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Hydrodesulfurization of 4,6-dimethyldibenzothiophene and dibenzothiophene over alumina-supported Pt, Pd, and Pt-Pd catalysts

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Abstract

The activity and selectivity of alumina-supported Pt, Pd, and Pt-Pd in the hydrodesulfurization (HDS) of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DM-DBT) were investigated, and all final, hydrocarbon products and partially hydrogenated intermediates were analyzed. Pd had a high activity in the hydrogenation of 4,6-DM-DBT, whereas the removal of sulfur from DBT and 4,6-DM-DBT and their intermediates occurred faster over Pt than over Pd. Bimetallic Pt-Pd catalysts were much more active than the combination of their monometallic constituents, proving a chemical synergism between the noble metals and the presence of alloyed particles. New sites with high hydrogenation activity explain why the hydrogenation of the products 3,3′-dimethylcyclohexylbenzyl and 3,3′-dimethylbiphenyl in the HDS of 4,6-DM-DBT, as well as the hydrogenation of 3,3′-dimethylbiphenyl in the presence of DBT, were significant only over the Pt-Pd catalysts. In contrast to the metal sulfide catalysts, the hydrogenation route over the noble metal catalysts was faster for 4,6-DM-DBT than for DBT, which almost compensated for the loss of activity via the desulfurization pathway.

Keywords: Hydrodesulfurization; 4,6-Dimethyldibenzothiophene; Dibenzothiophene; Platinum; Palladium; Pt-Pd catalysts

1. Introduction

Deep hydrodesulfurization (HDS) technology is needed to reduce the sulfur content in transportation fuels. Such molecules as 4,6-dimethyldibenzothiophene (4,6-DM-DBT), with alkyl groups adjacent to the sulfur atom, are often used as model molecules in deep HDS studies because they are very difficult to desulfurize and create problems in deep HDS [1,2]. The HDS of 4,6-DM-DBT occurs predominantly by hydrogenation followed by desulfurization [1–5] and is dependent on the hydrogenation activity of the catalyst. Metals are much better hydrogenation catalysts than metal sulfides and might be well suited as catalysts for deep HDS. Unfortunately, metal particles may transform into metal sulfide particles in the presence of sulfur-containing molecules and H_2S. The noble metals on the right-hand side of the Periodic Table are less sensitive to sulfur, and several investigations have shown that Pt and Pd are less susceptible than other metals to transformation into inactive sulfides [6,7]. Their sulfur resistance is further improved by the use of an acidic support and by alloying. Thus, noble metals may be used in the second reactor of a two-stage hydrotreating process, where the feed first undergoes HDS in a first reactor filled with a conventional metal sulfide catalyst. After removal of the H_2S formed in the first reactor, the amount of sulfur entering the second reactor may be low enough for the noble metals to maintain sufficient activity.

The reaction network of the HDS of 4,6-DM-DBT over Pd/γ-Al_2O_3 consists of two reaction routes, direct desulfurization (DDS) and hydrogenation (HYD) (Scheme 1) [8]. The HYD pathway, the dominant route, leads to sulfur-containing intermediates 4,6-dimethyltetrahydrodibenzothiophene (4,6-DM-TH-DBT), 4,6-dimethylhexahydrodibenzothiophene (4,6-DM-HH-DBT), and 4,6-dimethylperhydrodibenzothiophene (4,6-DM-PH-DBT), as well as desulfurized products 3,3′-dimethylcyclohexylbenzene (3,3′-DM-CHB) and 3,3′-dimethylbicyclohexyl (3,3′-DM-BCH). The DDS route yields 3,3′-dimethylbiphenyl (3,3′-DM-BP) with only 1% selectivity and thus contributes little to the HDS of 4,6-DM-DBT [8]. In con-

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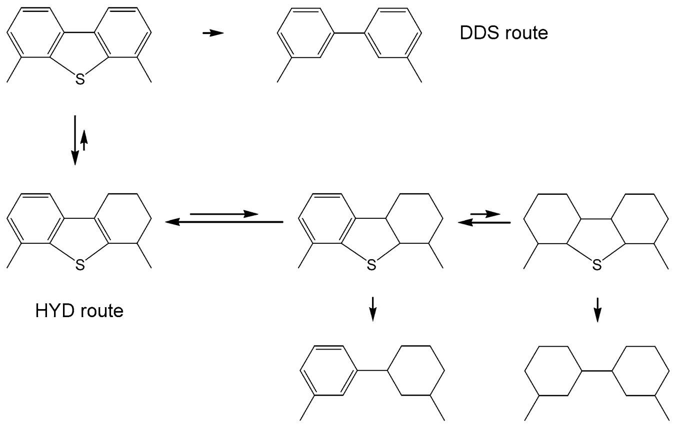


Scheme 1. Reaction network in the HDS of 4,6-DM-DBT at 300 °C and 5 MPa over Pd/γ-Al_2O_3.

trast to 4,6-DM-DBT, dibenzothiophene (DBT) converts predominantly by the DDS pathway. This difference has been attributed to the steric hindrance generated by the methyl groups adjacent to the sulfur atom in 4,6-DM-DBT [1,2,4,5,9–15]. DDS and HYD are assumed to take place on distinct types of active sites [16–22]. Pd was found to be more active than Pt in hydrogenation reactions in the presence of sulfur components [23–27]. Less is known about the different activity of the noble metal catalysts in the HDS of refractory sulfur-containing compounds. Lin et al. reported that adding a second metal, such as Pd to Pt, enhances the catalytic activity in the presence of sulfur [28]. This improvement was also observed in the conversion of substituted DBT derivatives over Pt-Pd catalysts [29,30]. A higher tolerance to sulfur due to a synergetic effect between the metals was suggested to explain these experimental results.

To gain better insight into the active sites involved in the transformation of sulfur-containing molecules, we studied the HDS of 4,6-DM-DBT and DBT over Pt, Pd, and Pt-Pd catalysts supported on γ-Al_2O_3 and analyzed not only the final hydrocarbon products, but also the (partially) hydrogenated intermediates. The possible further hydrogenation of the desulfurized products was investigated by carrying out experiments with 3,3′-DM-BP in the presence of DBT.

2. Experimental

All of the experiments were performed at 300 °C and 5 MPa total pressure in a continuous-flow fixed-bed reactor (Inconel 718) over 50 mg of noble metal catalyst supported on γ-Al_2O_3 (Condea; 35–60 mesh ≈ 250–400 µm; BET surface area, 220 m^2/g; total pore volume, 0.6 ml/g) diluted with SiC. The noble metal catalysts were prepared by incipient wetness impregnation of the calcined support with an appropriate aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (Aldrich, 99%) and/or $Pd(NH_3)_4(NO_3)_2$ (Alfa, 5 wt% in Pd). After impregnation, the catalysts were dried in air at ambient temperature for 3 h, then in an oven at 120 °C for 4 h, and finally calcined at 500 °C for 4 h (at a heating rate of 5 °C/min). Before the HDS experiments, the noble metal catalysts were activated by in situ reduction [8]. The HDS of 4,6-DM-DBT (Acros, 95%) was studied over monometallic 0.54 wt% Pt/γ-Al_2O_3 (referred to hereinafter as Pt/γ-Al_2O_3) and 0.50 wt% Pd/γ-Al_2O_3 (Pd/γ-Al_2O_3) catalysts, bimetallic 0.29 wt% Pt–0.24 wt% Pd/γ-Al_2O_3 (Pt-Pd/γ-Al_2O_3) and 0.46 wt% Pt–0.50 wt% Pd/γ-Al_2O_3 [Pt-Pd/γ-Al_2O_3 (2×)] catalysts, and a 1:1 physical mixture of 0.54 wt% Pt/γ-Al_2O_3 and 0.50 wt% Pd/γ-Al_2O_3. The gas-phase feed consisted of 130 kPa decane (as solvent), 8 kPa dodecane (as internal standard), 1 kPa 4,6-DM-DBT, and ~4.85 MPa hydrogen. After condensation of the reaction products, off-line samples were collected and analyzed with 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 µm) and a flame ionization detector. Investigations of the HDS of DBT (Fluka, 98%) and hydrogenation of 3,3′-DM-BP (Aldrich, 99%) were carried out under identical conditions over Pt/γ-Al_2O_3, Pd/γ-Al_2O_3, and Pt-Pd/γ-Al_2O_3.

Every series of HDS experiments over a freshly in situ reduced noble metal catalyst started with a stabilization period of at least one night (15 h) at the highest weight time (9 g min/mol) (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), and thus with decreasing weight times. 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, and we washed the condensers a few times. This corresponded to the removal of about 20 ml of product mixture from the condensers and ensured that the off-line samples were representative for the new conditions. This procedure was set up after many trial tests to determine how quickly the reaction system reached steady state. Furthermore, samples were taken with extreme care to avoid disturbance of the reaction pressure and steady state. Several samples were collected for each point at different times, and each sample was analyzed and quantified by gas chromatography (GC) to determine whether a stable composition had been reached yet. In this way, a set of five experimental points was measured in 2 days. However, we repeated all experiments at least once, yielding very similar results in all cases, and we also checked for possible catalyst deactivation by performing experiments with decreasing as well as increasing weight times. The difference in the conversion was only a few percent over the 2–3 weeks of the whole run with one catalyst, indicating that our stabilization procedure was reliable. As a result, stable conversions and selectivities were obtained a few hours after the start of the experiment.

Hydrogen chemisorption was used to determine the metal dispersion of the alumina-supported catalysts. Measurements were performed at 30 °C and a pressure of 0.1–95 kPa on a volumetric Micromeritics ASAP 2010C instrument. Before the analyses, the catalyst samples (500 mg) were reduced in situ in hydrogen at 350 °C for 2 h (at a temperature ramp of 10 °C/min). Measurements were repeated after an evacuation period of 45 min. The metal dispersions were calculated from the difference between both adsorption isotherms (strong H_2 adsorption) and its extrapolation to zero pressure.

3. Results

3.1. Characterization

In measuring the H_2 chemisorption of Pd-based samples, care must be taken to prevent the metal particles from absorbing large amounts of hydrogen. Experiments must be carried out at low H_2 partial pressures to avoid the formation of β-palladium hydride [31–33]. Thus, the metal dispersions of the alumina-supported catalysts were determined from the strong H_2 adsorption at 30 °C in the pressure range 0.1–2.0 kPa, assuming H/M = 1 at the metal surface. The corresponding metal particle sizes were calculated as done previously [34,35]. The results are presented in Table 1.

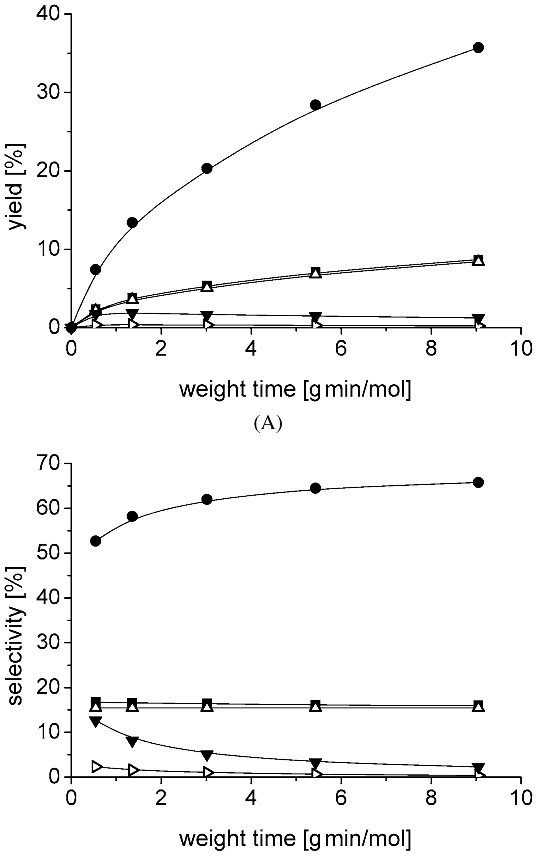
3.2. HDS of 4,6-DM-DBT

Six products were observed in the HDS of 4,6-DM-DBT over Pt/γ-Al_2O_3 (Fig. 1): 3,3′-DM-BP (the product of the DDS pathway), 4,6-DM-TH-DBT, 4,6-DM-HH-DBT, 3,3′-DM-CHB, 3,3′-DM-BCH (the intermediate and final products of the HYD pathway), and a trace of the fully hydrogenated sulfur-containing intermediate 4,6-DM-PH-DBT. The three desulfurized compounds showed continuously increasing yields and are the final products of the HDS network. They always represented the major part of the products, 85% at low weight time and 97% at high weight time. The selectivity of 3,3′-DM-BP was constant (15%) throughout the reaction (Fig. 1B), indicating that 3,3′-DM-BP does not hydrogenate further over Pt/γ-Al_2O_3 under the HDS conditions. Thus, 85% of the HDS of 4,6-DM-DBT occurs through the HYD pathway and 15% occurs through the DDS route. 3,3′-DM-CHB was always the most abundant product and showed increasing selectivity. The selectivity of 3,3′-DM-BCH was similar to that of 3,3′-DM-BP. The sulfur-containing molecules 4,6-DM-TH-DBT and 4,6-DM-HH-DBT were observed in small amounts, and their yields passed through a maximum. Apparently these intermediates desulfurize easily over Pt/γ-Al_2O_3.

The same sulfur-containing intermediates and hydrocarbons were observed over Pd/γ-Al_2O_3 as over Pt/γ-Al_2O_3, but with a different product distribution (Fig. 2). The sulfur-containing intermediates constituted 65% of the products at low weight time and 17% at high weight time, indicating that sulfur is more difficult to remove over Pd/γ-Al_2O_3. The yields of the sulfur-containing compounds passed through a maximum of 11% for 4,6-DM-TH-DBT, 6% for 4,6-DM-HH-DBT, and 3% for 4,6-DM-PH-DBT around $\tau = 1$ g min/mol, confirming that the sulfur-containing compounds are reaction intermediates. The concentrations of 4,6-DM-TH-DBT and 4,6-DM-HH-DBT evolved in parallel. As noted elsewhere [8], this suggests that the equilibrium between these partially hydrogenated sulfur components is rather rapid. The 3,3′-DM-BP selectivity remained constant at 1%, meaning that 99% of the 4,6-DM-DBT conversion occurred via the HYD route and only 1% occurred via the DDS route. 3,3′-DM-BCH was the major desulfurized product. The increasing selectivity of 3,3′-DM-CHB suggests that it did not hydrogenate under our conditions.

Table 1
Metal dispersions and estimated particle sizes as determined by strong hydrogen chemisorption at 30 °C (pressure range 0.1–2.0 kPa)

Catalyst	Dispersion [%]	Particle size [nm]
Pt	57	2.2
Pd	56	2.2
Pt-Pd	48	2.7
Pt-Pd (2×)	55	2.3



(A)

(B)

Fig. 1. Product yields (A) and selectivities (B) in the HDS of 4,6-DM-DBT over Pt/γ-Al_2O_3 as a function of weight time ((△) 3,3′-DM-BP; (▼) 4,6-DM-TH-DBT; (▷) 4,6-DM-HH-DBT; (●) 3,3′-DM-CHB; (■) 3,3′-DM-BCH).

The same six products were also observed over Pt-Pd/γ-Al_2O_3 (0.29 wt% Pt and 0.24 wt% Pd). 3,3′-DM-CHB was the most abundant product at low weight time, and 3,3′-DM-BCH was the most abundant at high weight time (Fig. 3). Both the yield and selectivity of 3,3′-DM-CHB passed through a maximum, suggesting that 3,3′-DM-CHB further hydrogenates to 3,3′-DM-BCH, which is then the only final product of the HDS network. The DDS product 3,3-DM-BP also showed a yield maximum and decreasing selectivity because of subsequent hydrogenation. Initially, 98.9% of 4,6-DM-DBT reacted by the HYD pathway and only 1.1% reacted by the DDS route over Pt-Pd/γ-Al_2O_3. The sulfur-containing intermediates rep-

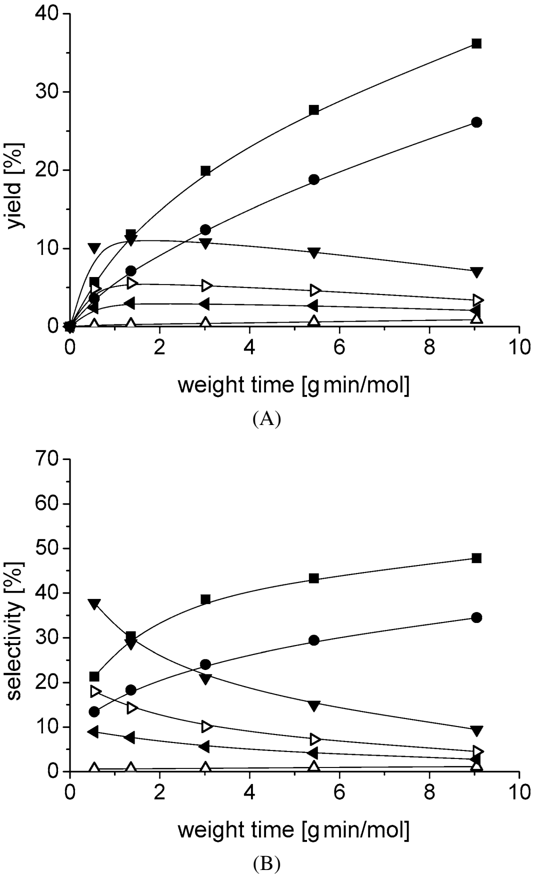


Fig. 2. Product yields (A) and selectivities (B) in the HDS of 4,6-DM-DBT over Pd/γ-Al_2O_3 as a function of weight time ((△) 3,3′-DM-BP; (▼) 4,6-DM-TH-DBT; (▷) 4,6-DM-HH-DBT; (◄) 4,6-DM-PH-DBT; (●) 3,3′-DM-CHB; (■) 3,3′-DM-BCH).

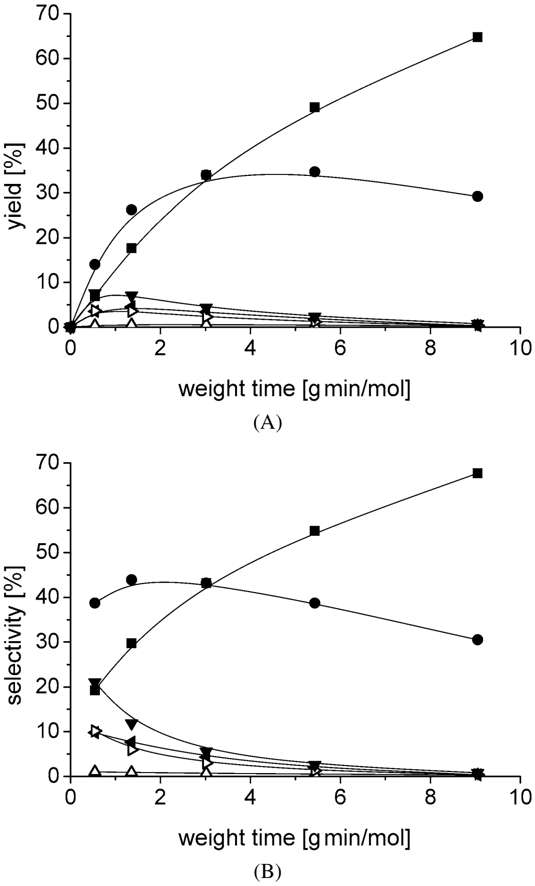


Fig. 3. Product yields (A) and selectivities (B) in the HDS of 4,6-DM-DBT over Pt-Pd/γ-Al_2O_3 as a function of weight time ((△) 3,3′-DM-BP; (▼) 4,6-DM-TH-DBT; (▷) 4,6-DM-HH-DBT; (◄) 4,6-DM-PH-DBT; (●) 3,3′-DM-CHB; (■) 3,3′-DM-BCH).

resented 41% of the reaction products at low weight time and 1% at high weight time. Surprisingly, the yield of 4,6-DM-PH-DBT was always slightly higher than that of 4,6-DM-HH-DBT.

Another Pt-Pd catalyst with about double loading of each noble metal (0.46 wt% Pt and 0.50 wt% Pd) was tested to investigate the effect of the total metal loading on the activity and reaction network of 4,6-DM-DBT. Product yields and selectivities were similar to those obtained over the Pt-Pd catalyst with lower loading. To enable a better comparison of the properties of the bimetallic catalysts with those of the monometallic components, a 1:1 physical-mixture catalyst of 0.54 wt% Pt/γ-Al_2O_3 and 0.50 wt% Pd/γ-Al_2O_3 was also tested. The activity of the physical-mixture catalyst was similar to that of the Pt catalyst (Fig. 4), whereas the selectivities of the products were between those selectivities observed over the monometallic catalysts.

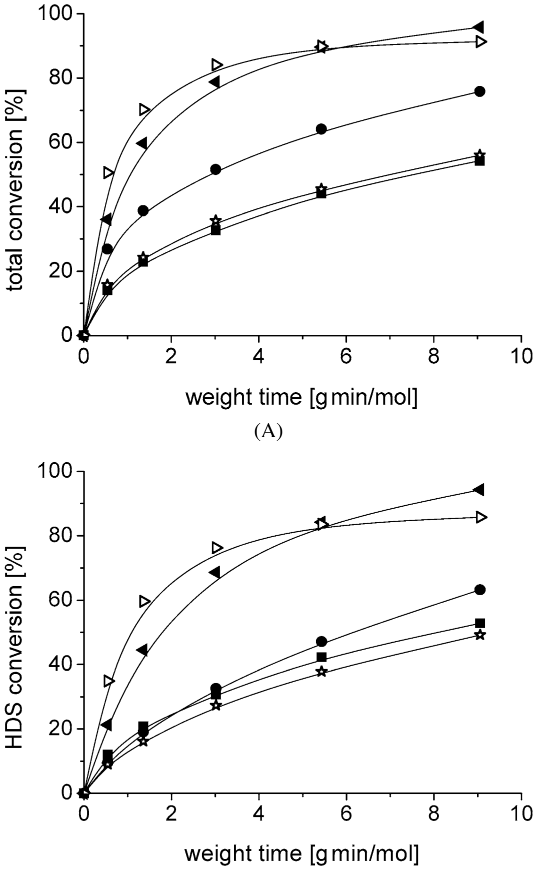
3.3. HYD of 3,3′-DM-BP

The hydrogenation of 1 kPa 3,3′-DM-BP over Pt/γ-Al_2O_3 was rapid in the absence of DBT but slow in the presence of 1 kPa DBT (to simulate the presence of a sulfur-containing compound during reaction of the hydrocarbon). The conversion of 3,3′-DM-BP reached only 6% at high weight time, even though the conversion of DBT was 96% (Fig. 5A). 3,3′-DM-CHB was more or less the only product (97–98%), showing that its hydrogenation to 3,3′-DM-BCH was very slow over Pt/γ-Al_2O_3. 3,3′-DM-BP also reacted very slowly in the presence of DBT over Pd/γ-Al_2O_3, reaching 7% conversion at high weight time and at 81% conversion of DBT (results not shown). The almost exclusive product was 3,3′-DM-CHB, confirming that hydrogenation did not occur easily.

Over Pt-Pd/γ-Al_2O_3, on the other hand, 3,3′-DM-BP showed appreciable conversion in the presence of DBT; at high weight time, 34% 3,3′-DM-BP and 100% DBT were converted (Fig. 5B). The selectivity to 3,3′-DM-CHB decreased from 96 to 88% with weight time, demonstrating not only that 3,3′-DM-BP hydrogenated to 3,3′-DM-CHB, but also that 3,3′-DM-CHB hydrogenated to 3,3′-DM-BCH.

3.4. HDS of DBT

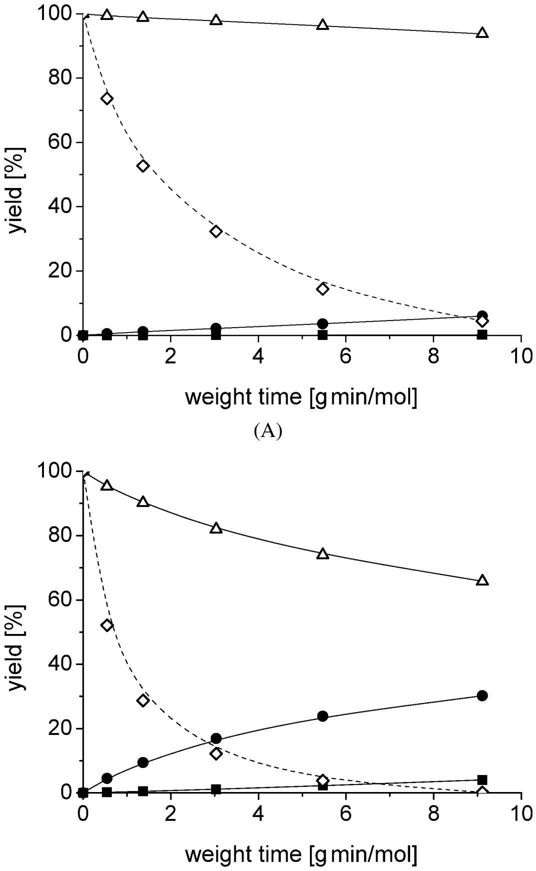
Five reaction species were observed in the HDS of DBT over Pt/γ-Al_2O_3 (Fig. 6): biphenyl (BP) as the DDS product and tetrahydrodibenzothiophene (TH-DBT), hexahydrodibenzothiophene (HH-DBT), cyclohexylbenzene (CHB), and bicyclohexyl (BCH) as the intermediate and final products of the HYD route. The main product was BP, with a constant selec-



(A)

(B)

Fig. 4. Total conversion (A) and HDS conversion (B) in the HDS of 4,6-DM-DBT over different alumina-supported catalysts ((■) Pt; (●) Pd; (✩) Pt + Pd; (◀) Pt-Pd; (▷) Pt-Pd, 0.46–0.50 wt%).



(A)

(B)

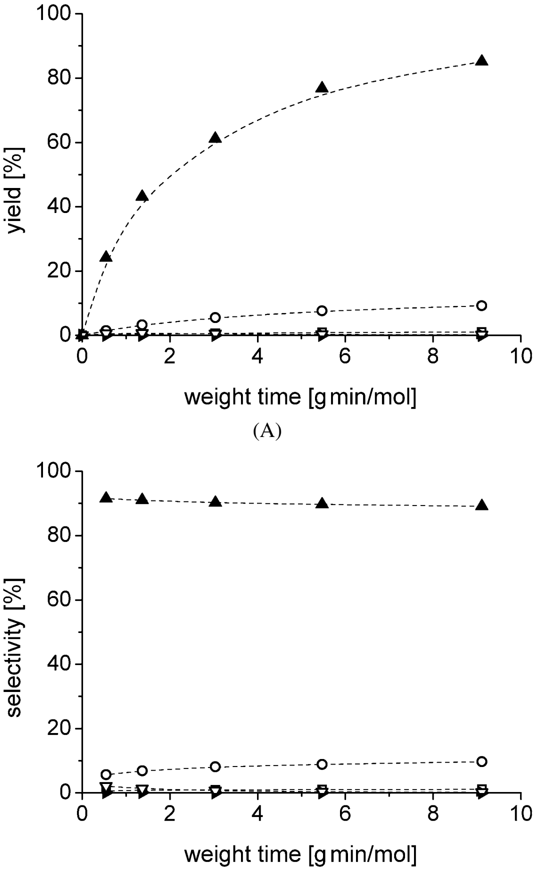
Fig. 5. Reaction profiles in the hydrogenation of 3,3′-DM-BP in the presence of DBT over Pt/γ-Al_2O_3 (A) and Pt-Pd/γ-Al_2O_3 (B) as a function of weight time ((◇) DBT; (△) 3,3′-DM-BP; (●) 3,3′-DM-CHB; (■) 3,3′-DM-BCH).

tivity of 91%. This indicates that no further significant hydrogenation occurred, and that the selectivity of the HYD pathway was only 9%. Moreover, the formation of BP seemed to occur easily, because its yield increased steeply at low weight time. TH-DBT was present in a very small amount, and HH-DBT was present in a trace amount. Their yields showed a maximum, and their selectivities decreased continuously, indicating that they are intermediates. The fully hydrogenated intermediate perhydro-dibenzothiophene (PH-DBT) was not detected, probably because of its slow formation and high reactivity under the experimental conditions.

CHB was the second major product; its selectivity increased from 6% at low to 10% at high weight time. CHB thus behaved like a final product and did not hydrogenate further to BCH. The third desulfurized component, BCH, was produced in small amounts (<1% selectivity). The high selectivity of the desulfurized products (98% at low weight time and 99.9% at high weight time) indicates that the removal of sulfur from DBT and from the sulfur-containing intermediates is rapid over Pt/γ-Al_2O_3.

Furthermore, over Pd/γ-Al_2O_3 the most abundant reaction product was BP, with a constant selectivity of 76%. It did not hydrogenate subsequently under our conditions (results not shown). Thus, 76% DBT reacted via the DDS route and 24% reacted via the HYD pathway over Pd/γ-Al_2O_3. The second major product was CHB; its yield was almost twice as high as over Pt/γ-Al_2O_3. Its selectivity increased from 15% at low weight time to 21% at high weight time and then leveled off. The third desulfurized compound, BCH, formed in small amounts (1.5% selectivity at high weight time). The two partially hydrogenated sulfur-containing intermediates were present in small quantities. Their selectivities decreased continuously and represented 8% at low weight time and 1% at high weight time.

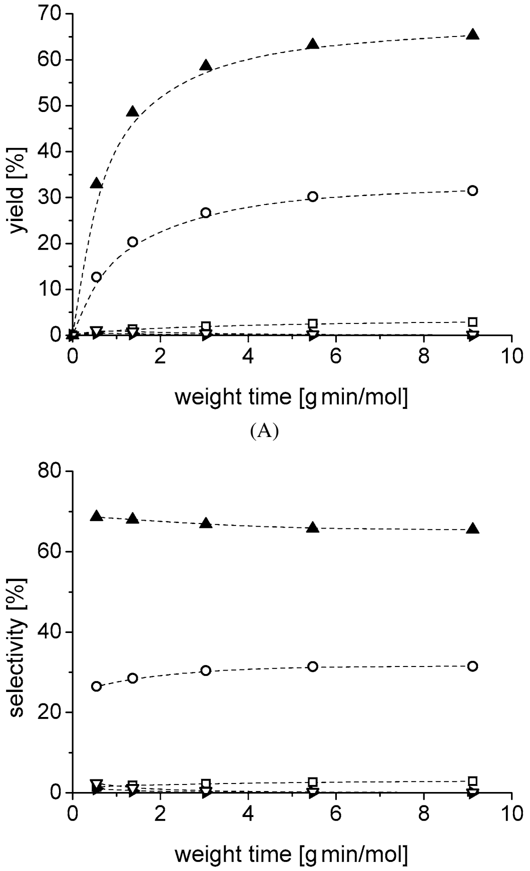
BP formed very rapidly over Pt-Pd/γ-Al_2O_3 and was the major product (Fig. 7), as it was over the monometallic catalysts. Its selectivity decreased slowly from 69% at low weight time to 65% at high weight time, indicating that hydrogenation of BP occurred over the bimetallic catalyst. Initially, 70% DBT converted through the DDS route and 30% converted through the HYD route. The second most abundant reaction product was CHB, with selectivity leveling off at 32%. The fully saturated and desulfurized compound BCH was produced in larger amounts than over the monometallic catalysts. It had a selectivity of 2.9% at high weight time. TH-DBT and HH-DBT were observed in very small amounts. Their selectivities decreased from 3% at low weight time to only 0.1% at high weight time.



(A)

(B)

Fig. 6. Product yields (A) and selectivities (B) in the HDS of DBT over Pt/γ-Al_2O_3 as a function of weight time ((▲) BP; (▽) TH-DBT; (►) HH-DBT; (○) CHB; (□) BCH).



(A)

(B)

Fig. 7. Product yields (A) and selectivities (B) in the HDS of DBT over Pt-Pd/γ-Al_2O_3 as a function of weight time ((▲) BP; (▽) TH-DBT; (►) HH-DBT; (○) CHB; (□) BCH).

4. Discussion

4.1. 4,6-DM-DBT

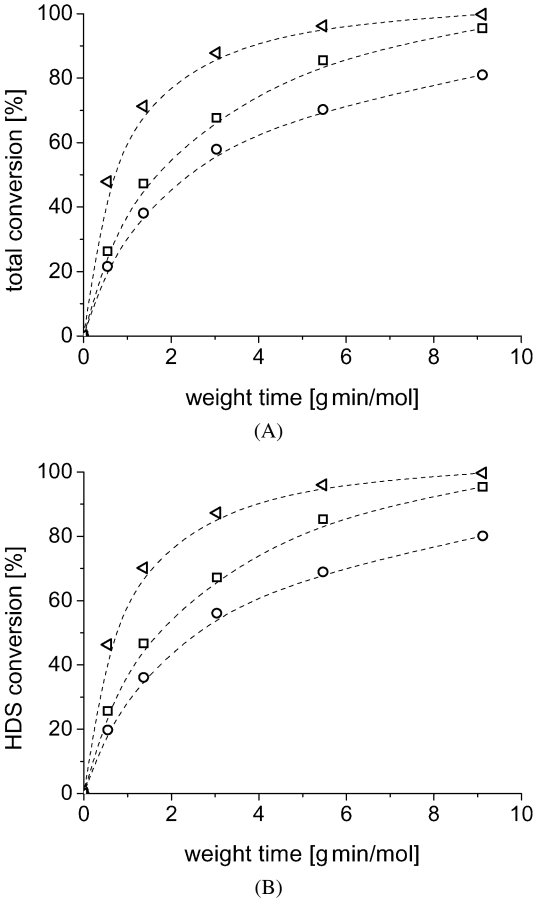
Because the HYD route is the main route in the HDS of 4,6-DM-DBT [1–5], the HDS of 4,6-DM-DBT is facilitated over catalysts with high hydrogenation properties—that is, Pd. Pd was more active than Pt in the conversion of 4,6-DM-DBT (Fig. 4A), whereas the bimetallic catalysts exhibited even higher activities. Nevertheless, doubling the metal Pt and Pd loadings brought about an increase in initial activity only (Fig. 4A). The lower activity at high weight time even suggests that the Pt-Pd (2×) catalyst was more sensitive to the inhibiting H_2S produced during the reaction. This might be due to a less homogeneous distribution of the two metal components over the alloy particles at higher metal loading. These results are in good agreement with the higher conversion of 4-ethyl-6-methyldibenzothiophene over a bimetallic Pt-Pd catalyst [29,36] and of substituted dibenzothiophenes in a light straight-run gas oil over a Pd catalyst compared with that over a Pt catalyst [30]. Pd was also much more active than Pt in the hydrogenation of small aromatic hydrocarbons in the presence of sulfur-containing molecules over various supports [23–27,37].

Similar hydrogen chemisorption data (Table 1) demonstrate that an effect of metal particle size can be ruled out as explanation for the varying activities. Assuming pseudo-first-order kinetics for the HDS of 4,6-DM-DBT, rate constants k were calculated at low conversions, where inhibition by H_2S was negligible (Table 2). As Figs. 4 and 8 show, the conversion of 4,6-DM-DBT and DBT, and therefore the concentration of the H_2S thus produced, varied from zero at low weight time to high at high weight time. This most probably means that the state of the catalysts is dependent on the conversion. At low conversion, the metal particles may adsorb little if any H_2S, whereas at high conversion, sulfur atoms may cover them to a large degree. Nevertheless, as explained in Section 2, no irreversible deactivation of the catalysts occurred. After changing from one weight time to another and back to the original weight time, the same conversion and selectivities were observed once steady state was reached.

The rate constant for Pd was twice as high as that for Pt, and the rate constant for the Pt-Pd catalyst was almost three times higher than that for the Pt catalyst. Doubling the Pt and Pd loadings in the bimetallic catalyst increased the initial reaction rate by a factor of 1.6. The Pt, Pd, Pt-Pd, and Pt + Pd catalysts contain about the same metal weight loadings but, due to different atomic weights, have different molar loadings. To correct for these effects, we expressed the activity as turnover frequency (TOF) per mmol surface metal (Table 2). The differences between the metals became smaller, with the TOF of Pd

Table 2
Pseudo-first-order rate constants (k, in mol/min g_{cat}), initial selectivities (in %), and turnover frequencies (TOF, in mol/min mmol) for the consumption of 4,6-DM-DBT over alumina-supported catalysts

Catalyst	k	HYD sel.	DDS sel.	TOF	TOF HYD	TOF DDS
Pt	0.28	85	15	18	15	2.7
Pt + Pd	0.32	95	5	15	14	0.8
Pd	0.58	99	1	22	22	0.2
Pt-Pd	0.83	99	1	46	45	0.5
Pt-Pd (2×)	1.30	99	1	33	33	0.3



(A)

(B)

Fig. 8. Total conversion (A) and HDS conversion (B) in the HDS of DBT over different alumina-supported catalysts ((□) Pt; (○) Pd; (◁) Pt-Pd).

only 20% higher than that of Pt. The bimetallic Pt-Pd catalyst was 2–2.5 times more active than the monometallic catalysts, and doubling both metal loadings decreased the TOF by 28%.

If the 4,6-DM-DBT molecules reacted independently on the Pt and Pd particles, then the TOF of the physical mixture (1:1 in weight but about 1:2 in molar ratio) should be the average of the activity of the monometallic Pt and Pd catalysts, that is, $(18 + 2 \times 22)/3 = 21$ mol/min mmol. But the observed TOF was slightly lower (15 mol/min mmol). The bimetallic Pt-Pd catalyst had almost the same metal composition as the physical mixture. Hence, if the metal particles in the Pt-Pd catalyst were completely segregated, then the activity of the Pt-Pd catalyst would be close to that of the physical mixture. Here the observed TOF was three times higher, suggesting alloying and a synergetic effect between Pt and Pd. A synergetic effect between Pt and Pd has also been reported for the HDS of DBT [25,38], substituted DBT compounds [30], and 4-ethyl-6-methyldibenzothiophene [29,36], as well as for the hydrogenation of tetralin in the presence of benzothiophene and of aromatics in a straight-run distillate diesel [28].

A synergetic effect can be caused by a textural effect or a chemical effect [39]. Textural synergism is due to an increase in the number of active sites on mixing of the individual metals. It may arise from a mutual influence of the metal salts during catalyst preparation, leading to a greater dispersion of the two metals than in the monometallic catalysts. In our case, the physical-mixture catalyst was prepared by mixing both separately prepared monometallic catalysts, to avoid any change in dispersion. The physical-mixture catalyst contained only sites of the same nature and strength as the monometallic catalysts, and they would be expected to catalyze the HDS reactions in parallel and independently on both types of metal sites. Chemical synergism means that either the bimetallic catalyst contains new sites not present in the monometallic catalysts or that the sites of one component catalyze one particular step (or steps) and those of the other component catalyze another step in the overall catalytic cycle. Either way, chemical synergism should lead to different selectivities of the reaction intermediates over the monometallic and bimetallic catalysts.

Although both metals reacted mainly through the HYD pathway, Pt showed a much higher DDS selectivity (15%) than Pd (1%) (Table 2). In other words, Pt has better desulfurization properties, and Pd is a very good hydrogenation catalyst. As expected, an intermediate DDS selectivity of 5% was obtained for the Pt + Pd physical-mixture catalyst (with a molar amount of Pd about twice that of Pt). In contrast, the bimetallic Pt-Pd catalyst did not show intermediate but did show different properties. First, the activity of the Pt-Pd catalyst was higher than that of the best (Pd) monometallic catalyst (Table 2). The HYD and DDS selectivities were the same as for the Pd catalyst, but the selectivity patterns in the HYD pathway differed (Figs. 2 and 3). These results suggest that the PtPd alloy particles have a Pd-rich surface and a Pt-rich core. Surface segregation of Pd in PtPd alloy particles has been observed in many experimental studies [40–43] and has been predicted by theoretical studies [41,44]. It is caused by the lower surface energy of Pd and higher cohesive energy of Pt [45,46]. Based on the similar values for the *trans*-decalin to *cis*-decalin ratio in the hydrogenation of tetralin over Pt-Pd and Pd, Matsui et al. concluded that Pt-Pd catalysts have surface properties similar to those of Pd [47].

TOFs for the DDS and HYD routes were calculated from the selectivity of the two HDS pathways and the total TOFs

(Table 2). The $\mathrm{TOF}_{\mathrm{DDS}}$ was 13 times higher for Pt than for Pd, but this is unimportant because the activities of the bimetallic catalysts are due mainly to their high hydrogenation activity, not their DDS activity. Compared with that of Pt, the $\mathrm{TOF}_{\mathrm{HYD}}$ was 1.5 times larger for Pd and 3 times larger for Pt-Pd. The higher activity of Pt-Pd catalysts toward aromatics in the hydrogenation of distillates has been ascribed to a higher sulfur tolerance of alloys [28,48–50], as well as to their better hydrogenation activity [51,52]. Sulfur poisoning of noble metals has been attributed to the fact that H_2S adsorption decreases the metal–support interaction and thus promotes the migration and growth of the Pt particles and the loss of Pt surface area [48–50]. Sulfur tolerance is related to the electron density of the metal. The addition of electrophilic Pd would decrease the electron density of Pt, inhibiting the adsorption of H_2S by weakening the S–Pt bond [28]. This helps maintain high dispersion of Pt in the presence of sulfur-containing compounds and stabilizes a larger number of small metal clusters. Fujikawa et al., in contrast, claimed that the alloying does not improve the sulfur tolerance, but significantly enhances the intrinsic hydrogenation activity [51,52].

The different product distributions in the HDS of 4,6-DM-DBT over Pt, Pd, and Pt-Pd (Figs. 1–3) show chemical synergism in the bimetallic Pt-Pd catalyst. The combination of Pt and Pd led to different catalytic properties than those of either Pt or Pd. Alloying Pd with Pt may form new active sites with different electronic and/or geometrical properties. These new active sites must have high hydrogenation activity, because the half-hydrogenated product, 3,3′-DM-CHB, was only hydrogenated to 3,3′-DM-BCH in the HDS of 4,6-DM-DBT over the Pt-Pd catalyst (Fig. 3). Similarly, 3,3′-DM-BP was hydrogenated to only a small extent over the Pt and Pd catalysts but to a significant extent over the Pt-Pd catalyst (Fig. 5), with TOFs of 0.6, 0.9, and 4.9 mol/min mmol for the Pt, Pd, and Pt-Pd catalysts, respectively (Table 3). These TOFs for the hydrogenation of 3,3′-DM-BP are four times smaller than the $\mathrm{TOF}_{\mathrm{HYD}}$ for the hydrogenation of DBT (Table 4). The surface of the Pt-Pd catalysts is strongly enriched in Pd, especially because the Pd-to-Pt molar ratio is higher than 1 (roughly 2). Therefore, the highly active hydrogenation sites in the Pt-Pd catalysts will probably consist of Pd atoms that are electronically influenced by underlying Pt atoms. This electronic influence may make the Pd atoms less sulfur-sensitive and thus more catalytically active.

Only trace amounts of 4,6-DM-PH-DBT were detected over Pt, whereas larger amounts were present over the Pd and Pt-Pd catalysts. This cannot mean that this sulfur-containing compound did not form over Pt, however, because 3,3′-DM-BCH, the product of the direct removal of sulfur from 4,6-DM-PH-DBT, formed in substantial quantities, and the hydrogenation of 3,3′-DM-CHB to 3,3′-DM-BCH was negligible in the presence of sulfur components. Hence, only very rapid desulfurization over Pt can explain the low concentration of 4,6-DM-PH-DBT. The major reaction product over Pt was 3,3′-DM-CHB, whereas that over Pd and Pt-Pd was 3,3′-DM-BCH. Thus, 4,6-DM-DBT reacted mainly to 4,6-DM-HH-DBT over the Pt catalyst and to 4,6-DM-PH-DBT over the Pd and Pt-Pd catalysts. This again points to the high hydrogenation properties of the Pd-based catalysts, on which the hydrogenation of 4,6-DM-HH-DBT to 4,6-DM-PH-DBT was faster than the desulfurization of 4,6-DM-HH-DBT to 3,3′-DM-CHB, and to the high desulfurization activity of Pt, on which the reverse occurred. Moreover, on the bimetallic catalysts, the partial pressure of 4,6-DM-PH-DBT was always slightly higher than that of 4,6-DM-HH-DBT, except at low weight time. This may be due to the slower reaction of 4,6-DM-PH-DBT by desulfurization to 3,3′-DM-BCH compared with that of 4,6-DM-HH-DBT by hydrogenation to 4,6-DM-PH-DBT and desulfurization to 3,3-DM-CHB.

The catalysts' desulfurization ability (i.e., their conversion to desulfurized products [HDS conversion]) was less than their total conversion of 4,6-DM-DBT (Fig. 4). The Pt curves show the smallest differences, because Pt converts 4,6-DM-DBT almost exclusively to desulfurized products. This is not the case for the Pd and Pt-Pd catalysts, which produce large quantities of sulfur-containing intermediates. The sum of the selectivities of the three sulfur-containing intermediates at 50% conversion of 4,6-DM-DBT was 3% for the Pt catalyst, 39% for the Pd catalyst, 32% for the Pt-Pd catalyst, and 15% for the physical-mixture catalyst. These findings confirm the very good desulfurization properties of Pt, with fewer (by 13 times) sulfur-containing intermediates detected than were detected over Pd. The desulfurization ability of the physical mixture was between that of the monometallic catalysts, whereas the Pt-Pd catalyst had a 20% lower selectivity for sulfur-containing intermediates than Pd. The necessary weight times to reach 50% conversion of 4,6-DM-DBT were 7.5 g min/mol for Pt, 2.8 g min/mol for Pd, 1.0 g min/mol for Pt-Pd, and 7.0 g min/mol for Pt + Pd. The value for the Pt-Pd (2×) catalyst was 0.5 g min/mol. More than anything else, these short weight times demonstrate the excellent properties of the bimetallic catalysts.

Table 3
Pseudo-first-order rate constants (k, in mol/min g_{cat}) and turnover frequencies (TOF, in mol/min mmol) for the hydrogenation of 3,3′-DM-BP over alumina-supported catalysts in the presence of 1 kPa DBT

Catalyst	$k_{3,3'\text{-DM-BP}}$	$\mathrm{TOF}_{3,3'\text{-DM-BP}}$
Pt	0.01	0.6
Pd	0.02	0.9
Pt-Pd	0.09	4.9

4.2. DBT

In contrast to the HDS of 4,6-DM-DBT, Pt had greater activity than Pd in the HDS of DBT (Fig. 8). The TOF for Pt was twice as large as for that Pd, whereas that for Pt-Pd was 1.9 times larger than that for Pt (Table 4). The different product distributions obtained over the bimetallic catalyst demonstrate the chemical synergism between Pt and Pd in the HDS of DBT. Pt had the highest initial DDS selectivity of 91% in the HDS of DBT (Table 4), as in the HDS of 4,6-DM-DBT (Table 2). Pd again showed lower DDS selectivity, with 76% DBT reacting by the DDS route. The DDS selectivity was lowest (70%) for the bimetallic Pt-Pd catalyst. Navarro et al. [53] and Kabe

Table 4
Pseudo-first-order rate constants (k, in mol/min g_{cat}), initial selectivities (in %), and turnover frequencies (TOF, in mol/min mmol) for the consumption of DBT over alumina-supported catalysts

Catalyst	k_{DBT}	HYD sel.	DDS sel.	TOF_{DBT}	TOF HYD	TOF DDS
Pt	0.56	9	91	35	3	32
Pd	0.44	24	76	17	4	13
Pt-Pd	1.19	30	70	66	20	46

et al. [25,38] also observed higher activity and DDS selectivity for Pt compared with Pd.

Because only small amounts of sulfur-containing intermediates were present in the HDS of DBT, the HDS conversions of the catalysts were only slightly lower than the total conversions (Fig. 8). The selectivity to TH-DBT and HH-DBT at a fixed conversion of DBT shows that sulfur removal was much faster over Pt than over Pd. The fully hydrogenated sulfur-containing intermediate PH-DBT was not detected over any of the three catalysts studied; however, small amounts of BCH were always produced. BCH can form through direct removal of sulfur from PH-DBT and through hydrogenation of CHB. The latter possibility can be disregarded here, because neither BP nor 3,3′-DM-BP hydrogenated under HDS conditions. Therefore, we conclude that BCH formed by desulfurization of PH-DBT and that PH-DBT was not detected due to its slow formation and high reactivity.

The TOFs (Table 4) show that the hydrogenation of DBT was 1.3 times faster over Pd and almost seven times faster over Pt-Pd than over Pt. The same trend can be observed for 4,6-DM-DBT (Table 2). This confirms that new sites were created, probably by alloying of the noble metals. In the DDS route of DBT, Pt was 2.5 times more active than Pd, confirming the weaker desulfurization activity of Pd, whereas Pt-Pd was 3.5 times more active than Pd. The major difference between the HDS of DBT and 4,6-DM-DBT is that DBT was transformed mainly by the DDS route, whereas 4,6-DM-DBT converted almost exclusively by the HYD route. This is due to the presence of the methyl groups at positions 4 and 6. In the DDS pathway, the reactant must adsorb in a σ mode through the sulfur atom, as suggested by experimental results [3,9,12,54] and confirmed by theoretical calculations [55]. However, the methyl groups strongly hinder the adsorption of 4,6-DM-DBT in this mode [3,9]. This explains the very low DDS rate constants and the need to decrease the strong steric hindrance by prehydrogenation of at least one aromatic ring before sulfur removal. Therefore, the HDS of 4,6-DM-DBT is facilitated over catalysts with high hydrogenation activity, such as Pd. In the case of DBT, the sulfur atom is easily accessible to direct desulfurization, leading to a high k_{DDS}. Its reactivity is further increased by the use of a catalyst with high desulfurization properties, such as Pt.

On the other hand, π adsorption is necessary in the hydrogenation pathway [3,9,12,54,55]. In this configuration, the substituents at positions 4 and 6 do not constitute a problem for adsorption, because they are located in the plane of the DBT molecule. The strong decrease in TOF_{DDS} going from DBT to 4,6-DM-DBT (Tables 2 and 4) leaves the HYD route as the main pathway for 4,6-DM-DBT. The loss of DDS activity is partially compensated for by the HYD activity. Comparing Tables 2 and 4 shows that the TOF_{HYD} values for the Pt, Pd, and Pt-Pd catalysts were much higher for 4,6-DM-DBT than for DBT. This is because the methyl groups donate electron density to the aromatic ring, enhancing the basicity and thus the adsorption of 4,6-DM-DBT relative to DBT on the catalyst surface. Consequently, the TOF of 4,6-DM-DBT was lower than that of DBT by only a factor of 2 for Pt and by a factor of 1.4 for Pt-Pd, whereas for Pd, the TOF of 4,6-DM-DBT was 1.3 times larger than that of DBT. The reason why Pd behaved differently was that the TOF_{DDS} for the HDS of DBT was much smaller for Pd than for Pt and Pt-Pd. Because the TOF_{DDS} of 4,6-DM-DBT was very small for all three catalysts, the TOF_{DDS} for Pd decreased much less than for Pt and Pt-Pd, and because the TOF_{HYD} for all three metals increased, the total TOF of Pd even increased when going from DBT to 4,6-DM-DBT. This enhanced HYD pathway makes the noble metals much more attractive than metal sulfides for the HDS of refractory molecules. Metal sulfides operate mainly by the DDS pathway in the HDS of DBT and by the HYD pathway in the HDS of 4,6-DM-DBT, because, as over the noble metals, the DDS pathway is strongly diminished by the presence of alkyl groups at positions 4 and 6. However, unlike over Pt and Pd, the HYD pathway over the metal sulfides is hardly enhanced by the methyl groups. The π adsorption of 4,6-DM-DBT on an extended metal surface probably enables more efficient electron donation of the methyl groups.

5. Conclusions

The desulfurization of DBT and 4,6-DM-DBT was faster over alumina-supported Pt than Pd, as indicated by the higher DDS selectivity and lower selectivity to sulfur-containing compounds. On the other hand, Pd had a high hydrogenation ability, especially for the refractory 4,6-DM-DBT. The bimetallic Pt-Pd catalysts were very active, much more than what would have been expected from a simple combination of their monometallic constituents. This demonstrates the occurrence of chemical synergism between the noble metals and confirms the presence of alloyed particles. The addition of Pt to Pd particularly improved the reactivity along the hydrogenation HDS pathway. New sites with high hydrogenation activity were probably created in the Pt-Pd catalyst. This was supported by the hydrogenation of the DDS products 3,3′-DM-CHB and 3,3′-DM-BP in the HDS of 4,6-DM-DBT, as well as by the hydrogenation of 3,3′-DM-BP in the presence of DBT, which was significant only over the Pt-Pd catalyst. DBT and 4,6-DM-DBT react basically by different reaction pathways, DBT mainly by direct desulfurization and 4,6-DM-DBT by hydrogenation followed by desulfurization. This is due to the presence of bulky substituents surrounding the sulfur atom, which strongly hinder σ adsorption in the DDS process. In contrast to metal sulfide catalysts, the hydrogenation over the noble metal catalysts was faster for 4,6-DM-DBT than for DBT and almost compensated for the loss of activity in the desulfurization.

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