



Reactivity of dibenzothiophene type molecules over Pd catalysts

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ABSTRACT

The reactivity of dibenzothiophene (DBT) over Pd/ γ -Al₂O₃ catalysts and the possible nature of the Pd active phase were analyzed. DBT conversion was studied as a function of the activating agent, the temperature, and in the presence of naphthalene (NP). Pd showed a high selectivity to the hydrogenation (HYD) route of DBT hydrodesulfurization (HDS). However, activation with H₂S decreased HYD selectivity. A reaction mechanism for the DBT conversion over Pd catalysts via HYD was proposed based on the mechanism usually accepted for aromatics hydrogenation. This mechanism comprises the initial saturation of one of the aromatic rings of DBT and a consecutive roll-over of the molecule onto the Pd surface. NP was found to inhibit HYD. Finally, the catalytic performance of Pd in HDS was found to agree well with the characteristics of a Pd metallic active phase.

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1. Introduction

The new generation of hydrotreating catalysts must have the capacity to desulfurize highly refractory alkyl-dibenzothiophenes (alkyl-DBTs) while performing the complete hydrogenation of aromatic molecules [1]. DBT and alkyl-DBTs react via two parallel routes: direct desulfurization (DDS) and hydrogenation (HYD) [2,3]. Desulfurization of DBT on sulfided CoMo and NiMo catalysts takes place via DDS, whereas conversion of alkyl-DBTs, in particular 4,6-dimethyl-DBT (4,6-DMDBT), proceeds mainly through HYD [2–5]. This difference is ascribed to strong steric effects induced by methyl groups in 4- and 6-positions [2,3]. The steric hindrance of alkyl-DBTs is reduced by hydrogenation of the DBT aromatic backbone [2,3,5]. Thus, developing highly hydrogenating selective catalysts is desirable for deep hydrodesulfurization (HDS) [2,6]. In this regard, it has been found that selectivity either to DDS or HYD is related to the adsorption mode of dibenzothiophene on the catalyst active sites [7,8].

Noble metal based catalysts have been tested in deep hydrodesulfurization and aromatics hydrogenation [9–13]. Compared to other HDS catalysts, monometallic Pd relatively shows a low desulfurization capacity [10–13]. Instead, Pd is able to selectively hydrogenate sulfur containing molecules. Mashkina and co-workers [14,15] hydrogenated thiophene and benzothiophene on Pd. Röthlisberger and Prins [11,16] tested Pd in the desulfurization of DBT and 4,6-DMDBT. Their results show that Pd has a

higher selectivity to HYD in the desulfurization of DBT as compared to NiMo and Pt catalysts [11]. On the other hand, significant amounts of partially hydrogenated products were found during the desulfurization of 4,6-DMDBT [16].

In this work, the performance of Pd catalysts on the hydrogenation of naphthalene (NP) and desulfurization of DBT were analyzed in terms of the reaction mechanism of their aromatic backbones. For this purpose, the HYD route over Pd was studied as a function of the activating agent, the temperature, and in the presence of naphthalene. DBT was used instead of 4,6-DMDBT in order to avoid steric effects in the selectivity of the catalyst [2,3]. Furthermore, to gain insight into the nature of the Pd active phase under a hydrotreating reaction environment, the thiotolerance of Pd sulfides in NP hydrogenation as well as the evolution of the catalytic performance were studied. Sulfided catalysts were characterized by XPS.

2. Experimental

2.1. Catalyst preparation

One Pd/ γ -Al₂O₃ catalyst prepared from a PdCl₂ precursor (Aldrich 99.0%) was chosen to study DBT desulfurization. The wet impregnation technique was used. The γ -Al₂O₃ used was a commercial Procatlyse: S_{BET} = 220 m²/g, V_p = 0.62 cm³/g, D_p = 11.6 nm. The support was previously calcined (2 h in air flow, T = 773 K), grounded and sieved to a particle size of 0.3–0.6 mm. The nominal content of Pd was adjusted to 2 wt.% and verified by atomic absorption. To obtain sulfided Pd catalysts with different chemical states of Pd and analyze their thiotolerance, two additional catalysts were prepared using Li₂PdCl₄ and palladium acetate

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(Pd(C₂H₃O₂)₂) (Aldrich 98.0%) as precursors. Impregnating solutions were obtained as follows: PdCl₂ was diluted in an aqueous solution of HCl to obtain PdCl₄²⁻ species [17]. Li₂PdCl₄ was diluted in water (deionized and distilled), and Pd(C₂H₃O₂)₂ was diluted in acetone. These solutions were kept in contact with the carrier until impregnation process completeness. Then, the exceeding solvent was vacuum evaporated. Drying (12 h) and calcination (4 h at 773 K) of these solids were performed under air flow. Catalyst labels were assigned according to the Pd precursor: Pd_{Cl} (PdCl₂), Pd_{Li} (Li₂PdCl₄), and Pd_{Ac} (Pd(C₂H₃O₂)₂).

2.2. Catalyst activation

Catalysts were *in situ* activated at 673 K after drying under N₂ flow (393 K). All catalysts were activated with a H₂S (15 vol.%) / H₂ mixture. Pd_{Cl} was also activated with pure H₂ or pure H₂S. According to the activating agent, the indexes: RS = mixture H₂S (15 vol.%) / H₂, R = pure H₂, and S = pure H₂S were added to catalyst labels. A thorough cleaning of the reaction system was made, by flushing with N₂ and H₂, before mounting the loaded reactor to perform catalyst's activation with H₂ (reduction). Afterwards, the *in situ* reduction of the catalyst was made according to the procedure mentioned above.

2.3. Catalysts characterization

The sulfided catalysts were analyzed by XPS. They were maintained in iso-octane before the XPS analysis to avoid air exposure. The XPS apparatus was an Axis Ultra spectrometer from Kratos working with non-monochromatic Mg radiation (10 mA, 15 kV) and a charge compensation device (charge balance fixed at -2.3 V). The pressure in the analysis chamber was around 10⁻⁶ Pa. The angle between the normal of the sample surface and the lens axis was 0°. The hybrid lens magnification mode was used with the slot aperture resulting in an analyzed area of 700 μm × 300 μm. The pass energy for the analyzer was 40 eV. In these conditions, the energy resolution gives a full width at half maximum (FWHM) of the Ag 3d_{5/2} peak of about 1 eV. The following sequence of spectra was recorded: C 1s, O 1s, Al 2p, Pd 3d, S 2p. The binding energies (BE) were calibrated by fixing the C-(C, H) contribution of the C 1s adventitious carbon at 284.8 eV. Peaks were considered to be combinations of Gaussian and Lorentzian functions in a 70:30 ratio working with a linear baseline. Data treatment was performed with the CasaXPS program (Casa Software Ltd., UK) [18].

2.4. Catalytic tests

Catalysts (0.5 g approximately) were tested in a continuous-flow high-pressure fixed-bed reactor. Four types of tests were performed: naphthalene or tetralin (TTL) hydrogenation without the presence of H₂S, naphthalene hydrogenation under an H₂S environment, dibenzothiophene desulfurization, and simultaneous DBT desulfurization and NP hydrogenation. Catalytic results were reproducible within a range of experimental error between each measurement of ca. 5%.

The composition of the liquid charge was systematically changed according to the reaction test performed. All reactants, NP, TTL, DBT, and hexadecane (Aldrich, 99%); used as chromatography internal standard (2 wt.%), were dissolved in cyclohexane (commercial grade). The total liquid feed flow was 30 mL/h. Reaction conditions were T = 543–603 K, P = 5 MPa, and the H₂/(liquid feed) ratio was fixed at 500 nL/L. Liquid products were analyzed using a HP 6890 GC equipped with an FID, an HP-1 capillary column (100 m × 0.25 mm × 0.5 μm), and a split injector. Catalytic tests were conducted until reaching steady state.

2.4.1. Hydrogenation of aromatic rings (NP and TTL)

Hydrogenation of mono-aromatic tetralin or di-aromatic naphthalene without the presence of H₂S was performed on reduced samples of Pd_{Cl} (Pd_{Cl}^R), in order to characterize the interaction of metallic Pd with aromatic rings. A concentration of 3 wt.% NP (commercial grade) or 2 wt.% TTL (Aldrich 98%) was used for these tests.

Naphthalene hydrogenation under a H₂S atmosphere was carried out on reduced Pd_{Cl}^R and reduced-sulfided Pd_{Cl}^{RS}, Pd_{Li}^{RS}, and Pd_{Ac}^{RS} catalysts, to analyze the effect of the chemical state of Pd in its thiotolerance in aromatics hydrogenation. NP content was the same as mentioned above, and H₂S (concentration ca. 4074 ppm) was generated from decomposition of dimethyldisulfide (DMDS) added to the reactor liquid feed. At the present conditions, all DMDS is transformed to H₂S [19].

2.4.2. Independent DBT desulfurization, and simultaneous DBT desulfurization and NP hydrogenation

These reactions were carried out only on samples of Pd_{Cl} activated with different agents (Pd_{Cl}^R, Pd_{Cl}^{RS} or Pd_{Cl}^S). Also, the effect of temperature on DBT desulfurization of Pd_{Cl}^R was studied. The concentration of DBT (Aldrich, 98%) used in both experiments was 2 wt.%. 3 wt.% naphthalene was used for the simultaneous desulfurization–hydrogenation reaction tests.

2.4.3. Expression of results

The activity results are presented in terms of reactant conversion (%C), product yield (%y_i), and the specific rate constant (k_i, L s⁻¹ g⁻¹). %y_i was defined as the concentration of each reaction product detected in the GC analysis of collected liquid samples per total concentration of detected reaction products. The k_i was calculated considering a pseudo-first order kinetics [20]. For naphthalene and tetralin tests without H₂S presence, the selectivity to *trans*-decalin over the *cis*-decalin isomer (*S*_{trans-}) was defined as the k_{trans-}/k_{cis-decalin} ratio. The value k_{TTL} was calculated from its conversion to decalins (DCLs), while k_{cis-decalin} and k_{trans-decalin} were calculated from their corresponding yields. In this manner, k_{TTL} values from naphthalene and tetralin hydrogenation can be compared directly. For naphthalene hydrogenation under a H₂S environment, turn over numbers (TON^{XPS}) were defined as the ratio k_{NP}, as obtained from an average of three samples at steady state conditions, to Pd/Al atomic relation determined by XPS as expressed by Eq. (1).

$$\text{TON}^{\text{XPS}} = k_{\text{NP}} / (\text{Pd/Al atomic ratio})^{\text{XPS}} \quad (1)$$

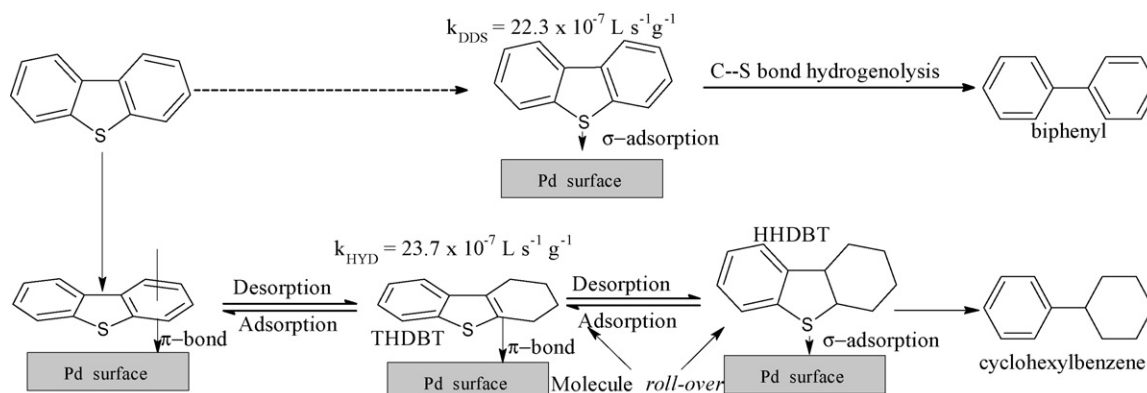
This calculation of TON^{XPS} provides a qualitative idea of the intrinsic activity of surface Pd atoms in steady state conditions. Considering that the alumina support can be taken as a common and valid reference to determine the relative distribution of Pd among these catalysts, the surface Pd/Al ratio is a good qualitative descriptor of the surface atomic dispersion. Even though this method is not fully accurate, the use of conventional methods to measure dispersion is not especially recommended in this case, given that sulfided phases are being examined [21].

To compare the thiotolerance of the reduced-sulfided (Pd_{Cl}^{RS}, Pd_{Li}^{RS}, and Pd_{Ac}^{RS}) catalysts to the one of reduced Pd_{Cl}^R during naphthalene hydrogenation, at steady state conditions, a % of the relative activity (%RA) was defined as k_{NP} for Pd_{Cl}^R minus k_{NP} for the corresponding reduced sulfided catalyst divided by k_{NP} for Pd_{Cl}^R:

$$\% \text{RA} = 100 \times (k_{\text{NP}}(\text{Pd}_{\text{Cl}}^{\text{R}}) - k_{\text{NP}}(\text{Pd}_{(\text{Cl}, \text{Li}, \text{Ac})}^{\text{RS}})) / k_{\text{NP}}(\text{Pd}_{\text{Cl}}^{\text{R}}) \quad (2)$$

where the corresponding catalyst has been indicated after k_{NP}.

For dibenzothiophene desulfurization reactions, k_i for the products resulting from HYD – i.e. tetra-hydro-dibenzothiophene (THDBT), hexa-hydro-dibenzothiophene (HHDBT) and cyclohexylbenzene (CHB) – were calculated considering a sequential



Scheme 1. Proposed reaction scheme for DBT conversion over Pd. Specific rate constants for the HYD route (k_{HYD}) and the DDS route (k_{DDS}) from the reaction over reduced Pd, as calculated from a pseudo-first order kinetics. $k_{\text{HYD}} = k_{\text{THDBT}}$ and $k_{\text{DDS}} = k_{\text{BP}}$, as reported in Table 4.

Table 1

XPS analysis of Pd/ γ -Al₂O₃ catalysts after activation by sulfidation either with a H₂S (15 vol.%)–H₂ mixture or H₂S.

Catalyst	% Atomic			Binding energy (BE) (eV)		FWHM		Atomic ratio	
	Pd 3d _{5/2}	S 2p	Al 2p	Pd 3d _{5/2}	S 2p	Pd 3d _{5/2}	S 2p	S/Pd	Pd/Al
Pd _{Cl} ^{RS}	0.27	0.39	30.98	336.43	162.01	2.2	2.7	1.4	0.009
Pd _{Li} ^{RS}	0.50	0.62	29.91	336.00	161.73	2.3	2.3	1.2	0.017
Pd _{Ac} ^{RS}	0.64	0.84	30.65	335.65	161.99	2.0	2.3	1.3	0.021
Pd _{Cl} ^S	0.18	0.48	31.09	336.55	162.34	1.7	2.7	2.7	0.006

conversion from DBT to THDBT → HHDBT → CHB (Scheme 1). Thus, k_{THDBT} represents the specific rate constant through HYD; i.e. calculated from the sum: $\%y_{\text{THDBT}} + \%y_{\text{HHDBT}} + \%y_{\text{CHB}}$. The catalytic selectivity was expressed in two different ways: as the $k_{\text{CHB}}/k_{\text{BP}}$ ratio ($S_{\text{HYD}}^{\text{DS}}$), i.e. between completely desulfurized products (BP = biphenyl) and the $k_{\text{THDBT}}/k_{\text{BP}}$ ratio ($S_{\text{HYD}}^{\text{T}}$), i.e. comparing the specific rate constant of HYD considering all of the HYD products. For the simultaneous reactions, two additional selectivities were defined: $S_{\text{HDA-HDS}}$, calculated as the $k_{\text{NP}}/k_{\text{HDS}}$ ratio (k_{HDS} was calculated from the sum: $\%y_{\text{BP}} + \%y_{\text{CHB}}$) representing the capacity of the catalyst to hydrogenate naphthalene over its desulfurization ability, and $S_{\text{NP-DBT}}$, calculated as the $k_{\text{NP}}/k_{\text{DBT}}$ ratio (k_{DBT} was calculated from the total conversion of dibenzothiophene considering all reaction products) indicating the capacity of the catalyst to hydrogenate naphthalene over converting dibenzothiophene.

3. Results

3.1. XPS analysis of the catalysts sulfided during activation

Table 1 shows the XPS results of the Pd catalysts sulfided during activation. As observed, the Pd/Al atomic ratio for the catalysts activated with the H₂S/H₂ mixture follows the order Pd_{Ac}^{RS} > Pd_{Li}^{RS} > Pd_{Cl}^{RS}. The S/Pd atomic ratio was found to remain almost constant for these catalysts. The BE of the Pd 3d_{5/2} peak decreases in the order Pd_{Cl}^{RS} > Pd_{Li}^{RS} > Pd_{Ac}^{RS}. All BE values are higher than the one of metallic Pd (335.0 ± 0.1 eV) [22]; hence,

the oxidation state of Pd is between +2 and +4 [23]. Given BE values for Pd 3d_{5/2} and S 2p and the S/Pd ratio, it is concluded that at similar activation conditions, this group of catalysts has similar sulfur saturation degrees but displays different electronic states of Pd. On the other hand, the S/Pd atomic ratio reported for Pd_{Cl}^S in Table 1 shows that activation with pure H₂S leads to an extensive sulfur saturation of the catalyst. Indeed, the S/Pd atomic ratio for Pd_{Cl}^S is almost twice that of Pd_{Cl}^{RS}. Additionally, activation with pure H₂S causes a larger positive BE shift of the Pd 3d_{5/2} peak.

3.2. Catalytic tests

The results for the independent naphthalene hydrogenation and dibenzothiophene desulfurization reactions are described first, and, afterwards, those corresponding to the simultaneous reactions.

3.2.1. Naphthalene or tetralin hydrogenation without the presence of H₂S

Reaction products detected were tetralin, *cis*-decalin, and *trans*-decalin. Table 2 presents the steady state values of the specific rate constant for naphthalene (k_{NP}), the various reaction products (k_{TTL} , $k_{\text{cis-decalin}}$, $k_{\text{trans-decalin}}$), and the selectivity *trans*- to *cis*-decalin ($S_{\text{trans-}}$) on Pd_{Cl}^R. It is observed that Pd is highly selective to tetralin. Moreover, the activity in tetralin hydrogenation to decalins is low. Concerning $S_{\text{trans-}}$, *trans*-decalin is always favored over *cis*-decalin.

Table 2

Steady state catalytic performance of Pd_{Cl}^R in naphthalene and tetralin hydrogenation without the presence of H₂S.

Reaction ^a	Activity, 10 ⁷ k (L s ⁻¹ g ⁻¹)				Selectivity
	k_{NP}	$k_{\text{TTL}}^{\text{b}}$	$k_{\text{trans-decalin}}$	$k_{\text{cis-decalin}}$	
Naphthalene hydrogenation	316	1.7	1.3	0.4	3.4
Tetralin hydrogenation	0	5.6	4.2	1.3	3.3

^a Reaction conditions: $T = 543 \text{ K}$; $P = 5 \text{ MPa}$; liquid feed flow = 30 mL/h; (H₂/liquid feed) ratio = 500 nL/L.

^b k_{TTL} determined in both cases from its conversion to DCLs.

^c $S_{\text{trans-}} = k_{\text{trans-decalin}}/k_{\text{cis-decalin}}$.

Table 3
Steady state performance of Pd/ γ -Al₂O₃ catalysts in naphthalene hydrogenation under a H₂S atmosphere.

Catalyst	10 ⁷ k _{NP}	%RA	TON ^{XPS}
Pd _{Cl} ^R	27.1	ND	ND
Pd _{Cl} ^{RS}	13.9	49	1.6
Pd _{Li} ^{RS}	21.3	21	1.3
Pd _{Ac} ^{RS}	13.9	49	0.7

Reaction conditions: $T = 563$ K; $P = 5$ MPa; liquid feed flow = 30 mL/h; (H₂/liquid feed) ratio = 500 nL/L; H₂S concentration in the reaction atmosphere ca. 4074 wppm. ND: non determinate.

This trend is similar either for naphthalene or tetralin, as in both cases S_{trans} remains constant. Similar results have been extensively reported in literature [24,25].

3.2.2. Naphthalene hydrogenation under an H₂S environment

Table 3 presents the steady state results for this reaction on Pd_{Cl}^R, Pd_{Cl}^{RS}, Pd_{Li}^{RS} and Pd_{Ac}^{RS}. All catalysts displayed very low activity and only yielded tetralin. This is in agreement with the low thiotolerance of monometallic noble metal based catalysts [26]. On the other hand, TON^{XPS} decreased in the order Pd_{Cl}^{RS} > Pd_{Li}^{RS} > Pd_{Ac}^{RS}. Thus, it can be said that, in general, Pd atoms on the surface of Pd_{Cl}^{RS} possess a relatively higher intrinsic activity than those of the other two catalysts.

3.2.3. Dibenzothiophene desulfurization

Fig. 1 shows the evolution of the catalytic performance with time on stream for Pd_{Cl} activated with different agents. In this figure, selectivity evolution is obtained from k_i values calculated from the reaction product distribution as determined per hour. Table 4 displays the steady-state catalytic behavior as a function of the activating agent and temperature. The reaction products detected were BP, CHB, THDBT and HHDBT.

3.2.3.1. Effect of the activating agent. Fig. 1 shows differences in the catalytic performance of Pd_{Cl} as a function of the activating agent. For Pd_{Cl}^R (Fig. 1a), a decrease in dibenzothiophene conversion is observed at the beginning of the reaction. Along with such lessening, a proportional decrease in the yields of BP and CHB was registered. Yields of THDBT and HHDBT remained constant. Hence, S_{HYD}^{DS} remained constant, whereas S_{HYD}^T slightly increased with time on stream. These trends demonstrate that HYD and DDS can proceed at similar ease over reduced Pd_{Cl}^R.

For Pd_{Cl}^{RS}, an initial raise in dibenzothiophene conversion was observed (Fig. 1b). Changes in yields of products are observed, as compared to Pd_{Cl}^R. Thus, a comparison between Pd_{Cl}^R and Pd_{Cl}^{RS} HYD product yields shows that the order of the former corresponded to CHB ~ THDBT > HHDBT, whereas the order of the latter corresponded to THDBT > CHB ~ HHDBT. Besides, the decrease in the kinetic rate constants registered for Pd_{Cl}^{RS} demonstrate that

Table 4
Steady state catalytic performance of Pd_{Cl} and temperature effect over Pd_{Cl}^R in independent DBT desulfurization.

Catalyst	T (K)	Activity 10 ⁷ k (L g ⁻¹ s ⁻¹)					Selectivity ^a	
		k_{THDBT}^b	k_{HHDBT}^b	k_{CHB}^b	k_{BP}	k_{DBT}^c	S_{HYD}^{DS}	S_{HYD}^T
Pd _{Cl} ^R	563	17.7	9.0	6.3	13.6	32.8	0.47	1.31
	583	23.7	13.1	10.5	22.3	49.5	0.48	1.07
	603	33.2	20.3	18.0	33.7	75.4	0.53	0.98
Pd _{Cl} ^{RS}	583	10.0	3.8	2.4	19.1	30.3	0.13	0.53
Pd _{Cl} ^S	583	17.2	9.2	7.0	22.7	42.8	0.31	0.76

Reaction conditions: $P = 5$ MPa; liquid feed flow = 30 mL/h; (H₂/liquid feed) ratio = 500 nL/L.

^a $S_{HYD}^{DS} = k_{CHB}/k_{BP}$; $S_{HYD}^T = k_{THDBT}/k_{BP}$.

^b Specific rate constants of the products resulting from the HYD pathway of DBT desulfurization were calculated considering a consecutive conversion from THDBT to CHB.

^c k_{DBT} is referred to the total conversion of DBT to (THDBT + HHDBT + BP + CHB).

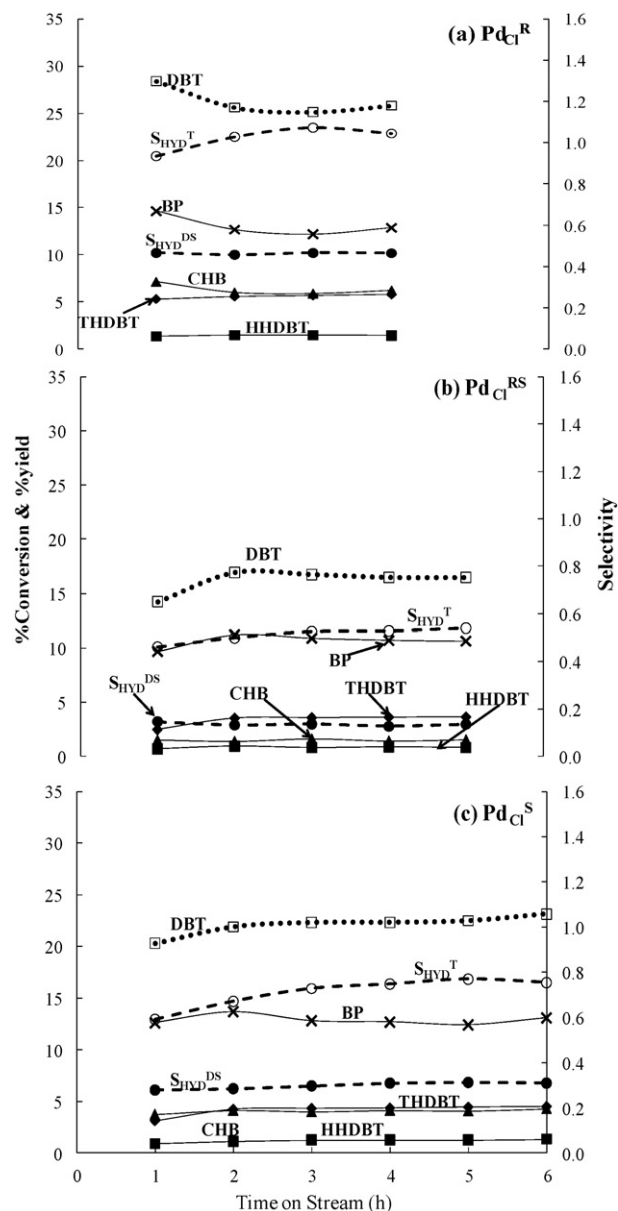


Fig. 1. Activity and selectivity versus time on stream for a Pd/ γ -Al₂O₃ catalyst, prepared from PdCl₂ precursor (Pd_{Cl}), in independent DBT desulfurization, as a function of the activating agent: (a) reduced in H₂ (Pd_{Cl}^R); (b) reduced-sulfided in H₂S (15 vol.%) / H₂ (Pd_{Cl}^{RS}); (c) sulfided with pure H₂S (Pd_{Cl}^S). Codes used: (···) catalytic conversion (%); (---) selectivity, and (—) %yield. (□) Dibenzothiophene (DBT); (×) biphenyl (BP); (▲) cyclohexylbenzene (CHB); (◆) tetrahydrodibenzothiophene (THDBT); (■) hexahydrodibenzothiophene (HHDBT); (○) $S_{HYD}^T = k_{HYD}/k_{BP}$; (●) $S_{HYD}^{DS} = k_{CHB}/k_{BP}$. Reaction conditions: $T = 583$ K, $P = 5$ MPa; liquid feed flow = 30 mL/h; (H₂/liquid feed) ratio = 500 nL/L.

Table 5
Steady state catalytic performance of Pd_{Cl} in simultaneous dibenzothiophene desulfurization and naphthalene hydrogenation reactions.

Catalyst	Activity 10 ⁷ k (Lg ⁻¹ s ⁻¹)						Selectivity			
	k _{NP}	k _{THDBT}	k _{HHDBT}	k _{CHB}	k _{BP}	k _{DBT}	S _{HYD} ^{DS}	S _{HYD} ^T	S _{HDA-HDS}	S _{NP-DBT}
Pd _{Cl} ^R	50.9	15.5	7.8	5.7	27.3	45.7	0.21	0.57	1.5	1.1
Pd _{Cl} ^{RS}	29.6	11.3	5.1	3.4	22.2	35.2	0.15	0.51	1.2	0.8
Pd _{Cl} ^S	31.0	18.9	9.6	7.1	22.5	41.0	0.31	0.84	1.0	0.8

Reaction conditions: T = 583 K, P = 5 MPa; liquid feed flow = 30 mL/h; (H₂/liquid feed) ratio = 500 nL/L.

inhibition of HYD can occur due to sulfidation of the catalyst. Notwithstanding, DDS was not deeply affected at steady state conditions (see k_{BP} in Table 4). Finally, the trends of Pd_{Cl}^S (Fig. 1c) are similar to those of Pd_{Cl}^{RS}.

In general, comparing k_{BP} for the three samples of the Pd_{Cl} catalyst in these experiments as a function of the activating agent (Table 4), only small changes are observed. Therefore, the activation procedure does not markedly impact DDS on Pd (see k_{BP}, Table 4). Conversely, as appointed before, HYD is negatively affected when activation by sulfidation is carried out. Thus, k_{THDBT} and S_{HYD}^T decreased in the order Pd_{Cl}^R > Pd_{Cl}^S > Pd_{Cl}^{RS}. Where, S_{HYD}^T of Pd_{Cl}^{RS} is half the one of Pd_{Cl}^R. Finally, S_{HYD}^{DS} of Pd_{Cl}^R is approximately thrice the one of Pd_{Cl}^{RS}.

3.2.3.2. Effect of reaction temperature on the selectivity of DBT conversion over Pd. The steady state catalytic performance of Pd_{Cl}^R in the dibenzothiophene reaction as a function of reaction temperature is presented in Table 4. Dibenzothiophene conversion increases with temperature, as in agreement with thermodynamics, but being much lower than equilibrium conversion at the present reaction conditions [27]. In general, S_{HYD}^T decreased and S_{HYD}^{DS} showed a small increase with temperature increase. Thus, higher temperatures enhanced the rate of hydrogenolysis of the C–S bond [27]. The results obtained evidence that dibenzothiophene desulfurization on Pd is kinetically controlled [27].

3.2.4. Reactivity of dibenzothiophene over Pd in the presence of naphthalene

Table 5 presents the steady state catalytic behavior of Pd_{Cl} as a function of the activating agent, and Fig. 2 features the catalytic conversion and the reaction product distribution – %y_i – as a function of time on stream.

As reported in Table 5 for Pd_{Cl}^R, a comparison of the results in dibenzothiophene desulfurization and those obtained in the simultaneous reactions demonstrates that the presence of naphthalene inhibits HYD. Therefore, on the reduced sample, k_i values (Tables 4 and 5) of HYD products decrease in the simultaneous reaction. Consequently, HYD selectivities, S_{HYD}^{DS} and S_{HYD}^T, are approximately half of those registered for the independent test. However, an increase in DDS can be observed, as comparing k_{BP} from Tables 4 and 5, respectively. Conversely, in this particular case, the evolution of dibenzothiophene conversion with time on stream shows a similar pattern to the one observed in the independent reaction (Figs. 1a and 2a, respectively). Additionally, it is remarkable that reduced Pd was more selective to naphthalene hydrogenation than to the conversion of dibenzothiophene, whether to desulfurized products (S_{HDA-HDS} = 1.5) or to all dibenzothiophene reaction products (S_{NP-DBT} = 1.1). Nevertheless, as observed in Fig. 2a, the initial conversion of naphthalene diminishes to a higher extent than the decrease in dibenzothiophene conversion.

For Pd_{Cl}^{RS}, the presence of naphthalene does not cause large changes on the performance in dibenzothiophene desulfurization (Fig. 2b). Therefore, steady state S_{HYD}^{DS} and S_{HYD}^T remained rather unchanged in the simultaneous reaction. Comparing the selectivity observed for Pd_{Cl}^{RS} to the one for Pd_{Cl}^R at steady state conditions (Table 5), a decrease in S_{NP-DBT} and S_{HDA-HDS} was obtained. However,

selectivity results still denote a higher favorability to the conversion of naphthalene than to the desulfurization of dibenzothiophene, i.e. conversion to desulfurized products. Similar trends in this reaction were observed for Pd_{Cl}^S.

Finally, comparing the selectivity trends of the sulfided samples of Pd_{Cl} (Pd_{Cl}^S and Pd_{Cl}^{RS}) to those of the reduced sample

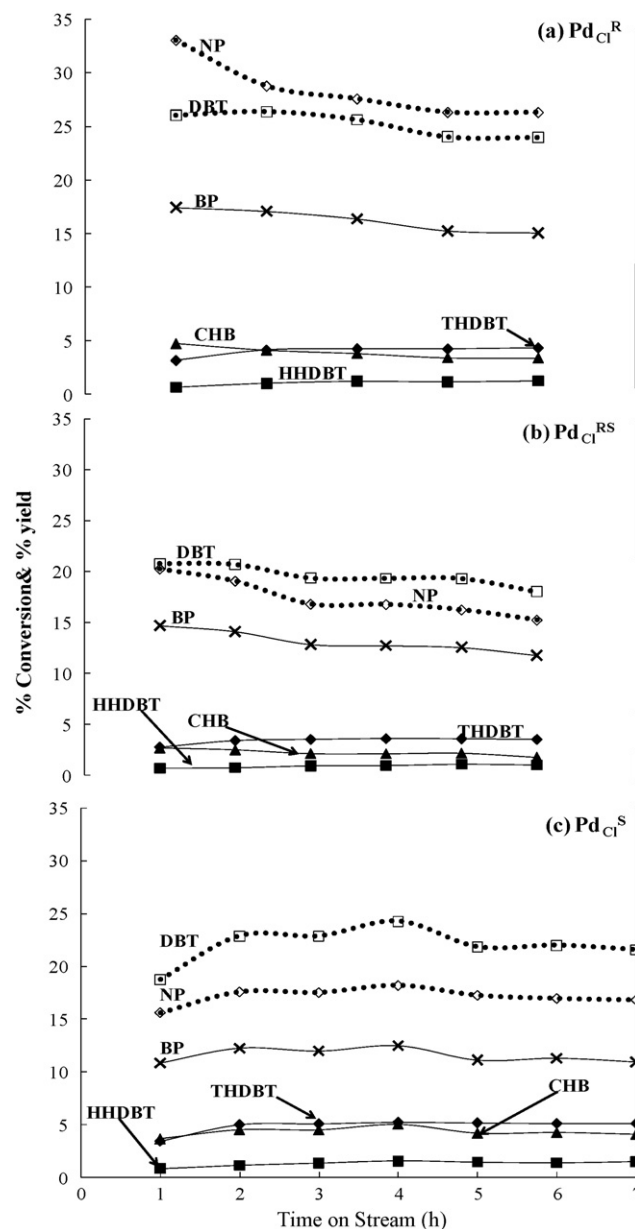


Fig. 2. Activity versus time on stream for Pd_{Cl} in simultaneous dibenzothiophene desulfurization and naphthalene hydrogenation, as a function of the activation agent. Codes as presented in Fig. 1, except for: (◇) naphthalene. Reaction conditions: T = 583 K, P = 5 MPa; liquid feed flow = 30 mL/h; (H₂/liquid feed) ratio = 500 nL/L.

(Pd_{Cl}^R), it is observed in Table 5 that selectivity to naphthalene hydrogenation ($S_{\text{HDA-HDS}}$ and $S_{\text{NP-DBT}}$) decreases when sulfidation was performed in the activation stage. This latter trend is similar to the one registered for HYD in dibenzothiophene desulfurization.

4. Discussion

The discussion is focused on the reactivity of DBT over Pd and the possible nature of Pd active phase under hydrotreating reaction conditions.

4.1. Reactivity of dibenzothiophene over Pd

Pd showed a high selectivity to the kinetically controlled HYD route, being highest than the one reported for MoS₂-based catalysts [4,5,9,28,29]. Selectivity trends can be explained in terms of an adsorption competition of DBT over catalyst active sites. It has been proposed that HYD comprises the formation of a π -complex between the DBT aromatic backbone and the catalyst active phase [7,8], whereas the hydrogenolysis of the S heteroatom over MoS₂ is considered to proceed via perpendicular σ -adsorption. Studies on DBT desulfurization over organometallic Pt complexes have shown certain similarities to this mechanism [30]. Thus, whereas DDS can be considered to occur on a “single step”, HYD comprises a series of sequential hydrogenation steps and a final hydrogenolysis of the C–S bond [4,5,28]; such mechanism is supposed to be similar as the one in DDS [5–7]. Egorova and Prins suggested that this is only possible after desorption and re-adsorption of the HHDBT intermediate [5]. Considering the above discussion and our results, we suggest that HYD over Pd takes place by the mechanism depicted in Scheme 1. This mechanism consists on a sequential series of adsorption–desorption steps, leading to the sequential saturation of one of the aromatic rings of DBT from THDBT to HHDBT. Then, the HHDBT intermediate rolls over the Pd surface to make possible the C–S bond hydrogenolysis as in DDS. Roll-over mechanisms have been suggested to explain aromatics hydrogenation on Pd [24,25,31]. The high selectivity of Pd to *trans*-decalin over *cis*-decalin ($S_{\text{trans-}}$) has been discussed by Weitkamp [24]. The conversion of TTL to *trans*-decalin implies an adsorption–desorption equilibrium between the $\Delta^{9,10}$ -octalin and the $\Delta^{1,9}$ -octalin intermediates on the Pd surface [24], whereas conversion to *cis*-decalin proceeds directly from the saturation of the olefin-type bond of $\Delta^{9,10}$ -octalin; the production of the *trans*-decalin isomer requires turning over of the octalin intermediate on the catalyst [24]. Other authors have also suggested a similar reaction mechanism for aromatics hydrogenation on Pd [25,31]. The results presented here suggest that the DBT aromatic backbone also interacts strongly with the Pd active phase given the high yield of HYD products observed. Therefore, it is possible that both hydrogenation reactions, namely, naphthalene hydrogenation and the HYD route of desulfurization, on Pd comprise roll-over type mechanisms.

4.2. Reactivity of dibenzothiophene over Pd in the presence of naphthalene

Selectivity changes observed in the simultaneous dibenzothiophene and naphthalene reactions indicate active site competition between these two molecules. In particular, the presence of naphthalene caused inhibition of the HYD route. Additionally, NP showed a higher conversion compared to DBT. These findings are in agreement with the proposed HYD mechanism on Pd, given the assumption that the naphthalene hydrogenation mechanism is similar to the one of HYD. Conversely, selectivity results point out

the preferential hydrogenation of the olefin-type bond of naphthalene in the presence of dibenzothiophene. In NP hydrogenation, the obtained results confirm that Pd is highly selective to TTL. Weitkamp ascribed this behavior to a preferential adsorption of naphthalene through the olefin-type bonds of the molecule [24]. Indeed, Pd is known to be the most selective catalyst to saturate olefin bonds attached to aromatic rings [24,32]. This trend has also been reported in the selective hydrogenation of the olefin-type bonds of thiophene and benzothiophene. Mashkina and Sakhaltueva [14] studied the selective hydrogenation of thiophene to tetra-hydro-thiophene over a series of transition metal sulfides and found that Pd was the most active in this reaction. Zirka et al. [15] hydrogenated benzothiophene to 2,3-dihydrobenzothiophene on Pd. Therefore, as in the case of NP hydrogenation to TTL, Pd has the capacity of selectively hydrogenate the olefin bond of these S-containing molecules. Such behavior matches the selectivity shift in DBT desulfurization in the presence of NP. Given that it appears that DDS is favored by HYD inhibition, it seems that naphthalene presence changes the mode of adsorption of the DBT molecule over the Pd active phase.

4.3. Pd active phase under a hydrotreating environment

The behavior of Pd under hydrotreating reaction conditions strongly suggests that its active phase is possibly not constituted by sulfur vacancies, having rather a metallic nature.

The XPS results of the catalysts activated with the H₂S/H₂ mixture (Pd_{Cl}^{RS}, Pd_{Li}^{RS} and Pd_{Ac}^{RS}) show that their sulfur coverage is comparable. According to the determined S/Pd ratio and the BE of the Pd 3d_{5/2} peaks, their stoichiometry corresponds to PdS_x, with $x < 1.5$. However, Pd sulfides stoichiometry cannot be accurately determined at the present conditions because sulfur can also be retained over the Al₂O₃ support [33]. Therefore, a mixture of different Pd sulfided species can be present as determined in previous studies [34–37]. According to Hensen et al. [34], activation with H₂S/H₂ can result in a mixture of metallic Pd, Pd₄S and PdS species, where, PdS is the most thermodynamically stable phase [34,36]. On the other hand, XPS analysis of Pd_{Cl}^S, i.e. activation with pure H₂S, leads to the formation of PdS₂ [34–36] along with H₂S adsorbed on the alumina support [33]. The different Pd species obtained during the activation step can be readily transformed under the HDT reaction environment [13,34,36–39]. This is evidenced in the evolution of the catalytic performance in the tests performed for the reduced and sulfided samples of Pd_{Cl} (Figs. 1 and 2). In such case, a dynamic equilibrium between the different Pd sulfided species, metallic Pd and the H₂S–H₂ atmosphere should be established. Considering the thermodynamic stability of Pd sulfides under H₂ atmospheres, it can be said that under the conditions used in this work, the equilibrium $\text{PdS}_{n(n=1,2)(s)} + \text{H}_{2(g)} \leftrightarrow \text{Pd}_{(s)} + \text{H}_{2}\text{S}_{(g)}$ is shifted to metallic Pd, i.e. the existence of thermodynamically stable Pd sulfide phases is not favored [9,34]. This, of course, does not completely rule out the formation of metastable Pd sulfided phases. Such phases can be formed, especially, from irreversible adsorbed sulfur species [40], as in reforming catalysts [38,40]. The fact that the evolution of the activity of Pd_{Cl}^R during the desulfurization experiments is contrary to the one of the sulfided samples (Pd_{Cl}^{RS} and Pd_{Cl}^S) indicates reduction-sulfidation dynamics of the Pd phases occurring under the reaction atmosphere. Indeed, Kabe et al. [13] studied DBT desulfurization over a series of γ -Al₂O₃ supported Pt and Pd catalysts. They proved that regardless the noble metal, the sulfided catalysts lost most of the sulfur present on their surface during the reaction. Conversely, the initial decrease observed in the activity of the reduced Pd_{Cl} sample, during the HDS tests, indicates that sulfidation under such conditions has a negative effect in both DBT desulfurization and NP hydrogenation. Furthermore, as discussed above, it is actually the HYD route of desulfurization of DBT which is mostly affected because DDS suffers rather small changes as a

function of the activating agent. These trends are in good agreement with the fact that the reduced sample of Pd_{Cl} is more thiotolerant than the sulfided catalysts (Pd_{Cl}^{RS}, Pd_{Li}^{RS} and Pd_{Ac}^{RS}) in NP hydrogenation. In addition, when correlating TON^{XPS} obtained for the reduced-sulfided catalysts with the BE of the Pd 3d_{5/2} peak, it can be said that those Pd atoms with a higher positive shifting of BE display a better activity in NP hydrogenation under and H₂S atmosphere. Such behavior is similar to that reported in thiotolerance tests of reduced noble metal catalysts [26,39,41]. Arcoya et al. [41] found that lower electron donating Pd^{δ+} species possess a higher thiotolerance in aromatics hydrogenation compared to metallic Pd⁰ species.

In conclusion, it seems that the active sites of Pd in desulfurization reactions should possess a more metallic character than expected, without discarding the existence of sulfided Pd phases, which, from the presented evidence, have a detrimental effect in HYD, as well as in naphthalene hydrogenation.

5. Conclusions

The reactivity of DBT over Pd/γ-Al₂O₃ under typical hydrotreating conditions and the possible nature of Pd active phase were analyzed. DBT transformation on Pd proceeds with a high selectivity to HYD being negatively affected by activation by sulfidation. From a comparison between the characteristics of Pd in the hydrogenation of aromatic rings, a reaction mechanism for the conversion of DBT was proposed. The mechanism has assumed that the C–S scission step is the same in either the DDS route or the final desulfurization step of HYD. HYD was assumed to be comprised of a series of consecutive adsorption–desorption steps leading to the sequential saturation of one of the aromatic rings of dibenzothiophene, and final scission of the C–S bond of the hexahydro-DBT intermediate. Such mechanism resembles to *roll-over* type mechanisms proposed for aromatics hydrogenation on Pd. This agreed with the observed inhibition of HYD by naphthalene. The activity and selectivity trends during the catalytic tests were found to be in accordance with a Pd active phase possessing a metallic character, rather than being constituted by sulfur vacancies.

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