{\text{desulfurization}}$	0.07 ± 0.03	0.06 ± 0.03
$k_{\text{dehydrogenation}}$	2.29 ± 0.10	2.43 ± 0.10

the sums of the selectivities of the products in each pathway and their extrapolation to  $\tau = 0$  quantify the initial proportions of the three independent routes. Based on these three proportions and a pseudo-first-order kinetic assumption, the rate constants  $k_{\text{HH-DMDBT}}$ ,  $k_{\text{hydrogenation}}$ ,  $k_{\text{dehydrogenation}}$ , and  $k_{\text{desulfurization}}$  of HH-DMDBT (C) over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at different H<sub>2</sub>S partial pressures were calculated (Table 2).

### 3.4. HDS of DH-DMDBT

The reactivity of the fully hydrogenated DH-DMDBT molecule over the Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 300 °C and 35 kPa H<sub>2</sub>S was much higher than that of HH-DMDBT. The major reaction product was DM-BCH (Fig. 8). Two other products were identified by a combination of mass spectrometry and chromatography; these had masses of 192 and 220 and behaved as primary products (Fig. 8b). The product

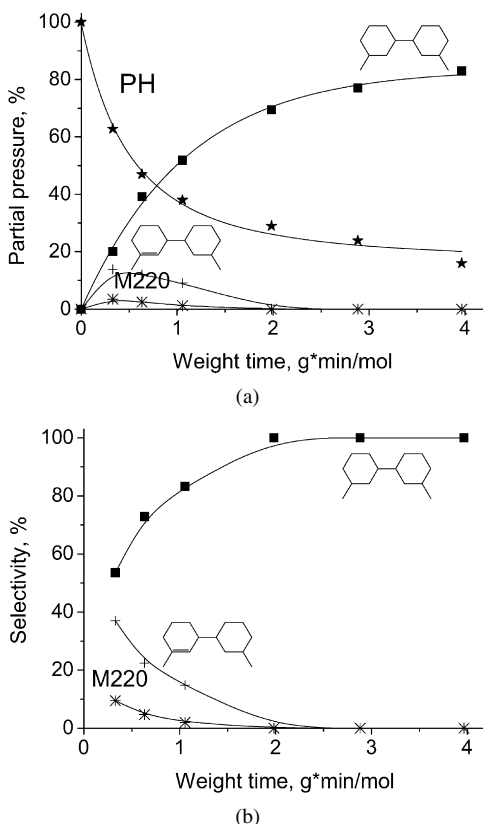


Fig. 8. Partial pressures of reactant and products (a) and product selectivities (b) in the HDS of DH-DMDBT over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C and 35 kPa H<sub>2</sub>S as a function of weight time.

with mass 192 is 1-methyl-3-(3-methylcyclohexyl)cyclohexene (3,3'-dimethylcyclohexylcyclohexene), a desulfurized product with one double bond. Actually, several isomers with mass 192 were observed; these could be isomers with different double-bond locations, or different stereoisomers (due to the presence of chiral centers). The low yields of these isomers did not allow further analysis. The product with mass 220 must be octahydro-4,6-dimethyldibenzothiophene (OH-DMDBT), the dehydrogenated reactant with two double bonds. These double bonds are most likely located in the thiophene ring. The products with mass 192 and 220 were not detected above  $\tau = 2.5$  g min/mol.

Four different isomers of DH-DMDBT were observed in the HDS experiments for TH-DMDBT and HH-DMDBT. The reactant in the HDS of DH-DMDBT itself had the 4,4a-cis;4a,9b-cis;5a,6-trans;5a,9a-trans;9a,9b-cis configuration of the hydrogen atoms on the six chiral centers of the molecule [15]. The selectivities of the main five isomers observed in the HDS of this DH-DMDBT reactant, normalized to the total amount of DH-DMDBT, showed that the 4,4a-cis;4a,9b-cis;5a,6-trans;5a,9a-trans;9a,9b-cis isomer isomerized quickly to four other DH-DMDBT isomers (Fig. 9). The structures of these isomers were not determined. Equilibrium between the isomers was not reached at the highest weight time used.

The influence of H<sub>2</sub>S on the HDS of DH-DMDBT was studied at 300 °C. At this temperature, no dehydrogenation products were observed except for OH-DMDBT, the product with mass 220. The conversion of DH-DMDBT at  $\tau = 0.3$  g min/mol was 45% in the absence of H<sub>2</sub>S and 25% in the presence of 100 Pa of H<sub>2</sub>S. The main HDS product was 3,3'-dimethylcyclohexylcyclohexene, the desulfurized alkene with mass 192. Its selectivity decreased from 75% in the absence of H<sub>2</sub>S to 70% in the presence of 100 kPa H<sub>2</sub>S. Assuming the reaction of DH-DMDBT to be first order with respect to the reactant, and taking into account the sum of the selectivities of the desulfurized products (DM-BCH and 3,3'-dimethylcyclohexylcyclohexene), we obtained pseudo-HDS rate constants of 1.65, 1.35, 1.09, and 0.74 mol/(g min) at 0, 10, 35, and 100 kPa H<sub>2</sub>S, respec-

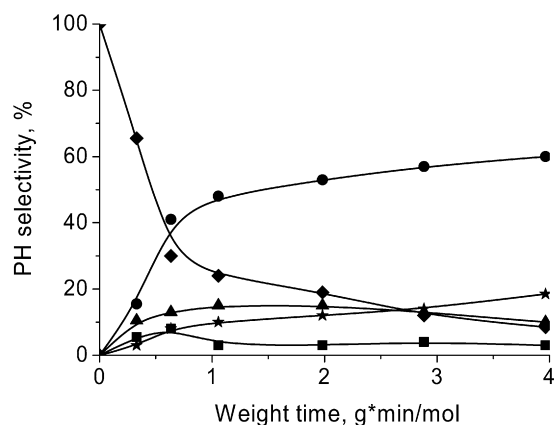


Fig. 9. Distribution of dodecahydro-isomers in the HDS of 4,4a-cis;4a,9b-cis;5a,6-trans;5a,9a-trans;9a,9b-cis-DH-DMDBT over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C as a function of weight time ((◆) 4,4a-cis;4a,9b-cis;5a,6-trans;5a,9a-trans;9a,9b-cis-DH-DMDBT; (▲), (★) and (■) other unknown DH-DMDBT isomers).

Table 3  
Product distribution in the HDS of DH-DMDBT at 340 °C,  $\tau = 0.3$  g min/mol, and different H<sub>2</sub>S partial pressures

H <sub>2</sub> S (kPa)	Conversion (%)	DM-BCH	M-192	DM-CHB	HH-DMDBT	TH-DMDBT	M-220	DM-DBT
0	92.0	33.0	33.9	7.6	4.0	5.5	3.6	4.4
10	83.1	30.0	25.7	6.5	1.9	11.3	4.7	3.0
35	79.1	27.4	23.7	6.1	3.3	11.8	2.9	3.9
100	63.7	40.1	1.4	3.3	4.2	10.2	0.9	3.6

tively. These findings indicate that the removal of sulfur from DH-DMDBT is suppressed with increasing partial pressure of H<sub>2</sub>S.

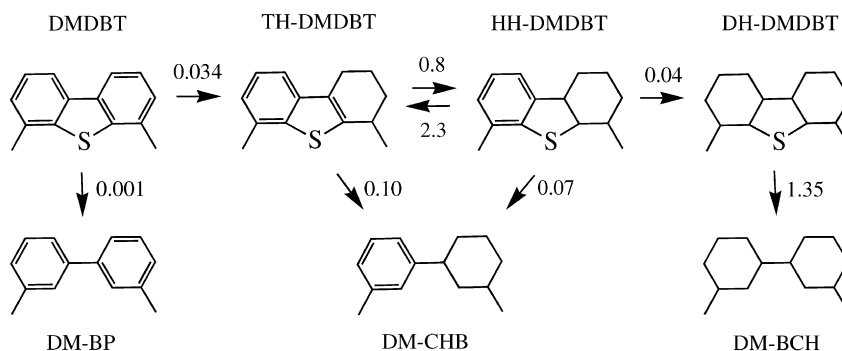
To allow a comparison with results obtained in the HDS of DMDBT at 340 °C [17], the HDS of DH-DMDBT was also studied at 340 °C. The DMDBT results had indicated that H<sub>2</sub>S has the same inhibitory influence on the sulfur removal step in the hydrogenation pathway as in the direct desulfurization pathway, but because the hydrogenation pathway of DMDBT consists of several consecutive and parallel reactions, results for the sulfur removal step were only semiquantitative. More accurate results can be obtained by taking the fully hydrogenated intermediate as a reactant, because this intermediate can react only by desulfurization. The HDS of DH-DMDBT demonstrates that the total conversion of DH-DMDBT and the sum of the desulfurized products (DM-BCH, product with mass 192, and DM-CHB) decreased with increasing partial pressure of H<sub>2</sub>S (Table 3). At the higher temperature of 340 °C, DH-DMDBT also underwent dehydrogenation to HH-DMDBT, TH-DMDBT, and DMDBT. Desulfurization of HH-DMDBT and/or TH-DMDBT occurred with the formation of DM-CHB, the yield of which decreased with increasing H<sub>2</sub>S partial pressure from 7.6 to 3.3% (Table 3). DMDBT was hardly desulfurized via the direct desulfurization pathway, because the amount of DM-BP never exceeded 0.1%. The product with mass 192 behaved as a primary product, and its production was suppressed by H<sub>2</sub>S almost as much as the production of DM-BCH up to 35 kPa H<sub>2</sub>S. At 100 kPa H<sub>2</sub>S, we observed only 1.4% of the product with mass 192, whereas the amount of DM-BCH was higher than at lower partial pressure of H<sub>2</sub>S.

#### 4. Discussion

The rate constants presented in Tables 1 and 2 and Scheme 3 were calculated from the experimental data at short weight

time by assuming first-order kinetics and by lumping the influences of the H<sub>2</sub> and H<sub>2</sub>S pressure into the kinetic constants. Because DMDBT and its hydrogenated intermediates have different aromaticity, their adsorption constants and thus their kinetic order could be different. Once we have synthesized more TH-DMDBT and HH-DMDBT, we will study this further. For the moment, note that the rate constants are pseudo-first-order rate constants that are valid only under the specified conditions. Nevertheless, these rate constants are valuable for a semiquantitative comparison.

The kinetic results of the HDS of DMDBT and its intermediates at low conversion over sulfided Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Scheme 3) show that the smallest measurable rate constant was obtained for the reaction of DMDBT to DM-BP. This rate constant (0.001 mol/(g min)) was 34 times smaller than the next smallest rate constant, that for the reaction of DMDBT to TH-DMDBT (0.034 mol/(g min)). Thus, the rate-determining steps in the HDS of DMDBT are the reactions of DMDBT itself. The next steps in the hydrogenation part of the HDS network—the hydrogenation of TH-DMDBT and dehydrogenation of HH-DMDBT—are more than an order of magnitude faster. This explains why it appears as if TH-DMDBT and HH-DMDBT quickly come to equilibrium (Figs. 4 and 6). The hydrogenation reaction rate constant of the subsequent reaction of HH-DMDBT to DH-DMDBT is, within the uncertainty of the measurement ( $\pm 0.01$  mol/(g min)), equal to that of DMDBT to TH-DMDBT, whereas the rate constant of the desulfurization reaction from HH-DMDBT to DM-CHB is about twice as large. The rate constant of the desulfurization reaction of DH-DMDBT to DM-BCH is the largest of all rate constants. The rate constant for desulfurization thus strongly increases from DMDBT (0.001 mol/(g min)) to HH-DMDBT (0.07 mol/(g min)) to DH-DMDBT (1.35 mol/(g min)). This must be due to weakening of the C–S bond (going from an arylthiol bond to an alkanethiol bond), as well as to decreased



Scheme 3. Pseudo-first-order rate constants (in mol/(g min)) in the reaction network of the HDS of DMDBT over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C and 10 kPa H<sub>2</sub>S.



steric hindrance. Hydrogenation of a phenyl ring makes the cyclohexyl ring in the hydrogenated DMDBT intermediate flexible and allows the methyl group to rotate away from the C(4a)–S–C(5a) plane (cf. Scheme 2A). Consequently, less open sites on the catalyst surface can bind the hydrogenated intermediates via the lone pair of the sulfur atom, and breaking of the C–S bond can occur faster.

Although the amounts of TH-DMDBT and HH-DMDBT that we had synthesized were sufficient to measure the rate constants of all reaction steps over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, insufficient material was available for measurements over NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The rate constants for the reactions of DMDBT to DM-BP and TH-DMDBT and for the desulfurization of TH-DMDBT to DM-CHB were larger over NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> than over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. This may be due to the more open structure of the Ni edges of NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> compared with the Mo and S edges of Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. According to DFT calculations [18–22], a Mo atom at the Mo edge is coordinated by six sulfur atoms and one at the S edge is coordinated by four sulfur atoms, but the Ni atoms on the metal edge of a NiMo catalyst (where the Ni atoms are preferentially located) are coordinated by four or five sulfur atoms. The rate constant for the hydrogenation of TH-DMDBT to HH-DMDBT (1.0 mol/(g min)) is similar to that over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0.8 mol/(g min)).

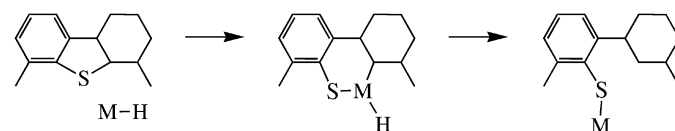
The hydrogenation rate constants for DMDBT and HH-DMDBT over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are about an order of magnitude smaller than over Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [14]. The dehydrogenation rate constants are much smaller as well. Over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, only a trace of DMDBT was observed in the HDS of TH-DMDBT, and only a trace of HH-DMDBT was found in the HDS of DH-DMDBT. This demonstrates that the rate constants for the dehydrogenation of TH-DMDBT and DH-DMDBT are very small (<0.001 mol/(g min)) over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under our conditions. Over Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, on the other hand, substantial amounts of DMDBT were measured in the HDS of TH-DMDBT, and in the HDS of DH-DMDBT, not only HH-DMDBT and TH-DMDBT, but also DMDBT, were found [14]. Over Pd, the hydrogenation of DMDBT and the hydrogenation and dehydrogenation of its hydrogenated intermediates were fast, and DMDBT as well as all hydrogenated intermediates were always observed regardless of the starting compound. The fast hydrogenation and dehydrogenation over Pd are probably due to stronger  $\pi$  bonding. The flat terraces of Pd crystallites offer a better opportunity for extended  $\pi$  bonding and hydrogenation than the curved edges of the MoS<sub>2</sub> and NiMoS<sub>2</sub> particles. This favors the demanding hydrogenation of the first and second phenyl rings of DMDBT. Hydrogenation of the 4a,9b double bond in 1,2,3,4-TH-DMDBT to HH-DMDBT and the reverse dehydrogenation require only a small part of the catalyst surface, however. This explains why the rate constants of these reactions are almost the same over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Metal-sulfide catalysts can break the C–S bond in aliphatic alkanethiols in two ways, by elimination and by hydrogenolysis, as demonstrated by experimental [23] and theoretical [9] studies of the HDS of ethanethiol by elimination to ethene and by hydrogenolysis to ethane. Low (atmospheric) pressure

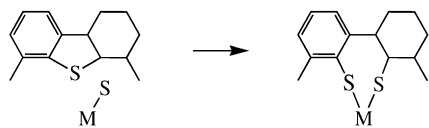
favors elimination, and high H<sub>2</sub> pressure favors hydrogenolysis [24,25]. The mechanism of the C–S bond-breaking in arylthiols (thiophenol) and cyclic sulfides (thiophene, tetrahydrothiophene, DMDBT, TH-DMDBT, HH-DMDBT, and DH-DMDBT) remains a matter of debate. Elimination and hydrogenolysis have not only been proposed for the C–S bond breaking in alkanethiols, but also for the breaking of the arylthiol C–S bond in thiophenol and the C–S sulfide bond in DBT and DMDBT. In the elimination mechanism, a phenyl ring must be hydrogenated before desulfurization by elimination of the SH group and a  $\beta$ -H atom can occur. A hydrogenated intermediate as a common precursor for the DDS and HYD pathways was first proposed by Singhal et al. [26]. However, this hydrogenation–elimination DDS mechanism needs a highly energetic 4,4a- or 4a,9b-dihydro-DMDBT compound as an intermediate and requires that H<sub>2</sub>S elimination occur by the less-favorable syn elimination [5,27]. Another difficulty is that hydrogenation of a double bond requires  $\pi$  adsorption, which makes it difficult to understand why the methyl groups constitute a steric problem in the DDS of DMDBT.

An alternative DDS mechanism assumes that the C–S bond is broken by hydrogenolysis [6–9]. Hydrogenolysis is known to occur because it is the only possible route for breaking the C–S bond of methanethiol, which quickly desulfurizes to methane over MoS<sub>2</sub> and WS<sub>2</sub> [28]. DFT calculations have confirmed that hydrogenolysis of CH<sub>3</sub>SH to CH<sub>4</sub> [8], C<sub>2</sub>H<sub>5</sub>SH to C<sub>2</sub>H<sub>6</sub> [9], 2,5-dihydrothiophene to 2-butene [29], and C<sub>6</sub>H<sub>5</sub>SH to C<sub>6</sub>H<sub>6</sub> [30] have relatively low activation energies. Studies in homogeneous solution have shown that organometallic complexes can insert into the C–S bonds of thiophene, benzothiophene, and DBT [31–34] (Scheme 4). HDS can then occur via M–C cleavage of the resulting metallathiacycle to a thiolate complex, which is known to desulfurize more easily than a cyclic sulfide. All of these results from heterogeneous and homogeneous catalysis studies indicate that hydrogenolysis is a likely mechanism for HDS.

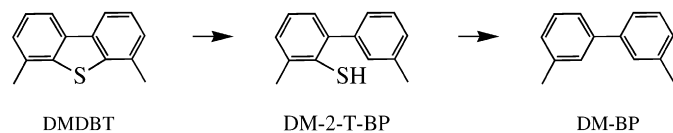
Another mechanism for the breaking of the first C–S bond in cyclic sulfides could involve acid-catalyzed ring opening by H<sub>2</sub>S to a dithiol or by a metal-sulfide fragment on the catalyst surface to a dithiolate as the first step. Such a reaction is analogous to the acid-catalyzed reactions of ethers to alcohols and is used in the synthesis of tetrahydrofurans to tetrahydrothiophenes and pyrrolidines [35]. In this way, tetrahydrothiophene could react with H<sub>2</sub>S on a metal cation site (Lewis acid) to 1,4-butanedithiol, which quickly reacts to a mixture of butane (by double hydrogenolysis), butene (by elimination and hydrogenolysis or by double elimination and hydrogenation), and butadiene (by double elimination). Similarly, HH-DMDBT could open the sulfur-containing ring to 4a,5a-dithio-DM-CHB



Scheme 4. Reaction of a cyclic sulfide to a metal thiolate via insertion of a metal hydride complex in a C–S bond.



Scheme 5. Formation of a dithiolate complex at the catalyst surface as intermediate for opening of the thiophene ring in DMDBT.

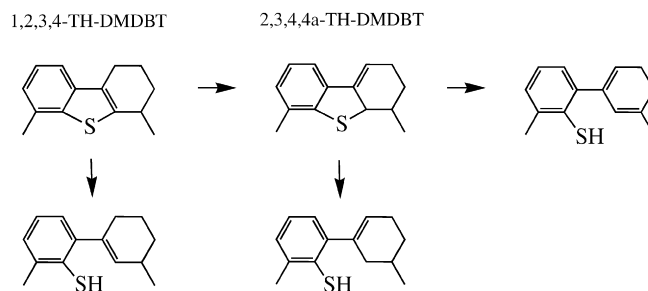


Scheme 6. Direct desulfurization of 4,6-dimethyldibenzothiophene (DMDBT) to 3,3'-dimethylbiphenyl (DM-BP).

and DH-DMDBT to 4a,5a-dithio-DM-BCH. These dithiols will undergo fast desulfurization by hydrogenolysis or by a combination of hydrogenolysis and elimination. The ring opening also could occur by reaction of the substrate with a metal atom and a sulfur atom at the catalyst surface to a dithiolate structure (cf. Scheme 5 for HH-DMDBT). The metal–dithiolate complex can react directly by hydrogenolysis of both C–S bonds. This acid-catalyzed ring opening is less likely for aromatic sulfides such as DBT and DMDBT, because aromatic nucleophilic substitution is much more difficult than aliphatic nucleophilic substitution [36].

DDS is the minor route for the removal of sulfur from DMDBT (Scheme 3). The DDS reaction must be a two-step process, with first a reaction to 2-methyl-6-(3-methylphenyl)thiophenol (3,3'-dimethyl-2-thiobiphenyl) and then a reaction to DM-BP (Scheme 6). The second step must be fast, because an intermediate thiophenol has never been observed in the HDS of either DBT or DMDBT. Moreover, in the HYD route, one C–S bond in a cyclic sulfide must be broken. Whichever C–S bond-breaking mechanism prevails, it most likely will be easier to break the first C–S bond of the hydrogenated intermediates TH-DMDBT, HH-DMDBT, and DH-DMDBT than that of DMDBT. The reason for this is that in the hydrogenation–elimination mechanism, hydrogenation to a dihydro-intermediate is not needed, whereas in the hydrogenolysis mechanism, the C–S bond should be more easily cleaved in an alkanethiol than in an arylthiol.

Our experimental results seem to indicate that the rate of C–S bond-breaking of TH-DMDBT over Mo/Al<sub>2</sub>O<sub>3</sub> is greater than that of HH-DMDBT, because the DM-CHB selectivity extrapolates to 12% at  $\tau = 0$  (Fig. 4b) in the former compared with only 3% in latter (Fig. 6b). However, TH-DMDBT and HH-DMDBT react mainly by interconversion, and thus the uncertainties in the much smaller rate constants for C–S bond breaking are substantial. Actually, the results of the HDS of TH-DMDBT and HH-DMDBT are quite similar if we omit the yields of HH-DMDBT from TH-DMDBT and TH-DMDBT from HH-DMDBT. The yields of DM-BCH and DM-CHB are about equal (Figs. 4a and 6a); only the yield of DH-DMDBT is different. It is lower in the HDS of TH-DMDBT, because DH-DMDBT is then a secondary product, not a primary product. Our experimental results do not allow an unequivocal answer



Scheme 7. Possible intermediates in the HDS of 1,2,3,4-tetrahydro-dimethyldibenzothiophene (TH-DMDBT).

to the question of whether C–S bond-breaking occurs in TH-DMDBT or whether this molecule is first hydrogenated to HH-DMDBT, which then undergoes C–S bond-breaking. 1,2,3,4-TH-DMDBT cannot undergo direct elimination, but a facile double-bond-shift isomerization from 1,2,3,4-TH-DMDBT to 2,3,4,4a-TH-DMDBT would allow elimination (Scheme 7). Hydrogenolysis of the C–S bond in TH-DMDBT is expected to be slightly easier than in DMDBT, because the C(4a)–S bond might be slightly easier to break in TH-DMDBT than in DMDBT, because of a weaker resonance effect between a sulfur atom and a cyclohexene ring compared with that between a sulfur atom and a phenyl ring. In principle, HH-DMDBT and DH-DMDBT can undergo elimination directly, and the first C–S bond-breaking in these molecules should be faster than in TH-DMDBT and DMDBT. Moreover, C–S bond-breaking of HH-DMDBT and DH-DMDBT by hydrogenolysis should be faster, because C(sp<sup>3</sup>)–S bonds are weaker than C(sp<sup>2</sup>)–S bonds.

It is not clear how the first C–S bond-breaking in HH-DMDBT and DH-DMDBT occurs. If it occurs by elimination, then molecules containing a double bond should be formed. HH-DMDBT should react to 1-methyl-3-(3-methylcyclohexenyl)benzene [also designated 1-methyl-3-(3-methylphenyl)cyclohexene or 3,3'-dimethylphenylcyclohexene], and DH-DMDBT should react to 3,3'-dimethylbicyclohexenyl, with a double bond in each of the two methylcyclohexyl rings. Neither of these two molecules was observed in our experiments. It could be that 3,3'-dimethylphenylcyclohexene is rapidly hydrogenated to DM-CHB. Unfortunately, 3,3'-dimethylphenylcyclohexene and even phenylmethylcyclohexene are not commercially available. Instead, we added phenylcyclohexene to the HDS of DBT and checked whether it reacts too rapidly to allow observation under HDS conditions. Although phenylcyclohexene reacted quite rapidly, we were able to observe it. Thus, it seems that fast hydrogenation of 3,3'-dimethylphenylcyclohexene to DM-CHB is not the reason for the absence of 3,3'-dimethylphenylcyclohexene in the HDS of DMDBT. Rather, it appears as if ring opening of a cyclic sulfide is slower by elimination than by hydrogenolysis and that an alkanethiol (or alkylthiolate), rather than an alkenylthiol, is predominantly formed. Acyclic alkanethiols, on the other hand, can undergo elimination, which would explain why the major product in the HDS of DH-DMDBT is 3,3'-dimethylcyclohexylcyclohexene. The first C–S breaking occurs inside a ring due to hydrogenolysis, whereas the second

C–S breaking of the acyclic cyclohexanethiol occurs mainly by elimination.

The HYD pathways in the HDS of DBT and DMDBT over NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are strongly inhibited by 2-methylpiperidine and 2-methylpyridine. In their presence, cyclohexylbenzene and DM-CHB, the final products of the HYD pathway, have been observed in small amounts only [37]. In the present study, we confirmed the strong inhibition by adding 0.1 kPa 2-methylpiperidine during the HDS of 1 kPa HH-DMDBT (isomer C) over Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 300 °C. At high weight time, only 1.5% conversion of HH-DMDBT occurred. This demonstrates a correlation between the ability to break the C–S bond of DBT and DMDBT and the ability to break the C–S bond of their hydrogenated intermediates.

## 5. Conclusion

The tetrahydro-, hexahydro-, and decahydro-intermediates in the HDS of DMDBT were synthesized and their rates of reaction under HDS conditions were measured. The slowest, rate-determining steps in the HDS of DMDBT turned out to be the hydrogenation and hydrogenolysis of DMDBT itself. The hydrogenation of TH-DMDBT to HH-DMDBT, its reverse dehydrogenation, and the desulfurization of DH-DMDBT were the fastest reactions in the network of the HDS of DMDBT. The correlation between the ease of breaking the C–S bond of DBT and DMDBT and that of breaking the C–S bond of their hydrogenated intermediates suggests that all C–S bonds are broken in the same way. Ring opening of the dihydrothiophene ring in HH-DMDBT and the tetrahydrothiophene ring in DH-DMDBT by hydrogenolysis rather than by elimination explains why the resulting products do not contain a double bond.

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