

Influence of nitrogen-containing components on the hydrodesulfurization of 4,6-dimethyldibenzothiophene over Pt, Pd, and Pt–Pd on alumina catalysts

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Pyridine and piperidine inhibited the hydrodesulfurization of 4,6-dimethyldibenzothiophene (4,6-DM-DBT) over alumina-supported Pt, Pd, and Pt–Pd catalysts. The Pd catalyst was least sensitive and the Pt–Pd catalysts were most sensitive to the nitrogen-containing compounds. Pyridine was a stronger inhibitor than piperidine at low initial pressure, but the reverse was true at high initial pressure. Hydrogenation of the tetrahydro to the hexahydro and on to the perhydro sulfur-containing intermediate as well as the removal of sulfur from these intermediates was slowed down by piperidine and pyridine. The hydrogenation pathway in the hydrodesulfurization of 4,6-DM-DBT was inhibited much more than the direct desulfurization pathway. The hydrogenation of the desulfurized products 3,3'-dimethylcyclohexylbenzene and 3,3'-dimethylbiphenyl over the Pt–Pd catalysts was suppressed by piperidine and pyridine. Piperidine and pyridine substantially decrease the ability of noble metal particles to convert refractory molecules like 4,6-DM-DBT and diminish the advantage of bimetallic Pt–Pd over monometallic Pt or Pd catalysts.

KEY WORDS: hydrodesulfurization; 4,6-dimethyldibenzothiophene; dibenzothiophene; platinum; palladium; Pt–Pd catalysts; alumina support; inhibition; pyridine; piperidine.

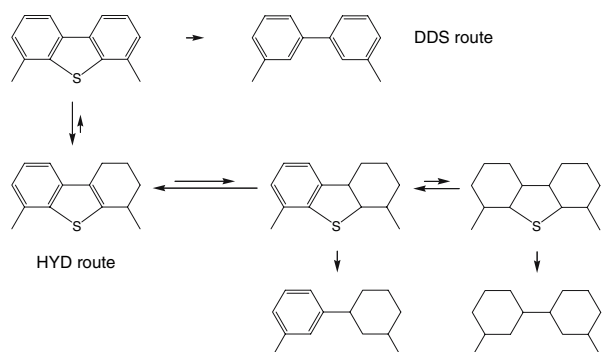
1. Introduction

In the future, the petroleum industry will have to deal with heavier feedstocks, rich in sulfur and nitrogen-containing components. Nitrogen-containing molecules strongly inhibit hydrodesulfurization (HDS) reactions on metal sulfide [1–10] and noble metal catalysts [11–15] because, with their high adsorption constants, they compete with sulfur-containing compounds for adsorption on the catalyst surface [2–5]. This is especially harmful in so-called deep HDS, where the sulfur content of the fuel must be decreased to a very low level and where the amounts of nitrogen- and sulfur-containing molecules become comparable. Therefore, the mutual influence of sulfur- and nitrogen-containing molecules in hydrotreating processes and the influence of nitrogen-containing molecules on the HDS of fuels and model molecules have been studied extensively, in particular over metal sulfide catalysts. Small nitrogen-containing molecules such as alkyl-substituted aniline [3,4,16], piperidine and pyridine [1,3,4,16,17], pyrrole and indole [9,16], and larger ones such as substituted carbazole [2,4,8–10,18], acridine [3,9,10,19], and quinoline [3,4,8,9] have been investigated. The degree of HDS inhibition has been correlated with the gas-phase basicity of the nitrogen-containing molecules and more basic molecules were found to have a stronger inhibiting effect [3,4]. Moreover, nitrogen-containing molecules were found to

inhibit the direct desulfurization (DDS) and hydrogenation (HYD) pathways in the HDS of dibenzothiophene (DBT) [3,8] and 4,6-dimethyldibenzothiophene (4,6-DM-DBT) [8,17] over metal sulfide catalysts to different extents. The HYD route was strongly suppressed, while the DDS pathway was less affected.

Similar information as for metal sulfide catalysts is not available for noble metal catalysts, even though Pt, Pd, and Pt–Pd alloy catalysts are very good hydrogenation catalysts, which can be used in the second stage of a two-stage HDS process [20]. Sulfur- and nitrogen-containing molecules adsorb quite strongly on noble metal surfaces and it has been shown that nitrogen-containing molecules inhibit the HDS of thiophene [12], DBT [14,19], 4,6-DM-DBT [15], and 4-ethyl-6-methyldibenzothiophene (4-E-6-M-DBT) [11,13,14] as well as the hydrogenation of aromatics [19,21–25]. Most of these studies have, however, only looked at total conversions and their inhibition, and studies of the influence of nitrogen-containing molecules on the different steps in the HDS networks are scarce. In previous work we studied the influence of noble metal catalysts (Pt, Pd, Pt–Pd) supported on alumina on the different DDS and HYD steps in the reaction network of the HDS of 4,6-DM-DBT (Scheme 1) [26,27]. In the present work, we investigated the influence of nitrogen-containing molecules on this network. Pyridine and piperidine were chosen as simple, aromatic and non-aromatic, heterocyclic nitrogen-containing model compounds.

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Scheme 1. Reaction network in the HDS of 4,6-DM-DBT over noble metal catalysts.

2. Experimental

The reactivity of 1 kPa 4,6-DM-DBT (Acros, 95%) in the presence of 20, 100, and 500 Pa piperidine (Fluka, 99%) and pyridine (Merck, 99%) was studied over monometallic 0.54 wt% Pt/ γ -Al₂O₃ and 0.50 wt% Pd/ γ -Al₂O₃ catalysts, bimetallic 0.29 wt% Pt – 0.24 wt% Pd/ γ -Al₂O₃ and 0.46 wt% Pt – 0.50 wt% Pd/ γ -Al₂O₃ catalysts, and a 1:1 physical mixture of 0.54 wt% Pt/ γ -Al₂O₃ and 0.50 wt% Pd/ γ -Al₂O₃. These catalysts will be referred to hereafter as Pt/ γ -Al₂O₃, Pd/ γ -Al₂O₃, Pt–Pd/ γ -Al₂O₃, Pt–Pd/ γ -Al₂O₃ (2x), and Pt + Pd/ γ -Al₂O₃, respectively. The catalysts were prepared by pore volume impregnation and the metal dispersions were 57% for Pt, 56% for Pd, and 48% for Pt–Pd, as determined by hydrogen chemisorption [27].

The HDS experiments were performed at 300 °C and 5 MPa total pressure in a continuous-flow fixed-bed reactor over 50 mg alumina-supported Pt, Pd, or Pt–Pd catalyst mixed with 8 g SiC and reduced in situ at 300 °C and 0.5 MPa for 2 h, as reported in [27]. In short, every series of HDS experiments over a freshly in situ reduced noble metal catalyst started with a stabilization period of at least one night at the highest weight time (lowest flow rate), to diminish a possible influence of catalyst deactivation. Then, experimental data were collected with increasing flow rates of the sulfur feed and hydrogen (at constant ratio), thus with

decreasing weight time. For each measuring point, we let the system stabilize for several hours (longer with low flow rates, shorter with high flow rates) after the change of flow conditions. We also checked for a possible deactivation of the catalysts by performing experiments with decreasing as well as increasing weight time. The difference in the conversion was only a few percent over the two to three weeks of the whole run with one catalyst. This means that stable conversions and selectivities were obtained after a few hours.

The gas-phase feed usually consisted of 130 kPa decane (Acros, 99 + %, solvent), 8 kPa dodecane (Lancaster, 99 + %, internal standard), 1 kPa 4,6-DM-DBT, and about 4.8 MPa H₂. The reaction product was condensed at room temperature and collected in a condenser. A needle valve to a second condenser allowed off-line sampling for analysis by means of a gas chromatograph (Shimadzu GC-14A) equipped with a DB-5 fused silica capillary column (J&W Scientific, length 30 m, inner diameter 0.25 mm, film thickness 0.25 μ m) and a flame ionization detector.

The effect of piperidine was also investigated in the HDS of 1 kPa 4,6-dimethyltetrahydrodibenzothiophene (4,6-DM-TH-DBT) over the Pd/ γ -Al₂O₃ catalyst. 4,6-DM-TH-DBT is a reaction intermediate in the HDS of 4,6-DM-DBT and was prepared in our laboratory [28]. Its HDS and that of the other hydrogenated intermediates, 4,6-dimethylhexahydrodibenzothiophene (4,6-DM-HH-DBT) and 4,6-dimethylperhydrodibenzothiophene (4,6-DM-PH-DBT), in the absence of nitrogen-containing components were described in [26].

3. Results

3.1. Effect of piperidine and pyridine over Pt/ γ -Al₂O₃

Piperidine significantly inhibited the conversion of 4,6-DM-DBT over Pt/ γ -Al₂O₃, as figure 1A and the rate constants *k*, determined at low weight time while assuming pseudo first-order reaction, show (Table 1). Piperidine decreased the yields of the two desulfurized products 3,3'-dimethylcyclohexylbenzene (3,3'-DM-CHB) and 3,3'-dimethylbicyclohexyl (3,3'-DM-BCH)

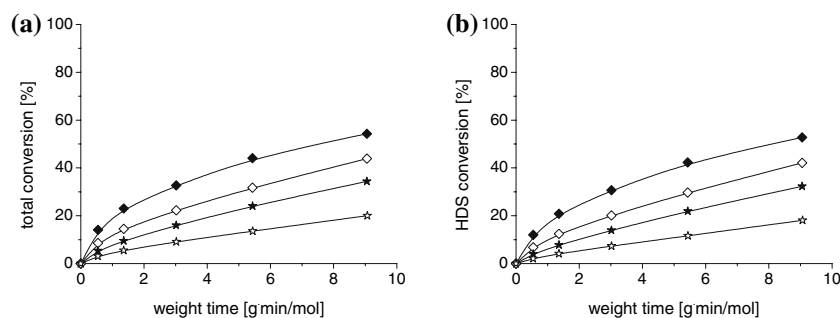


Figure 1. Total conversion (a) and HDS conversion (b) in the HDS of 4,6-DM-DBT over Pt/ γ -Al₂O₃ as a function of weight time at different piperidine pressures (◆ 0 Pa; ◇ 20 Pa; ★ 100 Pa; ☆ 500 Pa).

Table 1

Pseudo first-order initial rate constants k for the HDS of 4,6-DM-DBT over Pt, Pd, and Pt–Pd supported on γ - Al_2O_3 and of 4,6-DM-TH-DBT over Pd/ γ - Al_2O_3 in the presence of different pressures of piperidine (pip) or pyridine (py)

Metal	Amine	k [mol/min.g _{cat}]			
		Pressure of amine [Pa]			
		0	20	100	500
Pt	pip	0.28	0.17	0.10	0.06
Pt	py	0.28	0.15	0.12	0.09
Pd	pip	0.58	0.37	0.26	0.20
Pd	py	0.58	0.39	0.36	0.31
Pt + Pd	pip	0.32	0.17	0.13	0.08
Pt + Pd	py	0.32	0.18	0.14	0.11
Pt–Pd	pip	0.83	0.48	0.33	0.18
Pt–Pd	py	0.83	0.43	0.29	0.22
Pt–Pd (2x)	pip	1.30	0.74	0.51	0.25
Pt–Pd (2x)	py	1.30	0.59	0.42	0.29
Pd	pip	1.30		1.02	

(DM-TH-DBT)

strongly (figure 2), but hardly influenced the yield of 3,3'-dimethylbiphenyl (3,3'-DM-BP). As a result, the selectivities of 3,3'-DM-CHB and 3,3'-DM-BCH were lower at high piperidine pressure, whereas that of 3,3'-DM-BP increased from 16 to 36% (figure 3). The 3,3'-DM-CHB to 3,3'-DM-BCH ratio at high weight time increased from 4 to 7 when going from 0 to 500 Pa piperidine. The sulfur-containing compounds behaved differently than the hydrocarbon products. Since they are intermediates in the HDS of 4,6-DM-DBT, their yield-time curves went through a maximum, which shifted to higher weight time with increasing piperidine pressure (figure 2). The maximum yield of 4,6-DM-HH-DBT decreased, while that of 4,6-DM-TH-DBT remained about constant with increasing piperidine pressure. Because of the decreasing hydrocarbon yields, this resulted in an increased selectivity to 4,6-DM-TH-DBT with increasing piperidine pressure (figure 3).

The product distribution at constant (15%) conversion of 4,6-DM-DBT showed that the selectivity to 3,3'-DM-BP increased by 20% when the piperidine pressure

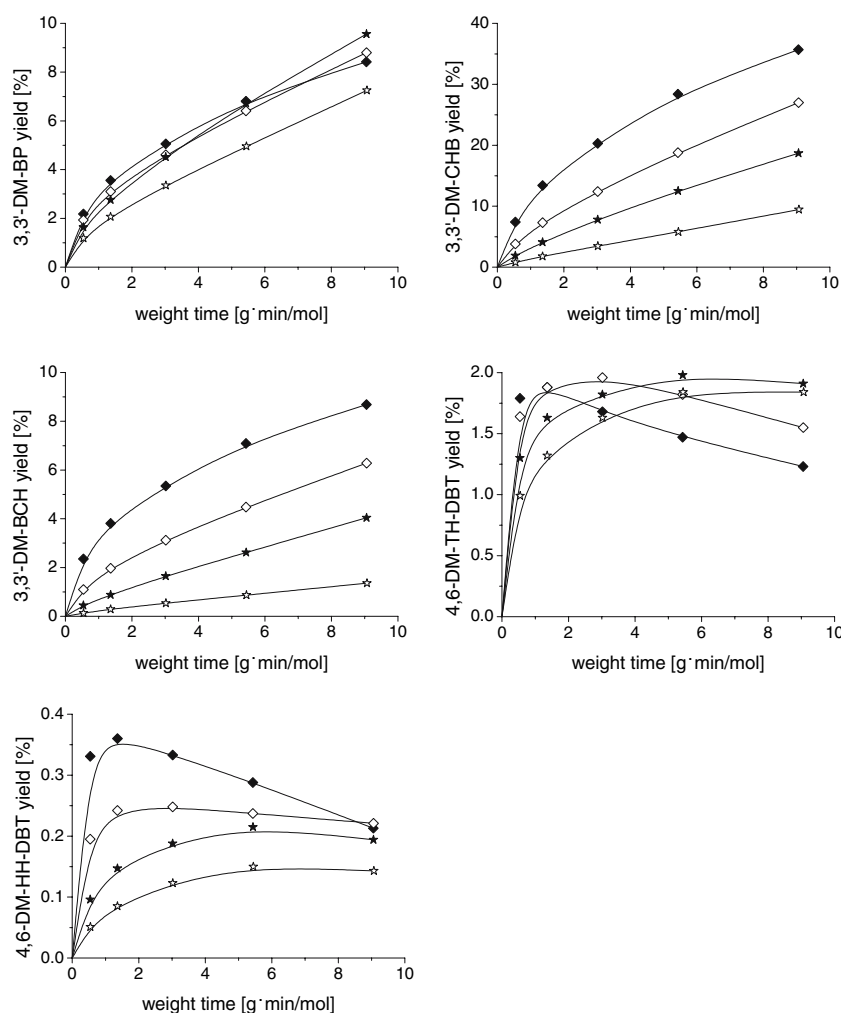


Figure 2. Product yields in the HDS of 4,6-DM-DBT over Pt/ γ - Al_2O_3 as a function of weight time at different piperidine pressures (\blacklozenge 0 Pa; \diamond 20 Pa; \star 100 Pa; \star 500 Pa).

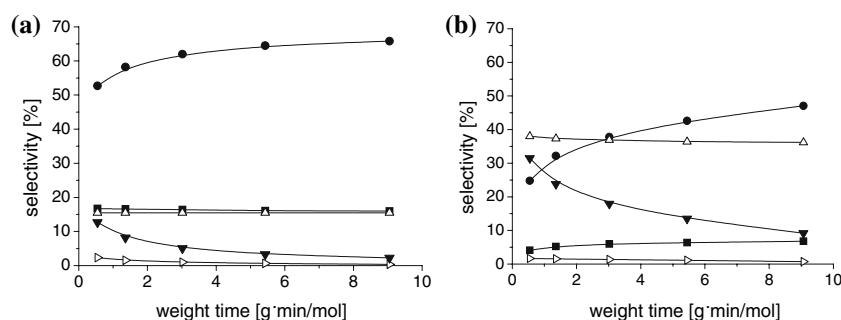


Figure 3. Selectivities in the HDS of 4,6-DM-DBT over Pt/ γ -Al₂O₃ in the absence (a) and presence of 500 Pa (b) piperidine as a function of weight time (\triangle 3,3'-DM-BP; \blacktriangledown 4,6-DM-TH-DBT; \triangleright 4,6-DM-HH-DBT; \bullet 3,3'-DM-CHB; \blacksquare 3,3'-DM-BCH).

was increased from 0 to 500 Pa, whereas the selectivity to 3,3'-DM-CHB and that to 3,3'-DM-BCH decreased by 10%. The other selectivities changed only slightly (Table 2). As a consequence, piperidine decreased the initial selectivity of the HYD pathway in the HDS of 4,6-DM-DBT from 84 to 63% and strongly increased the weight time necessary to reach 15% conversion from 0.7 to 6.2 g·min/mol. Since the influence of piperidine on the HDS conversion curves (figure 1b) was almost equal to that on the total conversion curves (figure 1a), similar fractions of sulfur-containing compounds (14%) were found in all cases.

Pyridine had a stronger inhibition effect on the conversion of 4,6-DM-DBT than piperidine at low pressure (20 Pa), but a weaker effect at higher pressures, as shown by the pseudo first-order initial rate constants k (Table 1). The product yields were influenced in a similar way as by piperidine (not shown). The conversion to desulfurized products (HDS conversion) at high weight time decreased from 53% in the absence to 19% in the presence of 500 Pa pyridine, like with piperidine. As a consequence of the similar yield behavior, the selectivities at 15% conversion were also similar to those obtained in the presence of piperidine. Hence, the initial HYD selectivity decreased from 84 to 72% and the weight time necessary to attain 15% conversion increased from 0.7 to 5.1 g·min/mol when the pyridine pressure was increased from 0 to 500 Pa, both values

being smaller than with piperidine. Furthermore, no significant change in the fraction of sulfur-containing compounds (14%) was found.

3.2. Effect of piperidine and pyridine over Pd/ γ -Al₂O₃

The inhibiting effect of piperidine on the conversion of 4,6-DM-DBT over Pd/ γ -Al₂O₃ was already strong at 20 Pa, but became weaker with increasing piperidine pressure (figure 4a and Table 1). Piperidine reduced the yield of 3,3'-DM-CHB and even more that of 3,3'-DM-BCH (figure 5). Whereas the yield of 3,3'-DM-BCH was larger than that of 3,3'-DM-CHB in the absence of piperidine, it was lower than that of 3,3'-DM-CHB at almost all piperidine pressures. The yield of 3,3'-DM-BP hardly changed, as over Pt/ γ -Al₂O₃. As a result, the HDS conversion decreased from 63% in the absence to 19% in the presence of 500 Pa piperidine at high weight time (figure 4B). The selectivity of 3,3'-DM-BCH decreased significantly and that of 3,3'-DM-CHB decreased slightly with increasing piperidine pressure (figure 6). As a result, the ratio 3,3'-DM-CHB/3,3'-DM-BCH changed from a value below one to a value above one. While over Pt/ γ -Al₂O₃ only two sulfur-containing intermediates were observed (4,6-DM-TH-DBT and 4,6-DM-HH-DBT), over Pd/ γ -Al₂O₃ also 4,6-DM-PH-DBT was observed. The sulfur-containing intermediates were affected differently by piperidine than the hydrocarbon products. The shape of the yield-time curves changed drastically, because of the shift of their maximum to higher weight time (figure 5). Piperidine had the same influence on the yields of 4,6-DM-TH-DBT and 4,6-DM-HH-DBT, but a different influence on the yield of 4,6-DM-PH-DBT. Since the hydrocarbon yields decreased and the yields of the sulfur-containing intermediates remained more or less constant, the selectivities of 4,6-DM-TH-DBT and 4,6-DM-HH-DBT increased at higher piperidine pressure (figure 6).

The selectivity of 3,3'-DM-CHB at constant (30%) conversion of 4,6-DM-DBT increased by 11% when the piperidine pressure was increased from 0 to 500 Pa, while the selectivity of 3,3'-DM-BCH decreased by 8% and the other selectivities only changed slightly (table 3).

Table 2

Effect of the piperidine pressure on the product selectivities and weight time (τ) at 15% conversion in the HDS of 4,6-DM-DBT over Pt/ γ -Al₂O₃

Selectivity [%]	Pressure of piperidine [Pa]			
	0	20	100	500
3,3'-DM-BP	16	22	28	36
3,3'-DM-CHB	53	50	48	43
3,3'-DM-BCH	17	14	10	7
4,6-DM-TH-DBT	12	13	13	13
4,6-DM-HH-DBT	2.3	1.7	1.3	1.0
$\tau_{15\%}$ [g·min/mol]	0.7	1.5	2.8	6.2

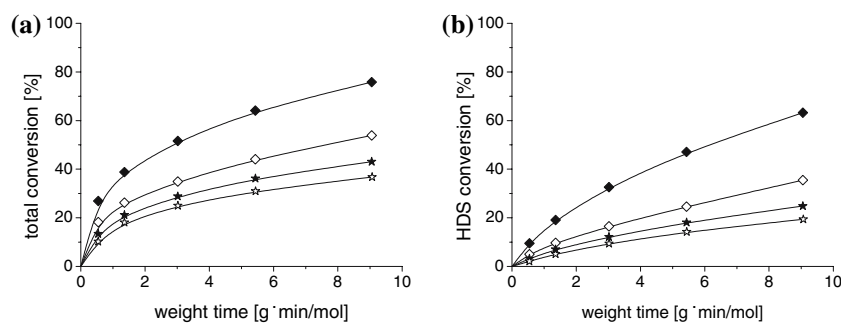


Figure 4. Total conversion (a) and HDS conversion (b) in the HDS of 4,6-DM-DBT over Pd/ γ -Al₂O₃ as a function of weight time at different piperidine pressures (\blacklozenge 0 Pa; \diamond 20 Pa; \star 100 Pa; \star 500 Pa).

The initial HYD selectivity decreased slightly from 99.4 to 98.1% with increasing piperidine pressure. Simultaneously, the weight time necessary to achieve 30% conversion increased substantially from 0.8 to 5.2 g·min/mol and the fraction of sulfur-containing products decreased from 61 to 56%. This means that the conversion to the desulfurized products (the sulfur removal)

is slightly less affected by piperidine than the total conversion of 4,6-DM-DBT.

Also pyridine caused the largest change in the yields of the reaction products at the lowest partial pressure (table 1). While piperidine and pyridine influenced the yields of the sulfur-containing intermediates (shift of their maximum yield to higher weight time) and 3,3'-

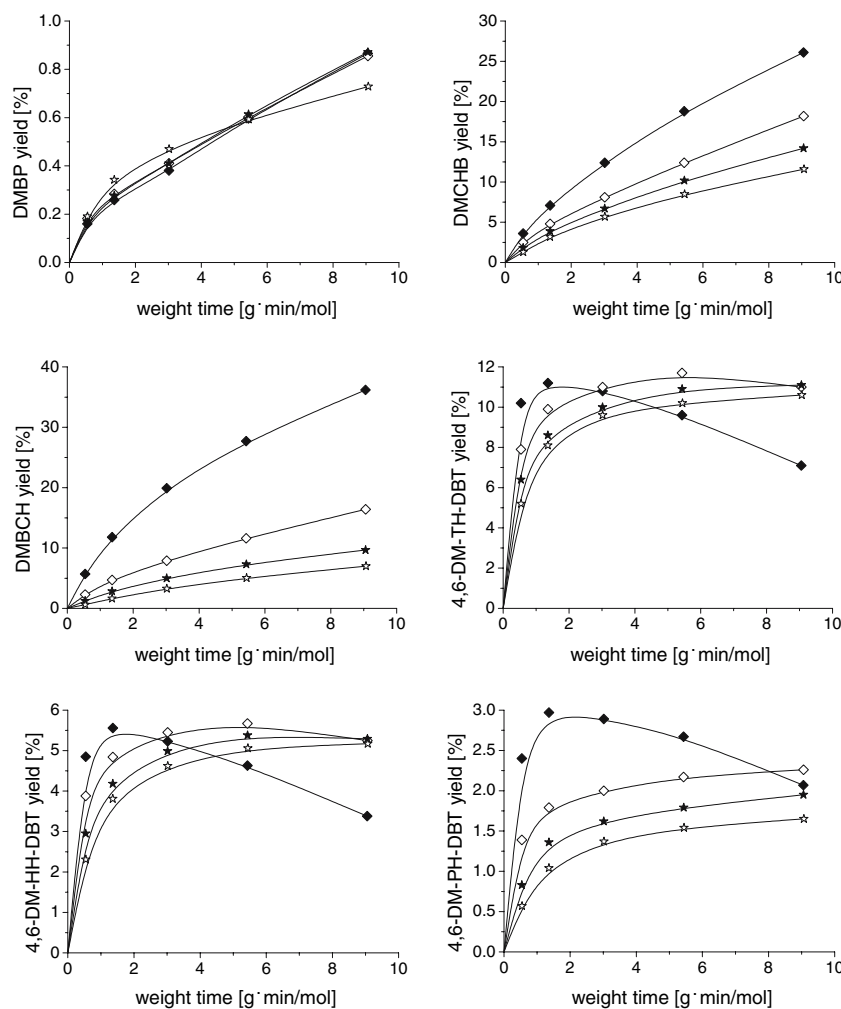


Figure 5. Product yields in the HDS of 4,6-DM-DBT over Pd/ γ -Al₂O₃ as a function of weight time at different piperidine pressures (\blacklozenge 0 Pa; \diamond 20 Pa; \star 100 Pa; \star 500 Pa).

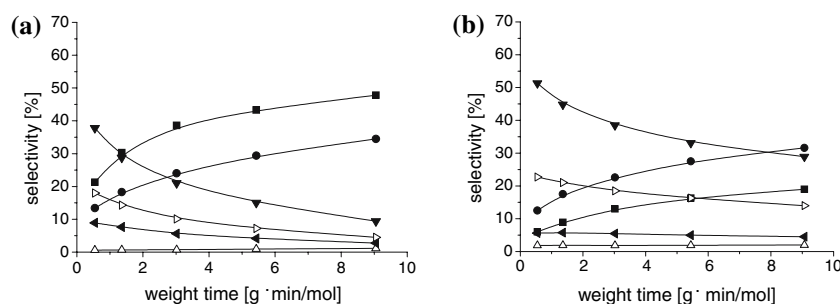


Figure 6. Selectivities in the HDS of 4,6-DM-DBT over Pd/ γ -Al₂O₃ in the absence (a) and presence of 500 Pa (b) piperidine as a function of weight time (Δ 3,3'-DM-BP; \blacktriangledown 4,6-DM-TH-DBT; \blacktriangleright 4,6-DM-HH-DBT; \blacktriangleleft 4,6-DM-PH-DBT; \bullet 3,3'-DM-CHB; \blacksquare 3,3'-DM-BCH).

Table 3

Effect of the piperidine pressure on the product selectivities and weight time (τ) at 30% conversion in the HDS of 4,6-DM-DBT over Pd/ γ -Al₂O₃

Selectivity [%]	Pressure of piperidine [Pa]			
	0	20	100	500
3,3'-DM-BP	0.6	1.1	1.5	1.9
3,3'-DM-CHB	15	21	24	26
3,3'-DM-BCH	24	20	18	16
4,6-DM-TH-DBT	35	35	34	34
4,6-DM-HH-DBT	17	17	17	17
4,6-DM-PH-DBT	8.6	6.3	5.5	5.0
$\tau_{30\%}$ [g·min/mol]	0.8	2.1	3.5	5.2

DM-BCH (lowering) similarly, they affected the yield of 3,3'-DM-CHB differently. The yield of 3,3'-DM-CHB was reduced by the addition of 20 Pa pyridine and then stayed constant with increasing pyridine pressure, but decreased continuously with increasing piperidine pressure. The conversion to desulfurized products at high weight time decreased from 63% in the absence to 22% in the presence of 500 Pa pyridine, close to the values obtained with piperidine.

The selectivity of 3,3'-DM-CHB at constant (30%) conversion of 4,6-DM-DBT increased and that of 3,3'-DM-BCH decreased with increasing pressure of pyridine, but less than with piperidine. The HYD selectivity decreased slightly from 99.4 to 98.7% with increasing pyridine pressure and the weight time necessary to reach 30% conversion increased from 0.8 to 3.0 g·min/mol, less strongly than with piperidine. The fraction of sulfur-containing products was larger with pyridine than with piperidine; it increased with the addition of 20 Pa pyridine from 61 to 67% and then decreased to 63% at 500 Pa pyridine.

3.3. Effect of piperidine and pyridine over Pt + Pd/ γ -Al₂O₃

The influence of piperidine and pyridine over a 1:1 physical mixture of Pt/ γ -Al₂O₃ and Pd/ γ -Al₂O₃ was

similar to that over its individual constituents. The conversion and initial pseudo first-order rate constant k were between those over Pt/ γ -Al₂O₃ and Pd/ γ -Al₂O₃, but closer to those over Pt/ γ -Al₂O₃ (table 1). The yields of the desulfurized products decreased with the addition of both nitrogen-containing molecules, which resulted in a decrease of the HDS conversion from 49% in the absence to 13% in the presence of 500 Pa piperidine and pyridine at high weight time. The selectivities to 3,3'-DM-CHB and 3,3'-DM-BCH decreased and to 4,6-DM-TH-DBT and 4,6-DM-HH-DBT increased with increasing piperidine or pyridine pressure. The product selectivities at 20% conversion of 4,6-DM-DBT were in general close to the averages of the values over the monometallic Pt/ γ -Al₂O₃ and Pd/ γ -Al₂O₃ catalysts. The initial HYD selectivity decreased slightly from 95 to 93% in the presence of piperidine. Because of the increasing inhibition with increasing piperidine pressure, longer weight times were needed to achieve 20% conversion (from 1.0 to 8.2 g·min/mol). Pyridine inhibited the total conversion of 4,6-DM-DBT similarly as piperidine, leading to very similar pseudo first-order rate constants (Table 1) and product distributions at 20% conversion. A minor increase in the initial HYD selectivity from 95 to 96% was observed in the presence of pyridine as well as longer weight times (from 1.0 to 7.5 g·min/mol) and a larger fraction of sulfur-containing compounds (from 37 to 44%) at 20% conversion.

3.4. Effect of piperidine and pyridine over Pt-Pd/ γ -Al₂O₃

Piperidine inhibited the total conversion of 4,6-DM-DBT over Pt-Pd/ γ -Al₂O₃, as shown in figure 7a and by the pseudo first-order rate constants k (table 1). Different from the Pt and Pd catalysts (figures 2 and 5), the Pt-Pd catalyst showed a maximum in the yield-time curves of 3,3'-DM-BP and 3,3'-DM-CHB in the absence of piperidine (figure 8), caused by the further reaction of both molecules by hydrogenation [27]. Piperidine did not change the rate of formation of 3,3'-DM-BP at low weight time, but shifted the maximum in the yield-time curve to higher weight time (figure 8), meaning that it slowed down its rate of hydrogenation. The initial rate

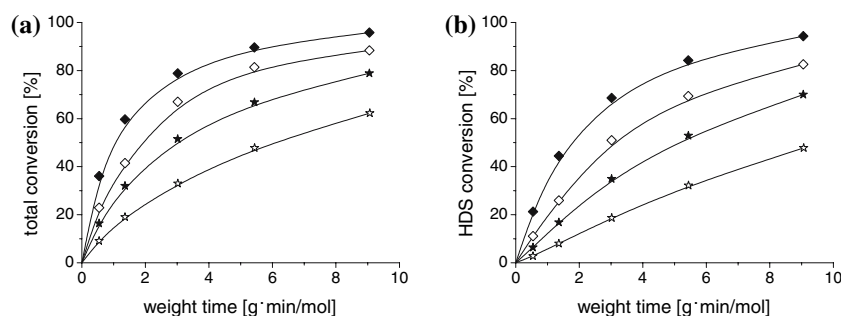


Figure 7. Total conversion (a) and HDS conversion (b) in the HDS of 4,6-DM-DBT over Pt-Pd/ γ -Al₂O₃ as a function of weight time at different piperidine pressures (◆ 0 Pa; ◇ 20 Pa; ★ 100 Pa; ☆ 500 Pa).

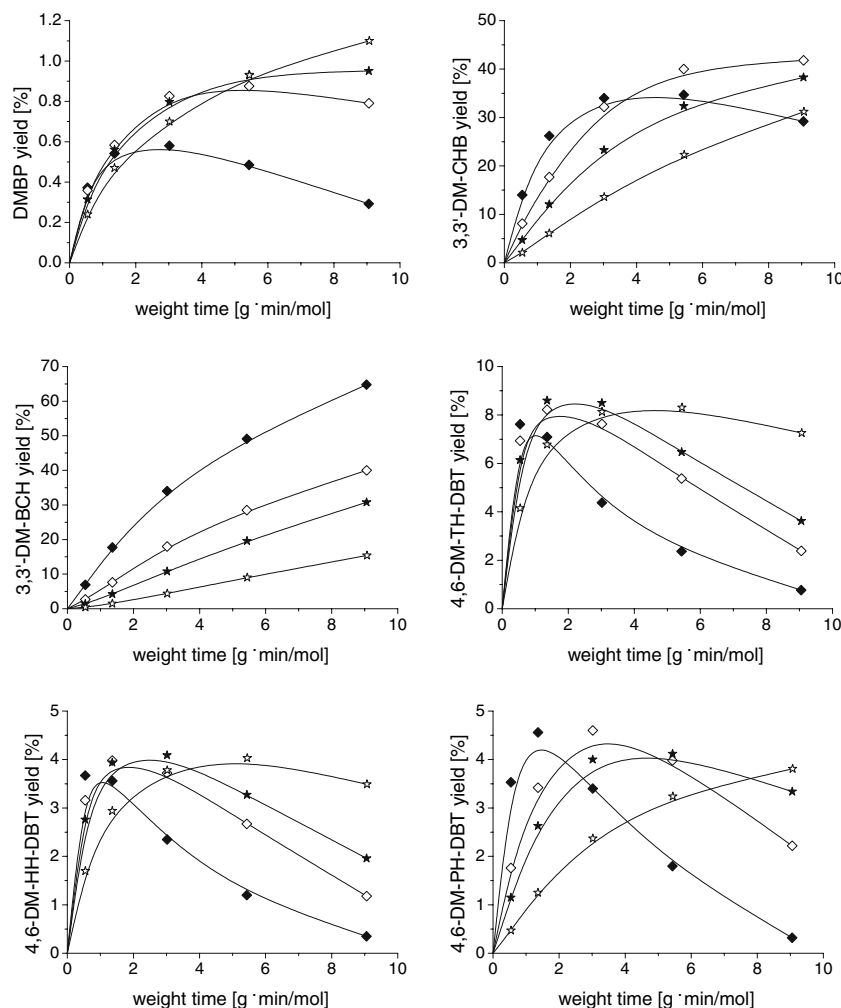


Figure 8. Product yields in the HDS of 4,6-DM-DBT over Pt-Pd/ γ -Al₂O₃ as a function of weight time at different piperidine pressures (◆ 0 Pa; ◇ 20 Pa; ★ 100 Pa; ☆ 500 Pa).

of 3,3'-DM-CHB production decreased with increasing pressure of piperidine and the maximum in its yield-time curve shifted to higher weight time, because the formation as well as the reaction (by hydrogenation) of 3,3'-DM-CHB were slowed down by piperidine. The results show that the hydrogenation of 3,3'-DM-CHB as well as of 3,3'-DM-BP is inhibited by piperidine. The rate of

formation of 3,3'-DM-BCH was strongly reduced and as a consequence the yield of the desulfurized products decreased from 94% in the absence to 48% in the presence of 500 Pa piperidine at high weight time (figure 7b). The rates of formation and reaction of 4,6-DM-TH-DBT and 4,6-DM-HH-DBT decreased in the presence of piperidine, resulting in a shift of their

maximum to higher weight time (figure 8). The rates of formation and reaction of 4,6-DM-PH-DBT decreased even stronger, as the strong decrease in the slope at low weight time and the much more important shift of the maximum of the yield-time curves show. The selectivity to 3,3'-DM-BCH decreased with increasing piperidine pressure, while those to 3,3'-DM-BP, 4,6-DM-TH-DBT, and 4,6-DM-HH-DBT increased (figure 9). As in the case of the Pd catalyst, piperidine had the same influence on the yields and selectivities of 4,6-DM-TH-DBT and 4,6-DM-HH-DBT; it is as if these two compounds are under all conditions in equilibrium, both on Pd and Pt-Pd.

The selectivity to 3,3'-DM-CHB at constant (50%) conversion of 4,6-DM-DBT increased by 5% when the piperidine pressure was increased from 0 to 500 Pa, whereas that of 3,3'-DM-BCH decreased by 6%, and the other selectivities changed less than 2% (table 4). The increase of the piperidine pressure caused a small decrease in the initial HYD selectivity from 98.9 to 97.2% and an increase in the weight time necessary to attain 50% conversion from 1.1 to 6.1 g·min/mol. The proportion of sulfur-containing compounds remained about constant (32–33%).

Pyridine gave comparable results as piperidine (table 1). It also inhibited the hydrogenation of 3,3'-DM-BP and 3,3'-DM-CHB. The yields of the sulfur-containing intermediates were slightly higher in the presence of pyridine than piperidine, while the yield of 3,3'-DM-BP was lower. The HDS conversion at high weight time decreased from 94% in the absence to 46% in the presence of 500 Pa pyridine. At constant (50%) conversion of 4,6-DM-DBT, pyridine first increased the selectivities of the three sulfur-containing intermediates by 4–8% and decreased them at higher pyridine pressure. The selectivity to 3,3'-DM-CHB showed the opposite behavior. Pyridine initially decreased the selectivity to 3,3'-DM-BCH, but above 20 Pa the selectivity stayed constant. The initial HYD selectivity decreased from 98.9 to 98.2% with pyridine, less pronounced than with piperidine, and the weight time necessary to reach 50% conversion increased from 1.1 to

5.9 g·min/mol. The fraction of sulfur-containing compounds increased from 32 to 49% with the addition of 20 Pa pyridine and decreased to 40% at higher pyridine pressure. It remained, however, larger than in the presence of piperidine.

3.5. Effect of piperidine and pyridine over Pt-Pd/ γ -Al₂O₃ (2x)

The Pt-Pd/ γ -Al₂O₃ (2x) catalyst with double Pt and Pd loading behaved similarly to the Pt-Pd/ γ -Al₂O₃ catalyst, as shown by the inhibition induced by piperidine (figure 10) and the corresponding pseudo first-order rate constants *k* (table 1). The selectivities of 3,3'-DM-CHB and 3,3'-DM-TH-DBT were lower and that of 3,3'-DM-BCH was higher than over Pt-Pd/ γ -Al₂O₃. The initial HYD selectivity decreased slightly from 99.0 to 97.8% with increasing piperidine pressure, the weight time necessary to achieve 60% conversion increased from 1.0 to 6.2 g·min/mol, and the fraction of sulfur-containing compounds increased from 24 to 28%. Pyridine gave similar results as piperidine. A small decrease of the initial HYD selectivity from 99.0 to 98.2% was obtained when increasing the pyridine pressure to 500 Pa and the weight time needed to reach 60% conversion increased from 1.0 to 7.7 g·min/mol. On the

Table 4

Effect of the piperidine pressure on the product selectivities and weight time (τ) at 50% conversion in the HDS of 4,6-DM-DBT over Pt-Pd/ γ -Al₂O₃

Selectivity [%]	Pressure of piperidine [Pa]			
	0	20	100	500
3,3'-DM-BP	1.0	1.4	1.6	1.9
3,3'-DM-CHB	42	45	44	47
3,3'-DM-BCH	25	21	21	19
4,6-DM-TH-DBT	16	17	17	17
4,6-DM-HH-DBT	7.8	8.3	8.4	8.0
4,6-DM-PH-DBT	8.5	7.7	7.6	6.7
$\tau_{50\%}$ [g·min/mol]	1.1	1.9	3.1	6.1

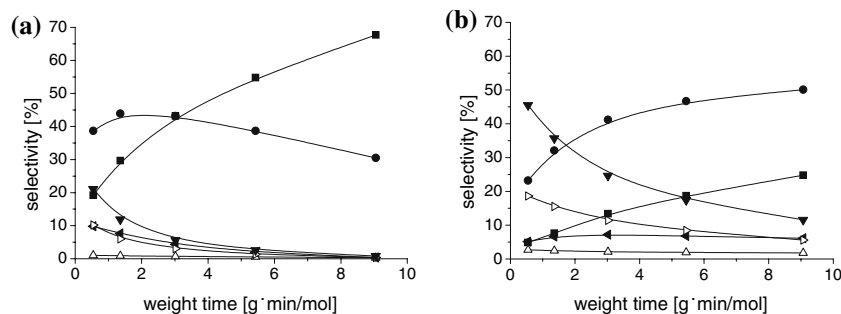


Figure 9. Selectivities in the HDS of 4,6-DM-DBT over Pt-Pd/ γ -Al₂O₃ in the absence (a) and presence of 500 Pa (b) piperidine as a function of weight time (Δ 3,3'-DM-BP; \blacktriangledown 4,6-DM-TH-DBT; \triangleright 4,6-DM-HH-DBT; \blacktriangleleft 4,6-DM-PH-DBT; \bullet 3,3'-DM-CHB; \blacksquare 3,3'-DM-BCH).

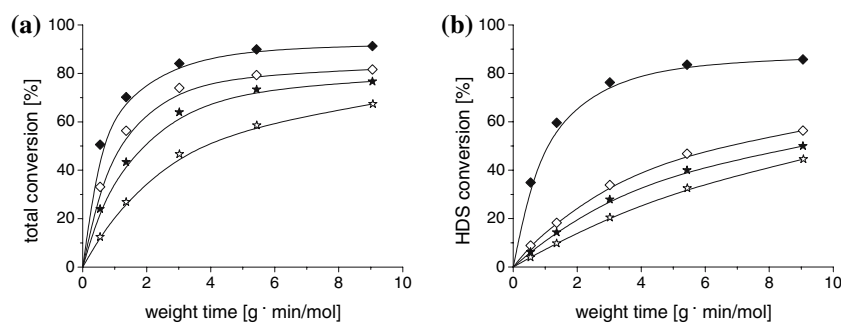


Figure 10. Total conversion (a) and HDS conversion (b) in the HDS of 4,6-DM-DBT over Pt-Pd/ γ -Al₂O₃ (2x) as a function of weight time at different piperidine pressures (\blacklozenge 0 Pa; \diamond 20 Pa; \star 100 Pa; \star 500 Pa).

other hand, the fraction of sulfur-containing compounds increased from 24 to 42% with the addition of 20 Pa pyridine and then decreased to 34% at high pyridine pressure.

3.6. Effect of piperidine on the HDS of 4,6-DM-TH-DBT over Pd/ γ -Al₂O₃

The influence of a nitrogen-containing compound was also investigated in the HDS of the reaction intermediate 4,6-DM-TH-DBT over Pd/ γ -Al₂O₃. As in the HDS of 4,6-DM-DBT over all noble metal catalysts, 100 Pa piperidine had an inhibiting effect on the total conversion and HDS conversion of 4,6-DM-TH-DBT (figure 11), but this inhibition was much weaker than for 4,6-DM-DBT. Thus, the pseudo first-order rate constant k decreased only by 22% (table 1). The yields of 4,6-DM-DBT, 3,3'-DM-CHB, and 3,3'-DM-BCH were lower in the presence of piperidine, while those of 4,6-DM-HH-DBT and 3,3'-DM-BP were higher, and that of 4,6-DM-PH-DBT was more or less the same (figure 12). The product selectivities followed the same trends (figure 13). Piperidine increased the fraction of sulfur-containing compounds. Hence, it seems that the desulfurization steps were more affected by piperidine than the overall conversion of 4,6-DM-TH-DBT.

4. Discussion

Piperidine and pyridine inhibited the HDS reaction of 4,6-DM-DBT over alumina-supported noble metal catalysts. The degree of inhibition (the ratio of the rate constants at 0 and 500 Pa piperidine or pyridine) was similar over all catalysts, with the exception of Pd/ γ -Al₂O₃ for which the inhibition was less strong (table 1). Thus, the degree of inhibition in the presence of piperidine was 4.7, 2.9, 4.0, 4.6, and 5.2 for Pt, Pd, Pt + Pd, Pt-Pd, and Pt-Pd (2x), respectively, while in the presence of pyridine it was 3.1, 1.9, 2.9, 3.8, and 4.5, respectively. As a result, at high piperidine or pyridine pressure the rate constants for the Pd, Pt-Pd, and Pt-Pd (2x) catalysts were similar (0.2–0.3 mol/min·g_{cat}), although k was larger for Pt-Pd than for Pd in the absence of piperidine or pyridine. The physical-mixture catalyst had an inhibition between those of the Pt and Pd constituents, but closer to that of Pt, as was the case in the absence of nitrogen-containing molecules. The difference in the inhibition of the metal catalysts by nitrogen-containing compounds cannot be attributed to the metal particle size, as all the alumina-supported catalysts have similar dispersions [27]. Because the Pt, Pd, and Pt-Pd catalysts contained about the same metal weight loading and had similar metal dispersions (57% for Pt, 56% for Pd, and 48% for Pt-Pd [27]), the turnover frequencies (TOF) of the

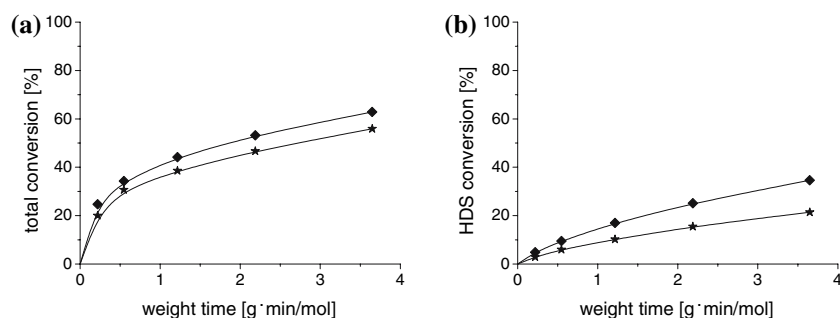


Figure 11. Total conversion (a) and HDS conversion (b) in the HDS of 4,6-DM-TH-DBT over Pd/ γ -Al₂O₃ as a function of weight time in the presence and absence of piperidine (\blacklozenge 0 Pa; \star 100 Pa).

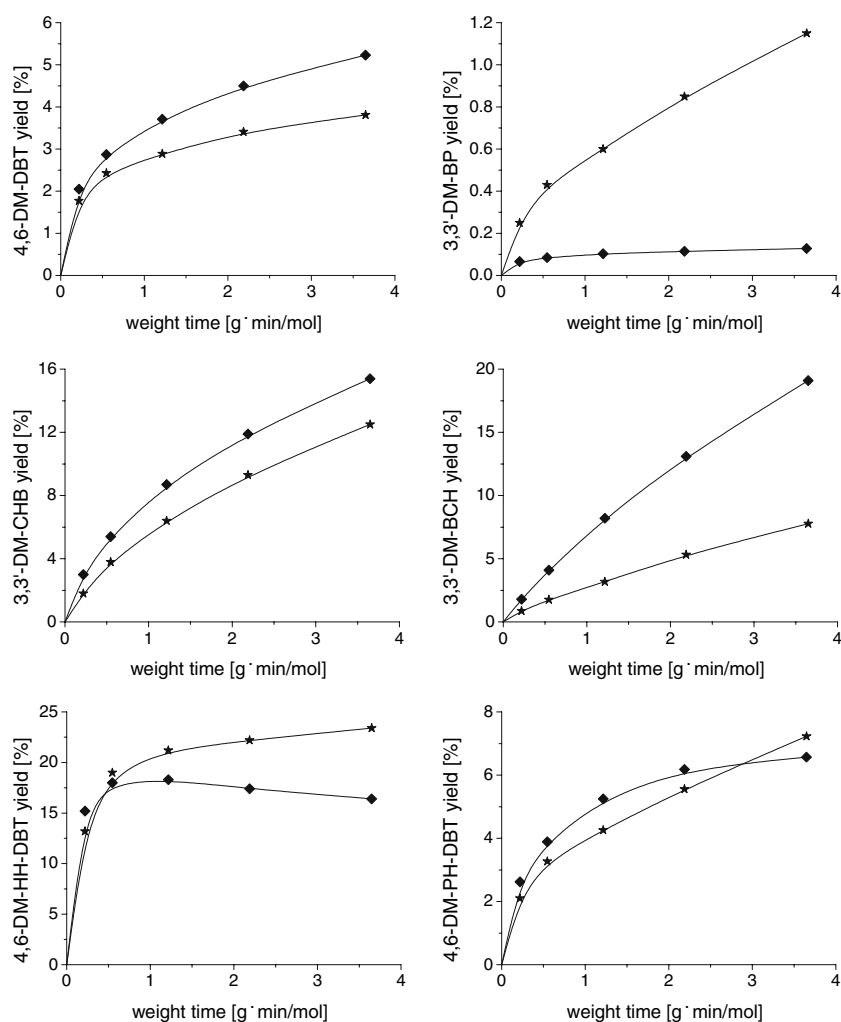


Figure 12. Product yields in the HDS of 4,6-DM-TH-DBT over Pd/ γ -Al₂O₃ as a function of weight time in the presence and absence of piperidine (◆ 0 Pa; ★ 100 Pa).

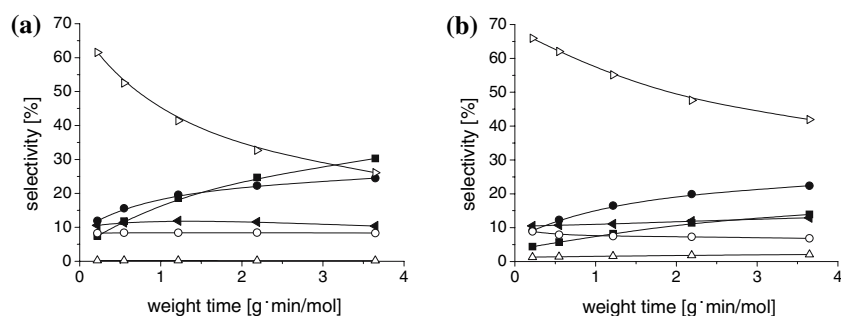


Figure 13. Selectivities in the HDS of 4,6-DM-TH-DBT over Pd/ γ -Al₂O₃ in the absence (a) and presence of 100 Pa (b) piperidine as a function of weight time (○ 4,6-DM-DBT; △ 3,3'-DM-BP; ▷ 4,6-DM-HH-DBT; ◀ 4,6-DM-PH-DBT; ● 3,3'-DM-CHB; ■ 3,3'-DM-BCH).

Pt–Pd catalyst were always larger than those of the Pd catalyst (table 5). While in the absence of piperidine or pyridine, the TOF of Pt–Pd was 100% higher and that of Pt–Pd (2x) 50% higher than those of the monometallic catalysts (46 respectively 33 mol/min.mmol versus 18 and 22 mol/min.mmol), in the presence of 500 Pa piperidine or pyridine all TOF values became close, 4–10 mol/min.mmol for piperidine and

6–12 mol/min.mmol for pyridine. These values confirm that piperidine and pyridine substantially decrease the ability of noble metal particles to convert refractory molecules like 4,6-DM-DBT and demonstrate that the advantage that bimetallic Pt–Pd has over monometallic Pt or Pd in the absence of nitrogen-containing molecules almost disappears in the presence of such molecules.

Table 5

Turnover frequencies (TOF) for the HDS of 4,6-DM-DBT over Pt, Pd, and Pt–Pd supported on γ -Al₂O₃ in the absence and presence of 500 Pa piperidine (pip) or pyridine (py)

Metal	TOF [mol/min.mmol]		
	Amine		
	–	pip	py
Pt	18	4	6
Pd	22	8	12
Pt–Pd	46	10	12
Pt–Pd (2x)	33	6	7

Pyridine was a stronger inhibitor than piperidine over the Pt, Pt–Pd, and Pt–Pd (2x) catalysts at low pressure (20 Pa), while the inhibition by pyridine was slightly weaker than piperidine for Pd and Pt + Pd. At 500 Pa, however, the inhibition by pyridine was weaker for all catalysts. A weaker inhibition by the aromatic nitrogen-containing molecules at high pressure was also observed over sulfided NiMo/ γ -Al₂O₃. 2-Methylpyridine was a weaker inhibitor than 2-methylpiperidine in the HDS of 4,6-DM-DBT [17] and pyridine was a weaker inhibitor than piperidine in the HDS of thiophene [4], in both cases at high pressure of the nitrogen-containing compound. Partial hydrogenation of pyridine to piperidine occurred during our HDS experiments in the presence of pyridine, in agreement with the fact that the hydrogenation of pyridine to piperidine is thermodynamically irreversible at 300 °C and 5 MPa [29]. At low pyridine pressure and high weight time the pyridine conversion was higher than 60% over our catalysts, while at higher initial pyridine pressures and shorter weight time it was lower. The hydrogenation of pyridine to piperidine can, however, not explain the crossover in inhibition between pyridine and piperidine over the Pt–Pd catalysts. It is known that the strength of adsorption of nitrogen-containing compounds correlates with their proton affinity [3,4] and the more basic piperidine will thus adsorb more strongly than pyridine and cause a higher inhibition [2,4,6,10]. If that were the only explanation, then piperidine should always have a stronger inhibition than pyridine at equal initial pressure, because the amount of piperidine that can form from pyridine can only approach the amount of piperidine used in the experiment with piperidine. For the same reason, if pyridine would adsorb and inhibit stronger than piperidine (as seems to be the case for the Pt–Pd catalysts from the results at 20 Pa), then inhibition should be higher for all experiments with pyridine and the crossover cannot be explained either. A possible explanation might be that a mixture of nitrogen-containing molecules gives a stronger inhibition than the pure constituents, as observed by Laredo et al. [30].

Another explanation for the crossover, with pyridine causing more inhibition at low pressure and piperidine

more at high pressure, could be a competition between adsorption of the nitrogen-containing compounds on the support and on the metal. The more basic piperidine would adsorb stronger on the support than on the metal and the reverse would be true for pyridine, which can have π bonding with the metal. This would explain the strong inhibition of the HDS activity upon addition of 20 Pa pyridine, which would largely adsorb on the metal, and the much more moderate further inhibition by 100 and 500 Pa pyridine. Piperidine, on the other hand, would initially adsorb preferentially on the slightly acidic alumina support and enough piperidine to adsorb on the metal would only be available at higher piperidine pressure. The fact that piperidine is almost always the stronger inhibitor at high pressure must mean that piperidine binds more strongly with the metal than pyridine. This would be in accordance with the fact that, whereas piperidine always adsorbs in σ mode on the metal, pyridine adsorbs in π mode at low pressure and in σ mode at high pressure to allow more molecules to adsorb. In σ mode, however, the bonding of the metal is always stronger with piperidine than with the less basic pyridine.

A more detailed look at the results of the HDS of 4,6-DM-DBT shows that the DDS and HYD reaction pathways were both inhibited by nitrogen-containing molecules, but to a different extent. The decrease of the initial HYD selectivity in the presence of piperidine or pyridine indicates that these molecules inhibit the HYD pathway more than the DDS pathway. The DDS rates over our catalysts were only weakly inhibited by piperidine and pyridine, as the increase in the yield of 3,3'-DM-BP at low weight time decreased only slightly or not at all in the presence of piperidine or pyridine over the Pt and Pd catalysts (figures 2 and 5), respectively. Over the Pt–Pd catalyst, the 3,3'-DM-BP yield showed a maximum that shifted to higher weight time with increasing piperidine or pyridine pressure (figure 8). The maximum is due to the hydrogenation of the 3,3'-DM-BP formed by DDS of 4,6-DM-DBT and the shift is due to the suppression of this hydrogenation by piperidine or pyridine. The initial steep increase of the 3,3'-DM-BP yield was only weakly influenced by piperidine or pyridine, however. This means that also over Pt–Pd/ γ -Al₂O₃ the DDS reaction is weakly suppressed by piperidine or pyridine and indicates that these molecules do not adsorb strongly on DDS sites. The strong inhibition of the HYD pathway leaves a higher pressure of 4,6-DM-DBT for the DDS pathway than in the absence of inhibitor and if k_{DDS} is not influenced by the amine, then the DDS conversion, and thus the 3,3'-DM-BP yield, should even increase. Higher yields of biphenyl were indeed observed in the HDS of DBT in the presence of different nitrogen-containing molecules over sulfided NiMo/ γ -Al₂O₃. This was explained by inhibition of the HYD route, so that more DBT becomes available for DDS [2,3,17,31,32]. The fact that in our

case the 3,3'-DM-BP yield decreased slightly indicates that piperidine and pyridine have a weak to moderate inhibiting effect on the DDS pathway.

We can only speculate about the structure of the sites that are responsible for DDS reactions and weakly influenced by nitrogen-containing molecules. The DDS reaction over noble metal catalysts is much slower for 4,6-DM-DBT than for DBT, due to the steric hindrance of the methyl groups [27]. Apparently, many sites that can catalyze the DDS of DBT are not able to perform the DDS of 4,6-DM-DBT. It suggests that metal atoms in terraces, or even in edges, cannot catalyze the DDS of 4,6-DM-DBT, but can catalyze the DDS of DBT, and that kink (and possibly edge) atoms act as the DDS sites for 4,6-DM-DBT. A metal particle, with truncated cubo-octaeder fcc structure and 50% dispersion (similar to the dispersion of our metal particles), has a substantial fraction of its surface atoms in small, (100) and (111) type planes, connected by edge and kink atoms (figure 14). A kink atom has enough space to create a σ bond to the sulfur atom of a 4,6-DM-DBT molecule, but only few kink sites are present in particles with a dispersion of 50% or lower. This would explain the low DDS activity for 4,6-DM-DBT.

Piperidine and pyridine caused a decrease of the conversion in the HDS of 4,6-DM-DBT over all catalysts, as figures 1, 4, 7, and 10 and the rate constants in table 1 demonstrate. Since the DDS contribution to the conversion decreased only weakly, the decrease in the conversion is mainly due to the decrease in the HYD contribution, as confirmed by the lower initial HYD selectivity when piperidine or pyridine were present. Similar results were obtained over sulfided catalysts. Thus, pyridine inhibited the hydrogenation of olefins stronger than the desulfurization of thiophene [1,33] and several nitrogen-containing molecules more strongly decreased the HYD route in the HDS of DBT [3,8,31,32] and 4,6-DM-DBT [17]. In our experiments, piperidine had a larger influence on the initial HYD selectivity than pyridine. The yields of the final, desulfurized products of the HYD pathway, 3,3'-DM-BCH and 3,3'-DM-CHB, decreased markedly with increasing pressure of pyridine and piperidine and the 3,3'-DM-

BCH to 3,3'-DM-CHB ratio decreased. This decrease was more significant with piperidine than with pyridine, as for the initial selectivity of the HYD route. It seems to be caused by a suppression of the hydrogenation of 4,6-DM-HH-DBT to 4,6-DM-PH-DBT (scheme 1). The decrease of the hydrogenation steps prior to this reaction and of the removal of sulfur from the sulfur-containing intermediates should not have a large impact on the 3,3'-DM-BCH to 3,3'-DM-CHB ratio. A higher pressure of the nitrogen-containing molecules inhibits the hydrogenation of 3,3'-DM-CHB to 3,3'-DM-BCH as well and further decreases the 3,3'-DM-BCH to 3,3'-DM-CHB ratio. Our explanation is in accordance with that of Matsui et al., who suggested that the decrease of the 3,3'-DM-BCH to 3,3'-DM-CHB ratio observed over Pt and Pd catalysts indicates that the loss in the HDS activity in the presence of nitrogen components is due to the loss in the hydrogenation activities of the aromatic rings of the sulfur-containing compounds [15].

The hydrogenation of 4,6-DM-DBT to 4,6-DM-TH-DBT was moderately inhibited by piperidine over Pt, as the change in the increase of the 4,6-DM-TH-DBT yield indicated (figure 2). The initial rate of hydrogenation decreased by a factor of 1.8, based on the data measured at the lowest weight time. The hydrogenation of 4,6-DM-TH-DBT to 4,6-DM-HH-DBT, on the other hand, was more strongly inhibited; the increase of the 4,6-DM-HH-DBT yield at low weight time indicates that it is inhibited by a factor of 6.6. Over Pd as well as over Pt-Pd the yield-time curves of 4,6-DM-TH-DBT and 4,6-DM-HH-DBT behaved exactly the same (figures 5 and 8). The decrease of the initial rise in the yield-time curves showed that the hydrogenation of 4,6-DM-DBT to 4,6-DM-TH-DBT (factor of 1.9) and of 4,6-DM-TH-DBT to 4,6-DM-HH-DBT (factor of 2.1) were almost equally inhibited by piperidine and also the yield decrease at longer weight time was almost identical. It thus looks as if 4,6-DM-TH-DBT and 4,6-DM-HH-DBT are in equilibrium at all piperidine pressures, which suggests that their rates of interconversion are fast relative to their rates of reaction to products. This is in agreement with the fast reaction of 4,6-DM-TH-DBT to 4,6-DM-HH-DBT over Pd (figure 12). The yield-time curve of 4,6-DM-PH-DBT behaved differently than the curves of 4,6-DM-TH-DBT and 4,6-DM-HH-DBT over Pd and Pt-Pd (figures 5 and 8); the hydrogenation of 4,6-DM-HH-DBT to 4,6-DM-PH-DBT was more strongly inhibited (factor of 4 for Pd and 7.5 for Pt-Pd).

A common effect of piperidine and pyridine on the three sulfur-containing intermediates in the HDS of 4,6-DM-DBT over the noble metal catalysts was to shift their maximum yield to higher weight time. Modeling the reaction network of Scheme 1 with pseudo first-order kinetics shows that this can be achieved by a decrease of the rates of formation and consumption of the intermediates by the nitrogen-containing molecules. This is in accordance with the observation that the

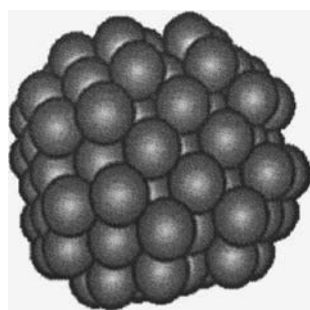


Figure 14. Model of a metal particle with fcc structure and 50% dispersion.

hydrogenation and the desulfurization steps were inhibited by pyridine and piperidine and that the fraction of sulfur-containing compounds was always higher in the presence than in the absence of piperidine and pyridine. Also, at a particular weight time the selectivities to the sulfur-containing intermediates increase while those to the desulfurized products of the HYD route decrease with increasing pressure of the nitrogen-containing molecules (figures 3, 6, and 9). Moreover, the fraction of sulfur-containing compounds was always higher in the presence of pyridine than of piperidine, indicating that pyridine inhibits the desulfurization of the intermediates more than piperidine.

Whereas the DDS pathway consists of only one step, from 4,6-DM-DBT to 3,3'-DM-BP, the HYD pathway consists of at least five steps, with three sulfur-containing intermediates and two final hydrocarbon products (scheme 1). Hydrogenation of 4,6-DM-DBT to 4,6-DM-TH-DBT, and on to 4,6-DM-HH-DBT and 4,6-DM-PH-DBT, is involved as well as desulfurization of 4,6-DM-HH-DBT to 3,3'-DM-CHB and of 4,6-DM-PH-DBT to 3,3'-DM-BCH. The desulfurization of 4,6-DM-HH-DBT and 4,6-DM-PH-DBT may occur analogously to the DDS of 4,6-DM-DBT, by σ adsorption and hydrogenolysis on kink sites. It may also occur on less exposed edge sites, because the methyl group(s) in the hydrogenated ring(s) of 4,6-DM-HH-DBT and 4,6-DM-PH-DBT can rotate away from the plane of the thiophene ring and thus create less steric hindrance. The hydrogenation of aromatic molecules is generally assumed to occur through π adsorption on domains with (100) and (111) arrangements at the surface of small metal particles (figure 14). These (100) and (111) domains may catalyze the hydrogenation reactions of the HYD pathway as well as the DDS reaction of DBT. The methyl groups of 4,6-DM-DBT prohibit the σ adsorption on these domains. As a consequence, these sites can catalyze the hydrogenation of 4,6-DM-DBT without competition of the DDS reaction, which would explain the much higher HYD rate constant for 4,6-DM-DBT than for DBT [27].

Piperidine also inhibited the conversion of 4,6-DM-TH-DBT, the first sulfur-containing intermediate in the HDS of 4,6-DM-DBT over Pd/ γ -Al₂O₃ (figure 11), but much less than the conversion of 4,6-DM-DBT. Both the forward (hydrogenation) and backward (dehydrogenation) reactions of 4,6-DM-TH-DBT were inhibited, but the hydrogenation to 4,6-DM-HH-DBT, and subsequent products 4,6-DM-PH-DBT, 3,3'-DM-CHB, and 3,3'-DM-BCH, was suppressed more than the dehydrogenation to 4,6-DM-DBT and its follow product 3,3'-DM-BP (figure 12). The yields of 4,6-DM-HH-DBT and 4,6-DM-PH-DBT increased at higher weight time because their maximum shifted strongly to higher weight time. This means that the reactions of 4,6-DM-HH-DBT and 4,6-DM-PH-DBT to subsequent products were suppressed and that the removal of sulfur from

these two intermediates was inhibited by piperidine. Like in the HDS of 4,6-DM-DBT, piperidine especially suppressed the formation of 3,3'-DM-BCH. The reason must be that 3,3'-DM-BCH is the product molecule that has undergone most reaction steps. 3,3'-DM-BCH can be formed from 4,6-DM-HH-DBT through 4,6-DM-PH-DBT or 3,3'-DM-CHB (scheme 1). In both cases, one additional hydrogenation step is needed to make 3,3'-DM-BCH than to make 3,3'-DM-CHB. Inhibition will thus have the strongest effect on the formation of 3,3'-DM-BCH.

5. Conclusions

Pyridine and piperidine inhibited the hydrodesulfurization of 4,6-dimethyldibenzothiophene (4,6-DM-DBT) over alumina-supported Pt, Pd, and Pt-Pd catalysts. The Pd catalyst was least sensitive and the Pt-Pd catalysts were most sensitive to the nitrogen-containing compounds. Pyridine was a stronger inhibitor than piperidine at low initial pressure, but the reverse was true at high initial pressure. This might be caused by a stronger adsorption of piperidine on the alumina support than on the noble metal particles, whereas the reverse is true for pyridine. At high pressure, both piperidine and pyridine adsorb in σ mode on the metal particles and piperidine is more strongly bonded. Hydrogenation of the 4,6-DM-TH-DBT to the 4,6-DM-HH-DBT intermediate and of the 4,6-DM-HH-DBT to the 4,6-DM-PH-DBT intermediate as well as the removal of sulfur from these intermediates was slowed down by piperidine and pyridine. The hydrogenation pathway in the hydrodesulfurization of 4,6-DM-DBT was inhibited much more than the direct desulfurization pathway. The hydrogenation of the desulfurized products 3,3'-dimethylcyclohexylbenzene and 3,3'-dimethylbiphenyl, which in the absence of piperidine and pyridine occurs only over the Pt-Pd catalysts, was suppressed by piperidine and pyridine. Piperidine and pyridine substantially decrease the ability of noble metal particles to convert refractory molecules like 4,6-DM-DBT. The turnover frequencies showed that the nitrogen-containing molecules diminish the advantage of bimetallic Pt-Pd over monometallic Pt or Pd catalysts.

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