Kinetic assessment of the simultaneous hydrodesulfurization of dibenzothiophene and the hydrogenation of diverse polyaromatic structures

Edgar M. Morales-Valencia¹, Carlos. O. Castillo-Araiza^{2*}, Sonia A. Giraldo¹ and Víctor G. Baldovino-Medrano^{1,3*}

¹Centro de Investigaciones en Catálisis (@CICATUIS), Parque Tecnológico

de Guatiguará (PTG), km 2 vía El Refugio, Universidad Industrial de Santander, Piedecuesta (Santander), 681011, Colombia.

²Grupo de Procesos de Transporte y Reacción en Sistemas Multifásicos, Departamento de IPH,

Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco No. 186, C.P. 09340

México D. F., México.

³Laboratorio de Ciencia de Superficies (#SurfLab-UIS), Parque Tecnológico Guatiguará (PTG),

Km. 2 vía El Refugio, Universidad Industrial de Santander, Piedecuesta (Santander), 681011,

Colombia.

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ABSTRACT

The elimination of sulfur from fossil fuels via hydrodesulfurization (HDS) is paramount to produce cleaner fuels. Ultra-deep HDS refers to reducing sulfur in fuels below 10 ppm. Nevertheless, under such conditions, dibenzothiophenes (DBTs) are to be desulfurized in the presence of highly complex aromatic structures that possibly exert inhibitory effects. Therefore, this contribution presents a kinetic study of the inhibition effect of diverse aromatic structures: naphthalene (NP), fluorene (FL) and phenanthrene (PHE), on the HDS of dibenzothiophene over a sulfided NiMo/y-Al₂O₃ catalyst. Kinetic modeling was based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) formalism and was submitted to regression analyses with the reparametrized form of the Arrhenius and van't Hoff equations. Before addressing inhibition effects, the kinetics of the HDS of DBT was revisited; in this sense, observations were better fitted when considering that the two parallel pathways for the HDS of DBT, i.e. the so called direct desulfurization (DDS) and hydrogenation mediated desulfurization (HYD) routes, take place on two different types of active sites. The developed model was used as a basis for the kinetic modeling of the inhibition of aromatics on the HDS of DBT. The kinetic parameters for the aromatics were estimated on both catalytic sites and exhibited thermodynamic consistency. Kinetic modeling indicated the following: (i) aromatic compounds and their reaction products are adsorbed on both DDS and HYD sites; (ii) the hydrogenation of naphthalene occurs on both sites while fluorene and phenanthrene only react on HYD sites; (iii) the entropy values suggested that mobility of the molecules is higher on HYD sites than on DDS sites except for fluorene and dibenzothiophene; and, (iv) fluorene strongly inhibits HYD sites due to its structure similarity with dibenzothiophene.

These findings are important because they provide an insight into the inhibition effects of polyaromatic compounds of different chemical structures on ultra-deep HDS.

1. Introduction

Increasingly stringent environmental requirements for fuels result in operational and economic challenges for the petroleum refining industry.^{1,2} Hydrodesulfurization (HDS) of fuel fractions is one of the major catalytic processes coping with environmental statutes for sulfur content. For instance, the maximum allowed concentration of sulfur in diesel fuels in the European Union is 10 ppm,³ 15 ppm in the U.S.A.,⁴ 10 ppm in Japan,⁵ and 50 ppm on overage in South America.⁶ When the sulfur content in fuels is around 10 ppm, refiners refer to ultra-deep HDS. Such demands drive constant research efforts for the development of new catalysts and processes. HDS catalysts, normally, sulfided CoMo/γ-Al₂O₃ and/or NiMo/γ-Al₂O₃, face ultra-deep HDS aiming to remove sulfur from refractory dibenzothiophenes (DBTs).^{7–9}

It is rather well established that DBTs react on the catalytic surface via the two parallel pathways shown in Scheme 1, namely, via the direct desulfurization (DDS), which yields biphenyl (BP), and via the hydrogenation mediated desulfurization (HYD) pathways. HYD comprises intermediate steps in which one of the benzene rings of DBT is firstly hydrogenated to tetra-hydro-dibenzothiophene (THDBT) and hexa-hydro-dibenzothiophene (HHDBT). These hydrogenation reactions are followed by the scission of the C-S-C bond to yield cyclohexylbenzene (CHB).^{10–13} On the other hand, the question of the number and nature of the active sites involved in DDS and HYD is not clear yet.

Some authors^{14–17} have proposed a common di-hydro-dibenzothiophene (DHDBT) intermediate for both the DDS and HYD reaction pathways. They suggest that this intermediate could be hydrogenated or desulfurized on the same active site. The difference in reactivity between the two pathways would thus be related to the different reaction rates to the transformation of DHDBT. Kinetic models based on this hypothesis have proposed one site on which DBT and its

reaction products competitively adsorb, and a second site for H_2 adsorption.^{14,18,19} However, a strong argument against this mechanism is that di-hydro-dibenzothiophene has not ever been detected in HDS reactions under standard operational conditions.

Other studies have suggested that the different reactivities of the two HDS pathways are determined by the adsorption mode of the DBTs. Particularly, two modes of adsorption can be taken into account. For the DDS and the final C-S-C bond scission in the HYD reaction route, adsorption is considered to occur by the direct attachment of the sulfur heteroatom in a σ adsorption mode. Meanwhile, HYD is considered to occur via π type adsorption of the aromatic structure of the molecule on the active site.^{20,21} These two different modes of adsorption require different active sites and different adsorption and kinetic constants for the DDS and HYD routes.^{22–24} However, these two adsorption modes for the transformation of DBTs and its derivatives has only been shown to be feasible via molecular simulations but not proven by experiments performed under actual reaction conditions.¹⁵

Assuming more than one active site for the adsorption of hydrocarbons increases the complexity of kinetic modeling by increasing the number of kinetic and adsorption parameters to be estimated. Kinetic expressions for the hydrodesulfurization of dibenzothiophene assuming that the hydrogenolysis and the hydrogenation reactions take place on two different active sites have been modeled scarcely. In this regard, pseudo-first-order order models²⁵ and the Langmuir-Hinshelwood-Hougen-Watson (LHHW) formalism have been used for the modeling kinetics mainly over CoMo/ γ -Al₂O₃ catalysts.^{26–28} Significantly less attention has been given to the study of kinetic models of HDS of DBT over NiMo/ γ -Al₂O₃.²⁹ Nevertheless, at present, for the high hydrogenation activity exhibited at high hydrogen partial pressure NiMo catalysts are preferred choosing for ultra-low sulfur diesel (ULSD) production^{13,30} and for the pretreatment stage for

hydrocracking with the primary objective of reducing aromatic and nitrogen compounds from the extra-heavy oils.^{31,32} For that reason, more rigorous kinetic modeling of the hydrodesulfurization over NiMo/ γ -Al₂O₃ catalyst are required for a proper description at a molecular level of the reactions taking place over the surface of this catalyst.

In ultra-deep HDS, DBTs must be desulfurized in the presence of highly complex aromatic structures.^{33–35} Several authors have studied the hydrodesulfurization of dibenzothiophene in the presence of aromatic compounds.^{34,36,37} Aromatic compounds with two and three fused rings have been found to inhibit HDS catalysts.^{36,38,39} The inhibiting effect on the aforementioned reaction routes is far from being understood, nonetheless. The studies, undertaken to determine possible inhibition effects of aromatics over the hydrodesulfurization of DBTs, often limit themselves to describing relative impacts of the presence of the aromatics on the conversion and selectivity of a selected model molecule.^{34,36,40} Furthermore, some contradictory trends have been reported since some authors observe that aromatics may inhibit the HYD route of desulfurization to a larger extent as compared to the DDS route,^{8,41} whereas some others report that both reaction routes are inhibited to the same extent.^{7,40,42}

Kinetic studies for the HDS of DBTs in the presence of aromatic compounds are limited. The pseudo-first-order model has been frequently used to correlate the inhibition effect of the aromatic compounds^{8,36,42}. Nevertheless, with this approach, the adsorption equilibrium constants for all the compounds involved in the reaction are not determined, which does not allow the elucidation of a reaction mechanism.³⁸ A simplified LHHW model assuming one site on which DBTs, aromatics, and the reaction products competitively adsorb has also been used.³⁴ However, physicochemical and statistical criteria were not employed to evaluate the estimated kinetic and adsorption parameters. To the best of our knowledge, a rigorous kinetic modeling that describes the

competitive adsorption of aromatic compounds and dibenzothiophene assuming the existence of two types of active sites, one for the hydrogenation reactions and the other for the C-S-C bond scission has not been published yet for a conventional NiMo/ γ -Al₂O₃.

Considering the above, the main objectives of this work were: first, to revisit the kinetic model for the hydrodesulfurization of dibenzothiophene over a conventional NiMo/ γ -Al₂O₃ catalyst to elucidate the role of the number of the catalytic centers involved in the reaction. Second, to propose kinetically viable reaction pathways for the mutual inhibition effects present in the simultaneous hydrodesulfurization of dibenzothiophene and hydrogenation of aromatics with different chemical structures: naphthalene (NP), phenanthrene (PHE), and fluorene (FL). To achieve the first objective, three kinetic models were developed, the first one was based on the assumption that HYD and DDS occur on the same type of active sites, whereas the second model assumed that the HYD and DDS routes take place on two different active sites. The third kinetic model also assumed that hydrocarbons are adsorbed on the two different active sites, but included the hydrogenation of biphenyl to cyclohexylbenzene in the reaction network. For the second objective, different kinetic models were developed to elucidate the structural effects of the polyaromatics on the simultaneous reactions of hydrogenation and HDS of DBT. Naphthalene and phenanthrene were used as models of aromatics with two and three fused rings, respectively; and fluorene as a model for aromatics with a structure equivalent to that of dibenzothiophene, i.e. aromatics with a fivecarbon-membered ring. All models were based on the Langmuir-Hinshelwood-Hougen-Watson formalism and submitted to regression analyses with the reparametrized form of the Arrhenius and van't Hoff equations. Owing to the latter, activation energies and pre-exponential factors, as well as the adsorption enthalpies and entropies of each compound were estimated. Statistical tests were performed to determine the overall significance of the regression and for the individual

significance of the parameters.^{43–45} This systematic study provided robust kinetic modeling for the inhibition of aromatics on the hydrodesulfurization of dibenzothiophene.

2. Catalytic tests

Catalytic tests were carried out in a high-pressure fixed-bed continuous flow reactor operated in integrated mode. The reactor was packed with particles of a NiMo/y-Al₂O₃ commercial catalyst (Procatalyse) which presented the following physical properties: BET specific surface area of 150 $m^2 \cdot g^{-1}$, BJH pore volume of 0.42 cm³ · g⁻¹, and average BJH pore diameter of 11.2 nm. Extrudates of NiMo/y-Al₂O₃ were ground and sieved so as to obtain particles within a diameter ranging from 300-600 µm. For the catalytic tests, 0.3 g of catalyst were dried in situ under N₂ flow (100 mL·min⁻ ¹) at 120°C for 1 h. Afterwards, the catalyst was sulfided during 4 h using a volumetric flow rate of 100 mL·min⁻¹ containing 15% of H₂S in H₂ at atmospheric pressure and 400°C. After sulfidation, reactants were fed to the reactor at a volumetric flow rate of 30 mL·h⁻¹. Then, the reactor pressure was increased with H₂ to 5 MPa and a hydrogen/(liquid feed) rate ratio of 500 NL·L⁻¹ was fixed for the experiments. Reaction temperatures were programmed to start at the highest testing temperature, i.e. 300°C, in order to stabilize the catalyst. Afterwards, temperature was decreased to 260°C followed by increases to 280°C and finally to 300°C, again. Such conditions were applied to check for possible deactivation of the catalyst during the experiments. Reactions were conducted until reaching steady state, considered herein as measurements where catalytic conversion and selectivity did not change more than $\pm 2\%$ over time on stream. The absence of heat and mass transport limitations was verified as stated elsewhere.^{37,46}

The reaction feedstock accounted for the following compounds employed either individually or in blends: dibenzothiophene (Sigma-Aldrich, 98%), as a model sulfur compound in ultra-deep HDS, naphthalene (Laboratorios León, 98%), fluorene (Merck, 95%), and phenanthrene (Sigma-Aldrich, 98%), as model aromatic compounds. Hexadecane (Sigma-Aldrich, \geq 99%) was used as an internal standard for chromatography and cyclohexane (commercial grade) was used as solvent. Two sets of experiments were carried out to evaluate the kinetic and inhibiting effect of aromatic compounds on the hydrodesulfurization of dibenzothiophene. In the first set of experiments, the reaction was performed in the absence of aromatic compounds. Temperature and space-time $(W_{cat}F_{DBT_0}^{-1})$ were varied between 260 - 300°C and between 33 - 182 $kg_{cat}kmol_{DBT}^{-1}h$, respectively. The second set of experiments was conducted in the presence of naphthalene, fluorene or phenanthrene. These experiments were carried out at a fixed space-time of DBT, i.e. 122 $kg_{cat}kmol_{DBT}^{-1}h$ but varying both the space-time of the aromatic compounds and the reaction temperature between 260 - 300°C.

Liquid products identification was based on chromatography and mass spectroscopy. Gas chromatography (GC) analyses were performed with a HP 6890 chromatograph equipped with an FID detector and an automatic injector. Two columns: an HP-1 (Agilent J&W, 100 m × 0.25 mm × 0.5 μ m) and an HP-5 MS (Agilent J&W, 50 m × 0.20 mm × 0.5 μ m) were used for GC and GC-MS, respectively. Analysis conditions were as follows: the GC oven temperature was programmed from 90 to 180°C (17 min) at 60°C min⁻¹, then to 260°C (10 min) using a temperature ramp of 80°C min⁻¹. Helium (Linde Colombia S.A, 99.99%) was used as carrier gas, with 19 cm s⁻¹ linear velocity (1.1 mL min⁻¹, at constant flow). Compounds in each sample were identified by means of a computer matching method, comparing their spectra with those provided in the Wiley, NIST, and QUADLIB libraries. The experimental error in the mass balance was found to be ±5%. The carbon balance calculated for each reaction is given in Tables S1 – S4, Section S4, of the Supporting Information.

Catalytic results were expressed in terms of conversion (%C_{*i*}), products selectivity (%S_{*j*}), and yield (%Y_{*j*}) percentages. Conversion was calculated as follows:

$$%C_i = \frac{F_i^0 - F_i}{F_i^0} \times 100\%$$
 (1)

Where, F_i^0 and F_i are the inlet and outlet molar flow rate of the hydrocarbon, respectively. Selectivity and yields were calculated as follows:

$$\% S_{j} = \frac{F_{j}}{F_{i}^{0} - F_{i}} \times 100\%$$
(2)
$$\% Y_{j} = \frac{F_{j}}{F_{i}^{0}} \times 100\%$$
(3)

Where, F_i is the outlet molar flow rate of the product *j*.

3. Kinetic modeling

3.1. Hydrodesulfurization of dibenzothiophene

Different kinetic models based on the LHHW formalism were developed. The first model; denominated DBT1S, considered a single active site, i.e. * sites, over which DBT and its reaction products adsorb and react via either DDS or HYD routes. The second model; named DBT2S, assumed that the HYD and DDS routes take place on two different active sites, i.e. π sites where the molecules are hydrogenated and σ sites over which the molecules are desulfurized. A third model; denominated DBTBP2S, was based on the same considerations as those made for the DBT2S model, but it included the hydrogenation of biphenyl to cyclohexylbenzene.^{11,27,29} The three kinetic models assumed the adsorption and heterolytically dissociation of H₂ occurring on β surface sites, which are different from the sites over which hydrocarbons adsorb.^{47,48}

The reaction mechanism for DBT1S is presented in Table 1. Therein, v_i is the stoichiometric number used for describing the number of times that each adsorption, desorption, and reaction steps must occur in order to complete one catalytic cycle according to the overall reaction *i*, the latter represented by global reactions 1 and 2. The dissociation of H₂ and the formation of SH species are considered to occur only on β sites: steps A, C, and G. Whereas, dibenzothiophene, biphenyl, and cyclohexylbenzene are considered to adsorb and react over * sites: steps B to H. The formation and later desorption of H_2S from β sites are represented in steps I and J, respectively. The direct desulfurization reaction pathway is represented by step C. HYD reactions include sequential hydrogenations steps: E for the conversion to THDBT and F for the hydrogenation to HHDBT. And, finally the hydrogenolysis of the HHDBT intermediate to cyclohexylbenzene is represented in step G.

Table 2 presents the reaction mechanism proposed for both DBT2S and DBTBP2S models. H₂ is dissociatively adsorbed on β sites; step A. DDS occurs on a single reaction on σ sites; step C. HYD is accounted for in a series of sequential hydrogenation steps; namely, F and G, on π sites and a final hydrogenolysis of C-S-C bond on σ sites; step J.^{26,27} Steps N to P were considered only for the model DBTBP2S where the hydrogenation of BP to CHB occurs as presented in step O. The global reaction represented in step 3 and the respective ν_3 are also exclusively for this model.

In general, the following assumptions were made: (i) an approximation to pseudo-equilibrium for adsorption and desorption steps; (ii) the concentration of hydrogen is constant during the reaction due to its large partial pressure. In consequence, H₂ concentration and sites β were lumped into the kinetic constant of the corresponding reaction rate; (iii) surface reactions are ratedetermining steps (RDS); (iv) the hydrogenolysis of THDBT and HHDBT are fast enough so as to be immediately desulfurized into cyclohexylbenzene and H₂S; and, (v) all products contribute to kinetic inhibition by competitive adsorption with dibenzothiophene. On the basis of these assumptions, the corresponding kinetic models can be written as follows:

DBT1S

$$r_{DBT,1} = -k_{DBTT,1}K_{DBT,*}C_{DBT}\theta_{*}$$
(4)
$$r_{DBT,2} = -k_{DBT,2}K_{DBT,*}C_{DBT}\theta_{*}$$
(5)

Where:

$$\theta_* = \frac{1}{1 + K_{DBT,*}C_{DBT} + K_{BP,*}C_{BP} + K_{CHB,*}C_{CHB} + K_{H_2S,*}C_{H_2S}}$$
(6)

DBT2S

$$r_{DBT,\sigma} = -k_{DBT,\sigma} K_{DBT,\sigma} C_{DBT} \theta_{\sigma}$$
(7)

$$r_{DBT,\pi} = -k_{DBT,\pi} K_{DBT,\pi} C_{DBT} \theta_{\pi} \qquad (8)$$

DBTBP2S

$$r_{DBT,\sigma} = -k_{DBT,\sigma} K_{DBT,\sigma} C_{DBT} \theta_{\sigma}$$
(9)
$$r_{DBT,\pi} = -k_{DBT,\pi} K_{DBT,\pi} C_{DBT} \theta_{\pi}$$
(10)
$$r_{BP,\pi} = -k_{BP,\pi} K_{BP,\pi} C_{BP} \theta_{\pi}$$
(11)

Where:

$$\theta_{\sigma} = \frac{1}{1 + K_{DBT,\sigma}C_{DBT} + K_{BP,\sigma}C_{BP} + K_{CHB,\sigma}C_{CHB} + K_{H_2S,\sigma}C_{H_2S}}$$
(12)
$$\theta_{\pi} = \frac{1}{1 + K_{DBT,\pi}C_{DBT} + K_{BP,\pi}C_{BP} + K_{CHB,\pi}C_{CHB} + K_{H_2S,\pi}C_{H_2S}}$$
(13)

Herein, k_i denotes the rate coefficient for the reaction *i*, $K_{n,j}$ correspond to the adsorption equilibrium coefficient for the component *n* on the site *j*, C_n the concentration for the component *n*, and θ_j denotes the fraction of free active sites *j*.

3.2. Hydrodesulfurization of dibenzothiophene simultaneous to the hydrogenation of aromatic compounds

After analyzing results that will be commented later (Section 3.1), the considerations proposed for the model DBTBP2S were used for the kinetic modeling of the hydrodesulfurization of dibenzothiophene simultaneous to the hydrogenation of aromatic compounds. Kinetic models were developed assuming that aromatic molecules and their reaction products react either only on π sites or on both π and σ sites. The reversibility of the hydrogenation of naphthalene, fluorene, and phenanthrene was considered for kinetic modeling. In what follows only the kinetic models that led to the best results are presented for the sake of brevity. Kinetic models describing the inhibiting effect on the simultaneous hydrodesulfurization of dibenzothiophene and hydrogenation of naphthalene, fluorene, and phenanthrene were named DBTNP, DBTFL, and DBTPHE, respectively. Kinetic expressions for each model were based on the mechanism of the HDS of DBT, i.e. Table 2, integrated with the mechanism of the respective hydrogenation of each aromatic molecule. In general, assumptions for the proposed models were based on both experimental results and literature review. The reader may refer to the Supporting Information (Section S1-S3) for data concerning other models tested in this work.

3.2.1. Hydrogenation of naphthalene simultaneous to the hydrodesulfurization of dibenzothiophene (DBTNP)

Scheme 2 (a) shows a simplified reaction network for naphthalene hydrogenation.^{49–51} In the presence of dibenzothiophene, the modeling of naphthalene hydrogenation was based on the following assumptions: (i) naphthalene is only hydrogenated to tetralin (TTL); (ii) naphthalene and tetralin competitively adsorb and react on both π and σ sites; and, (iii) naphthalene hydrogenation to tetralin is reversible. Table 3 presents the mechanism employed to describe naphthalene hydrogenated on σ sites: steps B and C, and on π sites: steps E and F. Finally, tetralin is desorbed: steps D and G.

The rate expressions considered for the simultaneous hydrodesulfurization of dibenzothiophene and hydrogenation of naphthalene were:

$$r_{DBTNP,\sigma} = -k_{DBT,\sigma} K_{DBT,\sigma} C_{DBT} \theta_{DBTNP,\sigma}$$
(14)

$$r_{DBTNP,\pi} = -k_{DBT,\pi} K_{DBT,\pi} C_{DBT} \theta_{DBTNP,\pi}$$
(15)

$$r_{BPNP,\pi} = -k_{BP,\pi} K_{BP,\pi} C_{BP} \theta_{DBTNP,\pi}$$
(16)

$$r_{NP,\sigma} = -(k_{NP,\sigma} K_{NP,\sigma} C_{NP} - k_{NP,\sigma} K_{TTL,\sigma} C_{TTL}) \theta_{DBTNP,\sigma}$$
(17)

$$r_{NP,\pi} = -(k_{NP,\pi}K_{NP,\pi}C_{NP} - k_{NP,\pi}K_{TTL,\pi}C_{TTL})\theta_{DBTNP,\pi}$$
(18)

Where, k_{NP} and k_{NP} are the reaction rate coefficients of the forward and backward of naphthalene hydrogenation. $K_{n,j}$ correspond to the adsorption equilibrium coefficient for the component *n* on the site *j*, and C_n the concentration for the component *n*.

From the above:

$$\theta_{DBTNP,\sigma} = \frac{1}{1 + K_{DBT,\sigma}C_{DBT} + K_{BP,\sigma}C_{BP} + K_{CHB,\sigma}C_{CHB} + K_{H_2S,\sigma}C_{H_2S} + K_{NP,\sigma}C_{NP} + K_{TTL,\sigma}C_{TTL}}$$
(19)

$$\theta_{DBTNP,\pi} = \frac{1}{1 + K_{DBT,\pi}C_{DBT} + K_{BP,\pi}C_{BP} + K_{CHB,\pi}C_{CHB} + K_{H_2S,\pi}C_{H_2S} + K_{NP,\pi}C_{NP} + K_{TTL,\pi}C_{TTL}}$$
(20)

Where, $\theta_{DBTNP,\sigma}$ and $\theta_{DBTNP,\pi}$ are the fraction coverage of vacant σ and π sites, respectively.

3.2.2. Hydrogenation of fluorene simultaneous to the hydrodesulfurization of dibenzothiophene (DBTFL)

A simplified hydrogenation network of fluorene based on the proposition by Lapinas et al.⁵² is presented in Scheme 2 (b). For the formulation of the kinetic model for fluorene hydrogenation in the presence of dibenzothiophene, the following assumptions were made: (i) only the hydrogenation of the first ring of fluorene to form 1, 2, 3, 4, 4a, 9a-hexahydrofluorene (HHFL) takes place; (ii) the hydrogenation of fluorene only occurs on π sites; and, (iii) the reversibility of the hydrogenation is neglected. Table 4 presents the mechanism to describe the hydrogenation of fluorene. Hydrogen and fluorene are adsorbed on β and π sites, respectively; steps A and B. Step C summarizes a series of sequential hydrogenation steps. Finally, on step D 1, 2, 3, 4, 4a, 9a-hexahydrofluo is desorbed.

The rate expressions for the simultaneous dibenzothiophene hydrodesulfurization and fluorene hydrogenation were thus described by the following equations:

$$r_{DBTFL,\sigma} = -k_{DBT,\sigma} K_{DBT,\sigma} C_{DBT} \theta_{DBTFL,\sigma}$$
(21)

$$r_{DBTFL,\pi} = -k_{DBT,\pi} K_{DBT,\pi} C_{DBT} \theta_{DBTFL,\pi}$$
(22)
$$r_{BPFL,\pi} = -k_{BP,\pi} K_{BP,\pi} C_{BP} \theta_{DBTFL,\pi}$$
(23)
$$r_{FL,\pi} = -k_{FL,\pi} K_{FL,\pi} C_{FL} \theta_{DBTFL,\pi}$$
(24)

Therefore:

$$\theta_{DBTFL,\sigma} = \frac{1}{1 + K_{DBT,\sigma}C_{DBT} + K_{BP,\sigma}C_{BP} + K_{CHB,\sigma}C_{CHB} + K_{H_2S,\sigma}C_{H_2S} + K_{FL,\sigma}C_{FL} + K_{HHFL,\sigma}C_{HHFL}}$$
(25)

 $\theta_{DBTFL,\pi}$

$$=\frac{1}{1+K_{DBT,\pi}C_{DBT}+K_{BP,\pi}C_{BP}+K_{CHB,\pi}C_{CHB}+K_{H_2S,\pi}C_{H_2S}+K_{FL,\pi}C_{FL}+K_{HHFL,\pi}C_{HHFL}}$$
(26)

Where, $\theta_{DBTFL,\sigma}$ and $\theta_{DBTFL,\pi}$ are the fraction coverage of vacant σ and π sites, respectively.

3.2.1. Hydrogenation of phenanthrene simultaneous to the hydrodesulfurization of dibenzothiophene (DBTPHE)

Phenanthrene is a polycyclic aromatic hydrocarbon composed of three fused aromatic rings. For the hydrogenation of phenanthrene different networks have been proposed in literature.^{39,53–56} Beltramone et al.³⁹ and Schachtl et al.⁵³ proposed two parallel pathways. The first route is the hydrogenation of phenanthrene to 9, 10-dihydrophenanthrene (DHPHE), and the second route is the hydrogenation of phenanthrene to 1, 2, 3, 4-tetrahydrophenanthrene (THPHE). Subsequently, DHPHE and THPHE are supposed to be hydrogenated to octahydrophenanthrene (1,8-OHPHE and 1,10-OHPHE) and thence to perhydrophenanthrene (PHPHE). Conversely, Ishihara et al.⁵⁴ proposed that phenanthrene is hydrogenated exclusively to DHPHE from where DHPHE is hydrogenated to THPHE and OHPHE, and finally to PHPHE. These two reaction networks are modeled herein but the network proposing two parallel pathways for the hydrogenation of phenanthrene in presence of dibenzothiophene led to a better fit of kinetic observations. The details for the other models evaluates are given in Section S3 of the Supporting Information. Thus, in what follows this reaction network and the corresponding kinetic model are presented. Scheme 2

(c) presents the reaction network for the hydrogenation of phenanthrene. 1.8octahydrophenanthrene and 1.10octahydrophenanthrene lumped were as octahydrophenanthrene. For the kinetic model, the following assumptions were made: (i) the hydrogenation of phenanthrene, 9, 10-dihydrophenanthrene, and 1, 2, 3, 4-tetrahydrophenanthrene only occur on π sites; and, (ii) the reversibility of the reactions is neglected. The corresponding reaction mechanism is shown in Table 5. Hydrogen and phenanthrene are assumed to adsorb on β and π sites, respectively: steps A and B. Steps C and D represent the hydrogenation of phenanthrene to 9, 10-dihydrophenanthrene and 1, 2, 3, 4-tetrahydrophenanthrene, respectively. The sequential hydrogenation to octahydrophenanthrene from 9, 10-dihydrophenanthrene and 1, 2, 3, 4-tetrahydrophenanthrene are representative in the steps E and F, respectively. Finally, desorption of products was represented by steps G to I.

The rate expressions for both the simultaneous hydrodesulfurization of dibenzothiophene and hydrogenation of phenanthrene are presented below:

$$r_{DBTPHE,\sigma} = -k_{DBT,\sigma}K_{DBT,\sigma}C_{DBT}\theta_{DBTPHE,\sigma}$$
(27)

$$r_{DBTPHE,\pi} = -k_{DBT,\pi}K_{DBT,\pi}C_{DBT}\theta_{DBTPHE,\pi}$$
(28)

$$r_{BPPHE,\pi} = -k_{BP,\pi}K_{BP,\pi}C_{BP}\theta_{DBTPHE,\pi}$$
(29)

$$r_{PHE-THPHE,\pi} = -k_{PHE-THPHE,\pi}K_{PHE,\pi}C_{PHE}\theta_{DBTPHE,\pi}$$
(30)

$$r_{PHE-DHPHE,\pi} = -k_{PHE-DHPHE,\pi}K_{PHE,\pi}C_{PHE}\theta_{DBTPHE,\pi}$$
(31)

$$r_{THPHE,\pi} = -k_{THPHE,\pi}K_{THPHE,\pi}C_{THPHE}\theta_{DBTPHE,\pi}$$
(32)

$$r_{DHPHE,\pi} = -k_{DHPHE,\pi}K_{DHPHE,\pi}C_{DHPHE}\theta_{DBTPHE,\pi}$$
(33)

Herein:

 $\theta_{DBTPHE,\sigma} =$

 $\overline{1 + K_{DBT,\sigma}C_{DBT} + K_{BP,\sigma}C_{BP} + K_{CHB,\sigma}C_{CHB} + K_{H_2S,\sigma}C_{H_2S} + K_{PHE,\sigma}C_{PHE} + K_{DHPHE,\sigma}C_{DHPHE} + K_{THPHE,\sigma}C_{THPHE} + K_{OHPHE,\sigma}C_{OHPHE} + K_{CHB,\sigma}C_{OHPHE} + K_{CH$

(34)

 $\frac{1}{1+K_{DBT,\pi}c_{DBT}+K_{BP,\pi}c_{BP}+K_{CHB,\pi}c_{CHB}+K_{H_2S,\pi}c_{H_2S}+K_{PHE,\pi}c_{PHE}+K_{DHPHE,\pi}c_{DHPHE}+K_{THPHE,\pi}c_{THPHE}+K_{OHPHE,\pi}c_{OHPHE}}$ (35)

Where, $\theta_{DBTPHE,\sigma}$ and $\theta_{DBTPHE,\pi}$ are the fraction of empty of σ and π sites, respectively.

3.3. Estimation of model parameters

Kinetic parameters were estimated by minimizing the objective function $RSS(\phi)$, which includes the residual sum of squares of the concentration of the different species:⁵⁷⁻⁵⁹

$$\operatorname{RSS}(\varphi) = \sum_{n=1}^{n_{resp}} w_n \sum_{k=1}^{n_{exp}} \left(F_{k,n} - \hat{F}_{k,n} \right)^2 \xrightarrow{\varphi_{1,},\varphi_{2,\dots,},\varphi_n} \min \quad (36)$$

Where φ is the optimal parameter vector, n_{exp} is the number of independent experiments, n_{resp} is the number of responses, $F_{k,n}$ and $\hat{F}_{k,n}$ are molar flows of the *n*-th experimental and predicted responses for the k-th observations, respectively. And, w_n is the weight factor assigned to the *n*-th response.

The subroutine VODE was used to solve the corresponding set of ordinary differential equations.⁶⁰ The initial minimization of the objective function, vide Eq. 36, in the model regression was carried out using the Rosenbrock method.⁶¹ Then the ODRPACK subroutines were called for fitting calculated values to the corresponding experimental data point.⁶² These subroutines can perform either weight orthogonal distance regression or nonlinear least square squares for explicit and implicit models using multi-response data with an implementation of the Levenberg-Marquard method.⁶³

The reparameterization of Arrhenius and van't Hoff expressions led to Eq. (37) and Eq. (38), respectively. The resulting parameters were used for the regression analysis. The activation energies and pre-exponential factors as well as the adsorption enthalpies and entropies were calculated from the parameter estimation procedure.

$$k_{i} = \exp\left[A_{i} - \frac{E_{A,i}}{R} \left(\frac{1}{T} - \frac{1}{T^{*}}\right)\right] \quad (37)$$
$$K_{n} = \exp\left[\frac{\Delta S_{n}^{0}}{R} - \frac{\Delta H_{n}^{0}}{R} \left(\frac{1}{T} - \frac{1}{T^{*}}\right)\right] \quad (38)$$

Where, for the *i*-th reaction, A_i is the natural logarithm of the pre-exponential factor, $E_{A,i}$ is the activation energy, *T* is the reaction temperature, T^* is the averaged reaction temperature, ΔS_n^0 is the standard adsorption entropy of component n, ΔH_n^0 is the standard adsorption enthalpy of component *n*, and R is the universal gas constant.

The significance of the overall regression for each model was tested after estimating the parameters of the model. This procedure was done by means of an F-test. The F-value for the global significance of the regression was defined as the ratio of the regression sum of squares to the residual sum of squares divided by their respective degrees of freedom. The significance of the individual parameters was evaluated by a *t*-test. Parity diagrams were also built to visualize the agreement between experimental observations and model fit.

3.4. Physicochemical tests on the parameters of the models

Typically, testing the fitting of the rate equation to the experimental data and calculating the confidence intervals of the estimated parameters should be enough when developing a kinetic model. However, this is not yet sufficient as for giving a physical meaning to the developed kinetic model. The kinetic and adsorption equilibrium constants contained in the rate expression need to be evaluated to verify whether they are physically reasonable and thermodynamically consistent. Boudart et al.⁶⁴ proposed several rules for evaluating kinetic parameters that are described next.

First, since adsorption is, with very few exceptions, exothermic, values for the estimated adsorption enthalpies must satisfy the inequality:

$$-\Delta H_n^0 > 0 \qquad (39)$$

Second, the adsorption entropy of the adsorbed species must be higher than zero and lower than the corresponding standard entropy of the corresponding species in the gas phase ($\Delta S_{n,g}^0$):

$$0 < \Delta S_n^0 < \Delta S_{n,g}^0 \qquad (40)$$

The following limits for the adsorption entropy must be met:

$$41.8 < -\Delta S_n^0 < 51.04 - 1.4\Delta H_n^0 \qquad (41)$$

Considering the above, the kinetic models developed in this work were tested as for their physical meaningfulness by using Boudart's criteria.

4. Results

4.1. Experimental evaluation

4.1.1. Hydrodesulfurization of dibenzothiophene in the absence and in the presence of aromatic compounds

Table 6 displays the conversion of dibenzothiophene and the selectivity to the reaction products as a function of space-time; $W_{cat}F_{DBT_0}^{-1}$. During the hydrodesulfurization of dibenzothiophene, only biphenyl and cyclohexylbenzene were detected. Partially hydrogenated intermediates; i.e. THDBT and HHDBT, of the HYD pathway were only observed as traces. As expected, the conversion of dibenzothiophene increased with space-time and the main reaction product was biphenyl.^{11,15,27} The selectivity to the DDS route, that is, the selectivity to biphenyl, decreased with space-time, whereas cyclohexylbenzene selectivity increased. This suggests that biphenyl was probably hydrogenated to cyclohexylbenzene, as has been mentioned by other authors.^{14,27,65}

The hydrodesulfurization of dibenzothiophene was studied in the presence of naphthalene, fluorene, and phenanthrene at the same space-time of dibenzothiophene, i.e. $122 W_{cat} F_{DBT_0}^{-1}$, but at different space-times for the aromatic compounds. The conversion of dibenzothiophene and the selectivity to biphenyl and cyclohexylbenzene were not significantly affected by the presence of naphthalene since the standard deviation calculated from these data was ca. 1.1 %. On the other hand, the conversion of dibenzothiophene decreased with the presence of fluorene and phenanthrene. For example, at 37 $W_{cat}F_0^{-1}$, dibenzothiophene conversion dropped from 70.8% to 58.6% and 50.7%, in the presence of fluorene and phenanthrene, respectively. On the other hand, the HYD pathway of the hydrodesulfurization of dibenzothiophene appeared diminished by fluorene, since the selectivity to biphenyl increased from ca. 86% to 89%. Whereas, phenanthrene seemed not to affect selectivity significantly. To this end, phenanthrene seems to inhibit DDS and HYD pathways to the same extent, while fluorene seems to inhibit the HYD route stronger than the DDS route.

4.1.2. Hydrogenation of naphthalene, fluorene, and phenanthrene in the absence and in the presence of dibenzothiophene

Besides analyzing dibenzothiophene reactivity in the presence of aromatics, it is also convenient to follow aromatics reactivity in the absence and in the presence of dibenzothiophene; Table 6 shows the corresponding results. In the absence of dibenzothiophene, aromatics conversion followed the order: $%C_{PHE} = 77 > %C_{NP} = 71.8 >> %C_{FL} = 12.7$. Therefore, fluorene exhibited a much lower hydrogenation activity than the other aromatics. The conversion of the aromatics was significantly affected by the presence of dibenzothiophene. The conversion of both naphthalene and phenanthrene dropped ca. 47% from the values observed in the absence of dibenzothiophene. On the other hand, the conversion of fluorene was affected more strongly as it dropped ca. 65%. The selectivity to phenanthrene products also varied in the presence of dibenzothiophene. THPHE and DHPHE, i.e. the products with one aromatic ring hydrogenated, increased their selectivity is ginificantly. Particularly, selectivity to THPHE increased from 19 to 38.8% whereas the selectivity to DHPHE increased from 28.1 to 39.9%. Meanwhile, the selectivity to OHPHE, the product with two hydrogenated aromatic rings, dropped ca. 60%. In conclusion, it

is evident that the hydrogenation of naphthalene, fluorene, and phenanthrene was strongly inhibited by the presence of dibenzothiophene which in turn affected the conversion and products distribution.

4.2. Kinetic modeling

4.2.1. Hydrodesulfurization of dibenzothiophene

Figure 1 depicts parity diagrams for the HDS of DBT over the NiMo/ γ -Al₂O₃ comparing the experimental with the calculated conversion of dibenzothiophene, and the yields of biphenyl and cyclohexylbenzene, for the three developed kinetic models: DBT1S, DBT2S, and DBTBP2S. The DBT1S model which assumes a single site for both HYD and DDS showed the worst fitting (Figure 1a). Conversely, the models assuming two different sites for the HYD and DDS pathways, DBT2S (Figure 1b) and DBTBP2S (Figure 1c), fitted adequately the experimental observations within an error margin lower than 10%. Between DBT2S and DBTBP2S, the latter fitted better the yield of cyclohexylbenzene. The global significance of the performed regressions for each model was assessed via calculation of the corresponding F-values. Although all models led to a statistically significant regression; i.e. F-value >> tabulated F-value ≈ 2.79 , DBTBP2S presented the largest F-value = 52317 which implies a closer fitting of the experimental data.

Considering the best fitting of the DBTBP2S model, the values calculated for its parameters are presented in Table 7 together with 95% probability confidence intervals and the corresponding *t*-values. In general, all parameters were found statistically significant. Furthermore, the values of adsorption enthalpies and adsorption entropies on both σ and π sites satisfied Boudart et al.⁶⁴ criteria, vide Eqs (39)-(41). Therefore, values of $-\Delta H_{i,\sigma}^0$ and $-\Delta H_{i,\pi}^0$ were indeed positive as well as $-\Delta S_{i,\sigma}^0$ and $-\Delta S_{i,\tau}^0$. The latter were also lower than the corresponding standard entropy of the gas phase species, i.e. they were below than 316, 384, and 205 J (mol K)⁻¹ for DBT, BP and H₂S, respectively. The second criterion for the adsorption entropy (Eq. 41) was also satisfied for values derived from the DBTBP2S model in all cases except for H₂S adsorption on π sites ($-\Delta S_{H_2S,\tau}^0$), probably due to poor adsorption of this compound on these sites. On the other hand, the activation energies obtained from the model were within the range proposed by Santaceraria⁶⁶, that is from 21 to about 210 kJ mol⁻¹. It is worth noting that activation energies lower than 21 kJ mol⁻¹ suggest the presence of external diffusion limitation, as values larger than 210 kJ mol⁻¹ are related to the existence of thermal gradients during the experimentation. To this end, activation energies obtained herein come from intrinsic kinetic observations rather than apparent ones.

4.2.2. Simultaneous HDS of DBT and hydrogenation of aromatics

For the kinetic models DBTNP, DBTFL, and DBTPHE both reactions are modeled simultaneous, i.e. the hydrodesulfurization of dibenzothiophene and the hydrogenation of respective aromatic compound. Considering that DBTBP2S was the model that better fitted the experimental results for the hydrodesulfurization of dibenzothiophene, was chosen as a basis for further kinetic analysis of the hydrodesulfurization of dibenzothiophene in the presence of the aromatic compounds. Figure 2 presents the reactions carried out in the presence of naphthalene, the DBTNP kinetic model was found to predict the subtle effect of naphthalene on the hydrodesulfurization of dibenzothiophene at studied space-times. The model was capable of fitting experimental observations with an error margin below 10%. Likewise, the models DBTFL and DBTPHE fitted adequately the experimental observation of the conversion of dibenzothiophene and product yields from the reaction in the presence of fluorene and phenanthrene as shown in the Figure 3 and Figure 4, respectively.

On the other hand, Figure 5 presents the experimental conversion of naphthalene, fluorene, and phenanthrene in the presence of dibenzothiophene compared to conversions predicted by the models DBTNP, DBTFL, and DBTPHE, respectively. The simulated conversions of fluorene appears not to satisfactorily close to observed values. However, it must be taken into account that the conversions of fluorene in the presence of dibenzothiophene are within the experimental error, i.e. ±5%. In general, the developed kinetic models also fitted the results for the hydrogenation of the studied aromatics. The particularly, F-values for the global significance of the regressions amounted to 15286, 252995, and 161765 for DBTNP, DBTFL, and DBTPHE respectively, thus evidencing a suitable statistical significance of these regressions. Values for the parameters of dibenzothiophene and its reaction products corresponding to the reactions under the presence of naphthalene, phenanthrene, and fluorine are also presented in Table 7. Tables 8 to 10 present the kinetic parameters related to the studied aromatic compounds and its reaction products. The DBTNP and DBTFL models led to statistically significant regressions, vide Table 8 and Table 9, respectively, since all parameters presented narrow confidence intervals and *t*-values larger than the tabulated *t*-values. The parameters estimated for the DBTPHE model, their corresponding 95% confidence intervals, and the calculated *t*-value are shown in Table 10. The thermodynamic consistency of these parameters was also verified except for those related to the production and adsorption of OHPHE. This behavior typically stems from a relatively weak chemisorption of the molecule in comparison to other compounds.⁵⁹

5. Discussion

5.1. Kinetics of the hydrodesulfurization of dibenzothiophene

Comparison of the kinetic model presented herein with previous works

Though the hydrodesulfurization of dibenzothiophene has been thoroughly studied in the past,^{10,67} the majority of kinetic studies have oversimplified the modeling using mainly pseudo-first-order rate equations.^{11,16,19,33,68} This approach is capable to fit well the experimental

observations. However, pseudo-first-order rate equations do not take into consideration elementary steps for the reaction mechanism and do not provide a description of the adsorption/desorption reactions for the different species on the catalyst.^{69,70} In order to understand the catalytic surface reactions for the hydrodesulfurization of dibenzothiophene, some mechanisms have been evaluated using Langmuir-Hinshelwood-Hougen-Watson (LHHW) model as shown in Table 11. Singhal et al.¹⁴ and Vrinat¹⁸ modeled the hydrodesulfurization of dibenzothiophene considering that the DDS and HYD pathways take place on the same catalytic site whereas Broderick et al.²⁶ and Vanrysselberghe et al.²⁷ assumed that the sites involved in hydrogenation and desulfurization are different. All of them, using one or two sites for the adsorption of dibenzothiophene and its products on the catalyst gave a good fit to the experimental data. Nevertheless, most of these kinetic model lack of a proper statistical and phenomenological analysis of the model itself and of the estimated kinetic parameters. Kinetic parameters should be not only capable to represent adequately the occurred physicochemical phenomena but also exhibit statistical significance and thermodynamic consistency.⁴⁴

Nature of the active sites

As already discussed in the results section, among the three kinetic models developed in this work, only those considering two active sites: one for hydrogenolysis and the other for hydrogenation, were able to properly describe experimental results. Few kinetic models for the hydrodesulfurization of dibenzothiophene have been developed assuming two different sites for the adsorption of DBT and its products.^{25–27} Nevertheless, several theoretical studies and DFT calculations have been carried out in the last years aiming to elucidate the atomic structure and nature of the active sites of hydrotreatment catalysts.^{24,71–74} Most authors accept that coordinately unsaturated sites (CUS) (sulfur vacancy sites) at the edges and corners of the catalyst play an

important role for the DDS route. These sites can be considered as equivalent to the σ sites included in the kinetic models developed herein. In this respect, the molybdenum sulfide (MoS_2) particles expose two types of edges: Mo-edge and S-edge. Under typical sulfidation conditions, nickel atoms might replace the molybdenum atoms from the Mo-edge to form the so-called NiMoS phase and, hence, promote the formation of CUS at the edges and corners due to the reduction of the sulfur binding energy.^{75,76} The desulfurization of DBTs via DDS preferably takes place on vacancies at corner sites via perpendicular adsorption through the sulfur atom.^{20,24,75,77} On the other hand, the nature of the sites for the HYD pathway is yet unclarified. Topsøe and coworkers^{22–24,73}, based on scanning tunneling microscopy (STM) images of the top of MoS₂ and CoMoS slabs, proposed that so-called *brim sites* are involved in hydrogenation reactions. Such sites can be assimilated to as the π sites of the kinetic models presented in this contribution. *Brim sites* are modeled as bridge sites presenting a metallic character and located at the cluster top, perimeter sites along the cluster edges. They are not sterically hindered as the adsorption of aromatic molecules does not require the formation of sulfur vacancies.^{78,79} As expected, on *brim sites* the adsorption of H₂S is negligibly weak, explaining the low inhibition effect of H₂S on HYD pathway.⁷⁸ Moreover, it is often theorized that aromatics adsorb flat on hydrogenation sites. Therefore, π -flat adsorption of dibenzothiophene and of other aromatic structure is feasible on brim sites. Considering the above arguments, the results obtained in this work can be interpreted considering that dibenzothiophene would preferably be adsorbed on corner CUS sites of a mixed NiMoS phase. Experimental evidence shows that in these sites,⁸⁰ the sulfur atom from dibenzothiophene might replace the sulfur atom from the CUS hence leading to direct hydrogenolysis for producing biphenyl. Furthermore, and provided the strongest kinetic viability of the model including the subsequent hydrogenation of biphenyl to cyclohexylbenzene, the former

product should re-adsorb on *brim sites*. On the other hand, the HYD route might be accounted to proceed via the adsorption of dibenzothiophene in a π -flat bonding between the benzene ring and the *brim site*, where partially hydrogenated intermediates are to be produced. These intermediates would desorb to react on CUS sites to further C-S-C bond scission. This proposition is summarized in Scheme 3. It is interesting to remark that the mechanism postulated herein resembles previous considerations for the reactivity of dibenzothiophene over noble metal based catalysts.^{37,46,81}

Considerations about the reaction mechanism

Given the scarcity of literature reports dealing with kinetic studies over NiMo catalysts, it was necessary to qualitatively compare the present results with reports for CoMo catalysts^{26,27} and with theoretical studies performed via molecular simulation^{24,72,74,78,79} According to Table 7, activation energies for dibenzothiophene on σ and π sites and of its DDS product over π sites followed the trend: $Ea_{BP,\pi} > Ea_{DBT,\pi} \gg Ea_{DBT,\sigma}$. This trend is in good agreement with literature reports, vide Table 11. As an exception, Broderick et al.²⁶ found that $Ea_{DBT,\sigma} > Ea_{DBT,\pi}$. However, their report may be criticized because they raised the denominator of their rate expression for hydrogenolysis to the square without providing a justification. Furthermore, these authors did not check their results for thermodynamic consistency. The order found for activation energies coincides with the high selectivity of NiMo sulfides to the DDS route. In addition, the highest value found for $Ea_{BP,\pi}$ also agrees with the experimental evidence on the low rate of the hydrogenation of biphenyl to cyclohexylbenzene. Theoretical studies have determined that this reaction is hindered by the fact that the two phenyl rings of biphenyl are not coplanar making difficult its adsorption on π sites.⁶⁵

On the other hand, calculated entropy values (Table 7) suggest that the mobility of dibenzothiophene on σ sites is greater than on π sites. Conversely, biphenyl, cyclohexylbenzene, and H₂S might present a higher mobility on π sites. Rangarajan et al.⁷⁸, using density functional

theory for evaluating the adsorption of different hydrocarbons on a CoMoS formulation, reported an apparent opposite result to the obtained herein, i.e. DBT and its alkyl-substituted aromatics presented a larger entropy when adsorbed on *brim sites* than on CUS. Nevertheless, the authors did not probe the adsorption of dibenzothiophene on a CUS located in corner sites. In fact, in a later work, these authors⁷⁴ considered the adsorption of dibenzothiophene on these corner type sites, suggesting that the C-S bond scission is rather more feasible to occur on these sites. Tuxen et al.²⁴ carried out a similar study but using scanning tunneling microscopy to investigate the atomic-scale adsorption of DBT and 4,6-DMDBT on MoS₂ and CoMoS nanoclusters. These authors, based on chemisorption calculations, elucidated also the preference of DBT to adsorb on corner type-sites. According to Ding et al.⁷⁶, the Co atom on a corner exhibits a square planar coordinated structure with four sulfur atoms, which allow for the high mobility of dibenzothiophene and the high hydrogenolysis activity. Given the values of entropy calculated herein, the same kind of explanation could apply to Ni promoted sulfides.

Concerning the calculated values for adsorption enthalpies, Yang et al.⁸² observed that a flat π -bonding on sites related to HYD route leads to larger values of this thermodynamic parameter as compared to the perpendicular adsorption of on σ sites. The authors related this observation to the type of interactions established between the sulfur atom (η 1S), thiophene (η 5), and the aromatic rings (η 6) of dibenzothiophene with the corresponding active sites of the catalyst. It is worth stressing that these theoretical analyses are in agreement with our calculated values, which indicate that adsorption enthalpy of dibenzothiophene is larger on π hydrogenation sites than on σ hydrogenolysis sites. To this respect, the adsorption enthalpy for dibenzothiophene on π and σ sites reported in the literature are according with values estimated here.^{26–28} For biphenyl, unlike as for cyclohexylbenzene, it was found that this product adsorbs more strongly on π sites; - Δ H⁰_{BP, π}=49.9

kJ mol⁻¹. Literature reports for adsorption enthalpies of biphenyl over hydrodesulfurization catalysts range from 38 to 50 kJ mol⁻¹.^{27,28} For cyclohexylbenzene, the relatively low values of adsorption enthalpy on π sites point to a high mobility under the conditions of the reaction atmosphere. Unfortunately, values derived from the present study could not be compared to theoretical or experimental data from literature, since they were not found in the literature survey.

Finally, in regards to H_2S , values calculated for its adsorption entropy and enthalpy on σ sites, 168 J (mol K)⁻¹ and 144 kJ mol⁻¹, respectively, were in a good agreement with literature.^{27,51,59} Furthermore, it has been postulated ^{11,16,72,83,84} that this compound selectively inhibits σ sites. In contrast, a low value of enthalpy; 1.25 kJ mol⁻¹, was found for the adsorption H₂S on π sites suggesting a weak adsorption on *brim sites*. In this sense, Lauritsen et al.⁷²; using high-resolution STM studies on hydrotreating HDS model systems, claimed that H₂S does not compete for adsorption on *brim sites*. Additionally, other reports^{11,16,83} have presented evidence of an increment of the selectivity to partially hydrogenated intermediates of DBT and 4,6 DMDBT with the partial pressure of H₂S. This agrees with the mechanism proposed for the hydrodesulfurization of dibenzothiophene in Table 2. On the HYD pathway the molecules are first hydrogenated on π sites and then moved to a σ sites to the C-S bond scission. Therefore, H₂S inhibits both the DDS pathway and the final desulfurization step in the HYD pathway, generating the increase of the concentration of partially hydrogenated intermediates of DBTs. Thermodynamic calculations performed from the kinetic modeling of this contribution are deemed relevant to developing a better understanding of the mechanism of hydrodesulfurization.

5.2. Kinetics of the hydrodesulfurization of dibenzothiophene and hydrogenation of aromatics

5.2.1. Simultaneous hydrodesulfurization of dibenzothiophene and hydrogenation of naphthalene

Reactivity of dibenzothiophene and naphthalene

Results showed that the presence of naphthalene did not modify the reactivity of dibenzothiophene over the tested sulfided NiMo/ γ -Al₂O₃ catalyst. However, the conversion of naphthalene significantly drop with the presence of dibenzothiophene. From the different models evaluated for the simultaneous hydrodesulfurization of dibenzothiophene and hydrogenation of naphthalene, the one assuming that the hydrogenation of naphthalene can be carried out on both σ and π sites showed the best fitting of the experimental data. In this regard, the fact that hydrodesulfurization selectivity was not affected suggests that naphthalene does not have a preferential site to adsorb. Considering the latter, the values of Arrhenius and van't Hoff parameters for the selected kinetic model were fixed for dibenzothiophene and its reaction products, vide Table 7, whereas the corresponding values for naphthalene and tetralin were estimated from the model, vide Table 8. In this instance, the calculated values for entropy indicate that naphthalene and tetralin might present more mobility on π sites than on σ sites. Conversely, entropy values for tetralin suggest a larger mobility of this compound as compared to naphthalene at both types of active sites. Such a result is reasonable considering their difference on either their aromaticity. The resonance energy of the aromatic ring is greater in tetralin than in naphthalene.^{50,85} On the other hand, the adsorption enthalpy of naphthalene and tetralin on π sites was found larger than on σ sites. This might be related to the fact that the π -flat adsorption of naphthalene and tetralin on π sites involves multipoint interactions so adsorption would be stronger than on σ sites where n6 is theorized to occur.⁵⁰ Though under the reaction conditions of this work, no significant impact of naphthalene on the hydrodesulfurization of dibenzothiophene was remarked, other authors have reported otherwise. Egorova et al.⁴⁰ investigated the inhibition effect of naphthalene on the hydrodesulfurization of DBT and 4,6 DMDBT, and found that naphthalene may inhibit the

hydrodesulfurization of DBT and 4,6 DMDBT but under conditions in which both the DDS and the HYD pathways were affected to the same extent. Consequently, these authors proposed that the hydrogenation of naphthalene occurred on both DDS and HYD sites. Conversely, Egorova et al.⁴⁰ also reported that the hydrogenation of naphthalene was inhibited by the presence of both organo-sulfur compounds.

Considerations about the reaction mechanism DBTNP

Some studies have elucidated how hydrogenation of small molecules such as naphthalene may take place on more than one type of catalytic sites. Gutiérrez et al.⁸⁶ proposed that the size of the molecules should dictate their accessibility to hydrogenolysis CUS sites. They speculated that the hydrogenation of *o*-propylaniline, a molecule with a single aromatic ring, occurs on both CUS and *brim sites* in view of their weak effect on the selectivities of hydrodenitrogenation and hydrodesulfurization reactions. Moreover, other authors have associated CUS sites not only with hydrogenolysis but also with hydrogenation reactions.^{51,87} Kinetic studies published^{38,49,51,88,89} for the hydrogenation of naphthalene in the absence and presence of other compounds assumed that naphthalene is only adsorbed and hydrogenated on one type of active sites. Cortés et al.⁵¹ developed a LHHW kinetic model for the hydrogenation of naphthalene over a NiMo/γ-Al₂O₃ assuming that the chemisorption of naphthalene and tetralin only occurred on CUS sites. Since there is a lack of information related to kinetic parameters on *brim sites*, a proper comparison of our results with those from literature is not carried out, however, our results are in agreement with those reported elsewhere.^{50,51,88}

5.2.2. Simultaneous hydrodesulfurization of dibenzothiophene and hydrogenation of fluorene

Reactivity of dibenzothiophene and fluorene

The presence of fluorene affected the conversion of dibenzothiophene and mainly inhibited the HYD pathway during the hydrodesulfurization reaction. There are few reports on this effect in open literature. Koltai et al.³⁴ reported that among the aromatic compounds: anthracene, phenanthrene, and fluorene, the latter had the strongest inhibiting effect on the transformation of 4,6 DMDBT. The authors ascribed this trend to the structural similarity between 4,6 DMDBT and fluorene. Unlike DBT 4,6 DMDBT principally reacts via HYD route. They argued that both molecules adsorbed in the same manner over the catalytic active sites, remarking a preference for hydrogenation sites. On the other hand, the very low conversion of fluorene compared with the other aromatic compounds was also reported by Koltai et al.³⁴

Considerations about the reaction mechanism DBTFL

The kinetic model proposed in this work effectively accounted for the effect of fluorene on dibenzothiophene reactivity. Furthermore, results from the model justify the assumption that fluorene and its partially hydrogenated product: hexahydrofluorene, adsorb on both π and σ sites but that fluorene hydrogenation can only be carried out on π sites. On the other hand, the activation energy for the hydrogenation of fluorene amounted to 78 kJ mol⁻¹; a value similar to the one reported by Lapinas et al.⁵² using a NiW/Al₂O₃. The chemisorption entropies indicate that fluorene, like dibenzothiophene, has higher mobility on σ sites than on π sites. The low conversion observed for fluorene is related the strong adsorption of this molecule on σ sites since here it cannot be hydrogenated. Besides, HHFL presents a higher chemisorption enthalpy on π sites than on σ sites, indicating that HHFL produced on π sites mainly contributes to the inhibition of hydrodesulfurization of dibenzothiophene on these sites.

5.2.3. Simultaneous hydrodesulfurization of dibenzothiophene and hydrogenation of phenanthrene

Reactivity of dibenzothiophene and phenanthrene

Phenanthrene had the strongest inhibition effect on dibenzothiophene hydrodesulfurization. In addition, this molecule affected both the DDS and the HYD pathways to the same extent. As in the case of the other aromatics, phenanthrene conversion was also inhibited by dibenzothiophene. The hydrogenation of phenanthrene has been studied by several authors and different reactions networks have been proposed.^{53–56} The product distribution during for the hydrogenation of phenanthrene in the absence of dibenzothiophene obtained herein was similar to that reported in the literature.^{53,56} Particularly, a high production of aromatics with two hydrogenated aromatic rings were detected, namely, 1,8-OHPHE and 1,10-OHPHE. Schachtl et al.⁵³ reported similar results for Ni promoted MoS₂/ γ -Al₂O₃ catalysts. Authors found that Ni favored the adsorption of phenanthrene leading to its deep hydrogenation and producing mainly 1.8-OHPHE and 1,10-OHPHE. On the other hand, the addition of dibenzothiophene to the reaction feed both decreased conversion and shifted selectivity to less OHPHE and more DHPHE and THPHE. The increase, particularly in the selectivity to THPHE, is according with Schachtl et al.⁵³ that suggested that the hydrogenation of the two aromatic rings of phenanthrene essentially occurred via the THPHE intermediate.

Considerations about the reaction mechanism DBTPHE

The kinetic model that best fitted the experimental values for the hydrodesulfurization of dibenzothiophene and hydrogenation of phenanthrene, assumed that both phenanthrene and its reaction products adsorb on both σ and π sites, but only react on π sites. The adsorption entropies of phenanthrene and its reaction products (Table 10) elucidated that aromatic molecules have a higher mobility on π sites than on σ sites. At π sites, the molecule mobility increased as the molecule became hydrogenated: PHE ($-\Delta S^{0}_{PHE,\pi}=81.7 \text{ J} \pmod{K}^{-1}$) < DHPHE ($-\Delta S^{0}_{DHPHE,\pi}=52.3 \text{ J} \pmod{K}^{-1}$). On the other hand, chemisorption enthalpy

of phenanthrene is similar on σ sites (93.2 kJ mol⁻¹) and π sites (91.6 kJ mol⁻¹), a result that is in agreement with the inhibition effect of this molecule during the hydrodesulfurization of dibenzothiophene where the selectivity to HYD and DDS pathways are affected in the same extend. According to results though, phenanthrene would only be hydrogenated on π sites, probably because the π sites are clearly less sterically hindered.⁷² Regarding the enthalpies for the primary products on π sites, THPHE showed a higher value than DHPHE. However, on σ sites results were in contraposition since the chemisorption enthalpy for DHPHE was higher than that found for THPHE. Concerning σ sites, the geometrical configuration of the aromatic rings of phenathrene dictate their accessibility. DHPHE and THPHE present their aromatic ring different positions, thus, according to Beltramone et al.³⁹ the central ring of the THPHE presents a steric constraint that limits its adsorption. This might be related to the larger adsorption enthalpy of DHPHE than of THPHE on σ sites. Finally, it is worth mentioning that the chemisorption enthalpy of OHPHE is not statistically significant, so a discussion on this parameter is not now possible. This statistical insignificance might be related to the lumping procedure carried out here, i.e. 1,8-OHPHE and 1,10-OHPHE were lumped as OHPHE.

6. Conclusions

A rigorous kinetic study of the hydrodesulfurization of dibenzothiophene was undertaken over NiMo/γ-Al₂O₃ catalysts, in the absence and in the presence of aromatic compounds with different chemical structures: naphthalene, phenanthrene, and fluorene. Among three proposed models for the hydrodesulfurization of dibenzothiophene in the absence of the aromatics, the one considering two different types of active sites, one for hydrogenation and the other for C-S-C bond scission, and considering the subsequent hydrogenation of biphenyl to cyclohexylbenzene was found to fit best observations. Furthermore, the developed model presented both physicochemical and

statistical significance. With respect to the nature of the HYD and DDS mechanisms, σ and π sites proposed in this work for carrying out the hydrogenolysis and hydrogenation reactions, present a large correlation with the active sites suggested for theoretical studies, CUS and *brim sites*, respectively. DDS pathway mainly take place on CUS sites whereas in a HYD pathway the molecules is first hydrogenated on the *brim sites* and then moved to a CUS site for the hydrogenolysis of C-S-C bond. The weak chemisorption of H₂S on π sites is according with the theoretical hypothesis that the adsorption of H₂S does not occur on the *brim sites*, but only on the CUS sites, inhibiting mainly the hydrogenolysis reaction.

The inhibition effect of the polyaromatic compounds on the hydrodesulfurization of dibenzothiophene is related to the size of the molecule. Phenanthrene was the molecule that most affected the conversion of dibenzothiophene, and naphthalene which affected it the least. However, regardless of size, both molecules do not have a preference for being adsorbed at a specific site, inhibiting to the same extent DDS and HYD pathways. The trend of fluorene to inhibit principally the HYD pathway is not correlated to the size but to the structure and geometry of the molecule. The similarity between dibenzothiophene and fluorene suggests the two molecules are adsorbed in the same manner on the hydrogenation sites, i.e. *brim sites*.

As concerned to the hydrogenation of the aromatics, the compounds are adsorbed on σ and π sites. However, the size of the molecules dictates their accessibility to σ sites to be hydrogenated. The kinetic models that best represent the experimental observation of the simultaneous hydrodesulfurization of dibenzothiophene and hydrogenation of aromatic compounds, proposed that naphthalene is hydrogenated on σ and π sites, whereas fluorene and phenanthrene are hydrogenated only on π sites.

Nomenclature

Roman letters

$A_{i}^{'}$	natural logarithm of pre-exponential factor, mm (g h) ⁻¹
C_n	conversion of component n , %
E_A	activation energy, kJ mol ⁻¹
F_n^0	inlet molar flow rate of the component <i>n</i> , mmol h^{-1}
F_n	molar flow rate of the component <i>n</i> , mmol h^{-1}
k_n	reaction rate coefficients of the forward, dep.
k_n^{i}	reaction rate coefficient of the backward, dep.
r_n	specific reaction rate of reaction <i>n</i> , mmol $(g h)^{-1}$
R	universal gas constant, kJ (mol K) ⁻¹
RSS	objective function
S_n	selectivity of component $n, \%$
T	temperature, K
Y_n	yield of component <i>n</i> , %
Wn	objective function weight factor of each response
W	mass of catalysts, g

Greek letters

*	active sites for the hydrogenation and hydrogenolysis reactions
β	active sites for the H ₂ adsorption
ΔH_n^0	standard enthalpy of adsorption for component n , kJ (mol K) ⁻¹
ΔS_n^0	standard entropy of adsorption for component n , J (mol K) ⁻¹
arphi	vector of parameters accounted for in the objective function
π	active sites for the hydrogenation reactions
σ	active sites for the hydrogenolysis reactions
$ heta_i$	fraction coverage of vacant of <i>i</i> site
v_{j}	Horiuti number
-	

Subscripts

cat	Catalyst
exp	experiment
g	gas phase
n	component <i>n</i>
obs	Observed
tab	Tabulated

Superscripts

\wedge	Calculated		
0	inlet, standard		

AUTHOR INFORMATION

Corresponding Author

Email for C.O.C.A: coca@xanum.uam.mx

Email for V.G.B.M: vicbaldo@uis.edu.co

ORCID 💿

Edgar M. Morales-Valencia: 0000-0003-3401-2811

Carlos O. Castillo-Araiza: 0000-0001-8719-0473

Víctor G. Baldovino Medrano: 0000-0003-3227-0251

Notes

The authors declare no competing financial interest.

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Table Captions

Table 1. Reaction mechanism and catalytic cycles for the kinetic model DBT1S.

Table 2. Reaction mechanism and catalytic cycles for the kinetic models DBT2S and DBTBP2S.

Table 3. Reaction mechanism and catalytic cycles for the kinetic model DBTNP to describe the hydrogenation of NP.

Table 4. Reaction mechanism and catalytic cycles for the kinetic model DBTFL to describe the hydrogenation of FL.

Table 5. Reaction mechanism and catalytic cycles for the kinetic model DBTPHE to describe the hydrogenation of PHE.

Table 6. Conversion and selectivity observed at different conditions and obtained evaluating the conversion of DBT or aromatic compound individually or in blend.^a

Table 7. Kinetic parameters values and corresponding 95% probability confidence intervals for the kinetic model DBTBP2S used to describe the HDS of DBT.

Table 8. Kinetic parameters values and corresponding 95% probability confidence intervals for the kinetic model DBTNP used to describe the HDS of DBT and hydrogenation of NP.

Table 9. Kinetic parameters values and corresponding 95% probability confidence intervals for the kinetic model DBTFL used to describe the HDS of DBT and hydrogenation of FL.

Table 10. Kinetic parameters values and corresponding 95% probability confidence intervals for the kinetic model DBTPHE used to describe the HDS of DBT and hydrogenation of PHE.

 Table 11. Kinetic expressions for dibenzothiophene hydrodesulfurization based on Langmuir-Hinshelwood-Hougen-Watson approach.

C4 am	Mashanian		
Step	Wechanism	<i>v</i> ₁	v_2
A	$H_2 + 2\beta \leftrightarrow 2H\beta$	2	5
В	$DBT + * \leftrightarrow DBT *$	1	1
C	$DBT * + 3H\beta \rightarrow BP * + SH\beta + 2\beta$	1	0
D	$BP * \leftrightarrow BP + *$	1	0
E	$DBT * + 4H\beta \rightarrow THDBT * + 4\beta$	0	1
F	$THDBT * + 2H\beta \leftrightarrow HHDBT * + 2\beta$	0	1
G	$HHDBT * + 3H\beta \rightarrow CHB * + SH\beta + 2\beta$	0	1
Н	$CHB * \leftrightarrow CHB + *$	0	1
Ι	$SH\beta + H\beta \leftrightarrow H_2S\beta + \beta$	1	1
J	$H_2 S\beta \leftrightarrow H_2 S + \beta$	1	1
	Global Reactions		
1	$DBT + 2H_2 \rightarrow BP + H_2S$	1	0
2	$DBT + 5H_2 \rightarrow CHB + H_2S$	0	1

Table 1. Reaction mechanism and catalytic cycles for the kinetic model DBT1S.

Step	Mechanism	<i>v</i> ₁	v_2	v_3
А	$H_2 + 2\beta \leftrightarrow 2H\beta$	2	5	3
В	$DBT + \sigma \leftrightarrow DBT\sigma$	1	0	0
С	$DBT\sigma + 3H\beta \rightarrow BP\sigma + SH\beta + 2\beta$	1	0	0
D	$BP\sigma \leftrightarrow BP + \sigma$	1	0	0
E	$DBT + \pi \leftrightarrow DBT\pi$	0	1	0
F	$DBT\pi + 4H\beta \rightarrow THDBT\pi + 4\beta$	0	1	0
G	$THDBT\pi + 2H\beta \leftrightarrow HHDBT\pi + 2\beta$	0	1	0
Н	$HHDBT\pi \leftrightarrow HHDBT + \pi$	0	1	0
Ι	$HHDBT + \sigma \leftrightarrow HHDBT\sigma$	0	1	0
J	$HHDBT\sigma + 3H\beta \rightarrow CHB\sigma + SH\beta + 2\beta$	0	1	0
K	$CHB\sigma \leftrightarrow CHB + \sigma$	0	1	0
L	$SH\beta + H\beta \leftrightarrow H_2S\beta + \beta$	1	1	0
М	$H_2S\beta \leftrightarrow H_2S + \beta$	1	1	0
N	$BP + \pi \leftrightarrow BP\pi$	0	0	1
0	$BP\pi + 6H\beta \leftrightarrow CHB\pi + 6\beta$	0	0	1
Р	$CHB\pi \leftrightarrow CHB + \pi$	0	0	1
	Global Reactions			
1	$DBT + 2H_2 \rightarrow BP + H_2S$	1	0	0
2	$DBT + 5H_2 \rightarrow CHB + H_2S$	0	1	0
3ª	$BP + 3H_2 \rightarrow CHB$	0	0	1

Table 2. Reaction mechanism and catalytic cycles for the kinetic models DBT2S andDBTBP2S.

^aThe global reaction 3 and the respective v_3 are exclusively for DBTBP2S model.

Table 3.	Reaction	mechanism	and	catalytic	cycles	for th	e kinetic	model	DBTNP	to	describe
the hydr	ogenatior	ı of NP.									

Sten	Mechanism	12.	11-
Step	Wittenamsin	<i>v</i> ₁	<i>v</i> ₂
А	$H_2 + 2\beta \leftrightarrow 2H\beta$	2	2
В	$NP + \sigma \leftrightarrow NP\sigma$	1	0
С	$NP\sigma + 4H\beta \leftrightarrow TTL\sigma + 4\beta$	1	0
D	$TTL\sigma \leftrightarrow TTL + \sigma$	1	0
E	$NP + \pi \leftrightarrow NP\pi$	0	1
F	$NP\pi + 4H\beta \leftrightarrow TTL\pi + 4\beta$	0	1
G	$TTL\pi \leftrightarrow TTL + \pi$	0	1
	Global Reactions		
1	$NP + 2H_2 \leftrightarrow TTL$	1	1

Table 4. Reaction mechanism and catalytic cycles for the kinetic model DBTFL to describethe hydrogenation of FL.

Step	Mechanism	<i>v</i> ₁
Α	$H_2 + 2\beta \leftrightarrow 2H\beta$	3
В	$FL + \pi \leftrightarrow FL\pi$	1
С	$FL\pi + 6H\beta \leftrightarrow HHFL\pi + 6\beta$	1
D	$HHFL\pi \leftrightarrow HHFL + \pi$	1
	Global Reactions	
1	$FL + 3H_2 \rightarrow HHFL$	1

Table 5. Reaction mechanism and	nd catalytic cycles for the kinetic	c model DBTPHE to describe
the hydrogenation of PHE.		

Step	Mechanism	v_1	v_2	v_3	v_4
А	$H_2 + 2\beta \leftrightarrow 2H\beta$	1	2	3	2
В	$PHE + \pi \leftrightarrow PHE\pi$	1	1	0	0
С	$PHE\pi + 2H\beta \rightarrow DHPHE\pi + 2\beta$	1	0	0	0
D	$PHE\pi + 4H\beta \rightarrow THPHE\pi + 4\beta$	0	1	0	0
E	$DHPHE\pi + 6H\beta \rightarrow OHPHE\pi + 6\beta$	0	0	1	0
F	$THPHE\pi + 4H\beta \rightarrow OHPHE\pi + 4\beta$	0	0	0	1
G	$DHPHE\pi \leftrightarrow DHPHE + \pi$	1	0	0	0
Н	$THPHE\pi \leftrightarrow THPHE + \pi$	0	1	0	0
Ι	$OHPHE\pi \leftrightarrow OHPHE + \pi$	0	0	1	1
	Global Reactions				
1	$PHE + H_2 \rightarrow DHPHE$	1	0	0	0
2	$PHE + 2H_2 \rightarrow THPHE$	0	1	0	0
3	$DHPHE + 3H_2 \rightarrow OHPHE$	0	0	1	0
4	$THPHE + 2H_2 \rightarrow OHPHE$	0	0	0	1

 Table 6. Conversion and selectivity observed at different conditions and obtained evaluating

 the conversion of DBT or aromatic compound individually or in blend.^a

Feed	WCatal Fo ⁻¹	%Срвт	%Selectivity to DBT products		%CNP	%Сы	%Сриг	%Selectivity to PHE products		
	VV Catal. I 0	/000b1 <u>-</u>	%Sbp	%Schb		/ UCIE	/ CT IIE	%Sthphe	%Sdhphe	%Ѕонрне
	46	33.4	87.9	12.1						
NDT	91	57.9	87.5	12.5						
DDI	122	70.8	86.1	13.9						
	182	88.7	85.1	14.9						
NP	56				71.8					
FL	73					12.7				
PHE	73						77.0	19.0	28.1	52.9
DDT+ND ^b	56	72.2	86.7	13.3	38.1					
	28	70.1	86.5	13.5	29.2					
DDT+FI b	73	65.3	89.3	10.7		4.5				
DDITL	37	58.6	89.1	10.9		3.4				
DBT_PHE ^b	73	56.8	86.3	13.7			42.6	38.8	39.9	21.2
DDITIE	37	50.7	85.9	14.1			36.4	41.7	40.6	17.6

^{*a*} Reaction conditions: T=300°C, P=5 MPa, liquid-flow rate of 30 mL \cdot h⁻¹ and H₂/liquid feed ratio of 500.

^b The $W_{cat}F_0^{-1}$ is respect of the aromatic compound. $W_{Catal}F_{DBT_0}^{-1}$ is constant and equal to 122 $kg_{cat}kmol_{DBT}^{-1}h$.

Table 7. Kinetic parameters values and corresponding 95% probability confidence intervalsfor the kinetic model DBTBP2S used to describe the HDS of DBT.

Parameter	Estimated value	Lower limit	Upper limit	<i>t</i> -value
A _{DBT,σ} mmol (g h) ⁻¹	5.56E-01	5.52E-01	5.61E-01	2.51E+02
Adbt, a mmol (g h)-1	1.70E-01	1.67E-01	1.72E-01	1.33E+02
$A_{BP,\pi} \operatorname{mmol} (g h)^{-1}$	1.13E-02	9.89E-03	1.27E-02	1.60E+01
Ea DBT, s kJ mol ⁻¹	4.71E+01	4.54E+01	4.88E+01	5.58E+01
E _{a DBT,π} kJ mol ⁻¹	1.85E+02	1.76E+02	1.94E+02	4.05E+01
E _{a BP,π} kJ mol ⁻¹	1.98E+02	1.90E+02	2.06E+02	4.99E+01
$-\Delta S^0{}_{DBT,\sigma} J \ (mol \ K)^{-1}$	6.95E+01	6.93E+01	6.96E+01	9.60E+01
$-\Delta S^0{}_{BP,\sigma} J \ (mol \ K)^{-1}$	9.54E+01	9.13E+01	9.95E+01	4.56E+01
$-\Delta S^0_{CHB,\sigma} J \ (mol \ K)^{-1}$	6.43E+01	6.38E+01	6.48E+01	2.64E+02
$-\Delta S^0{}_{H28,\sigma} J \ (mol \ K)^{-1}$	1.68E+02	1.43E+02	1.92E+02	1.33E+02
$-\Delta S^{0}_{DBT,\pi} J \ (mol \ K)^{-1}$	1.02E+02	1.01E+02	1.03E+02	2.78E+02
$-\Delta S^{0}{}_{BP,\pi} J \ (mol \ K)^{-1}$	4.29E+01	4.26E+01	4.32E+01	3.06E+02
$-\Delta S^0_{CHB,\pi} J \pmod{K}^{-1}$	4.10E+01	4.07E+01	4.13E+01	3.09E+02
$-\Delta S^{0}_{H_{2}S,\pi} J \ (mol \ K)^{-1}$	1.07E+02	1.06E+02	1.09E+02	1.29E+02
$-\Delta H^0_{DBT,\sigma} kJ mol^{-1}$	2.95E+01	2.89E+01	3.02E+01	9.11E+01
-ΔH ⁰ _{BP,σ} kJ mol ⁻¹	3.31E+01	2.85E+01	3.78E+01	1.39E+01
-ΔH ⁰ _{CHB,σ} kJ mol ⁻¹	2.19E+01	2.06E+01	2.33E+01	3.15E+01
$-\Delta H^0_{H_2S,\sigma} kJ mol^{-1}$	1.44E+02	1.23E+02	1.65E+02	1.33E+01
- $\Delta H^0_{DBT,\pi} kJ mol^{-1}$	4.79E+01	4.69E+01	4.88E+01	9.90E+01
$-\Delta H^{0}_{BP,\pi} \text{ kJ mol}^{-1}$	4.99E+01	4.64E+01	5.35E+01	2.77E+01
-ΔH ⁰ CHB,π kJ mol ⁻¹	1.79E+00	1.71E+00	1.86E+00	4.69E+01
$-\Delta H^0_{H_2S,\pi} kJ mol^{-1}$	1.25E+00	1.15E+00	1.35E+00	2.46E+01

Note: F-value = 52317. F-value_{tab} = 2.97, *t*-value_{tab} = 1.97 at $1-\alpha = 0.95$ and 410 degrees of freedom.

 Table 8. Kinetic parameters values and corresponding 95% probability confidence intervals

 for the kinetic model DBTNP used to describe the HDS of DBT and hydrogenation of NP.

Parameter	Estimated value	Lower limit	Upper limit	<i>t</i> -value
	7.44E-03	6.85E-03	8.03E-03	2.47E+01
$A_{NP,\pi} \text{ mmol } (g h)^{-1}$	7.26E-02	7.13E-02	7.40E-02	1.07E+02
$A_{NP,\sigma} \operatorname{mmol} (g h)^{-1}$	1.00E-05	8.29E-06	1.17E-05	1.15E+02
$A_{NP`,\pi} \operatorname{mmol} (g h)^{-1}$	7.45E-02	6.90E-02	7.99E-02	2.68E+01
Ea NP,σ kJ mol ⁻¹	7.61E+01	7.27E+01	7.96E+01	4.33E+01
E _{a NP,} kJ mol ⁻¹	4.62E+01	4.45E+01	4.80E+01	5.20E+01
$E_{a NP,\sigma} kJ mol^{-1}$	5.11E+01	4.40E+01	5.82E+01	1.41E+01
$E_{a NP`,\pi} kJ mol^{-1}$	7.34E+01	6.18E+01	8.49E+01	1.25E+01
$-\Delta S^{0}{}_{NP,\sigma} J \ (mol \ K)^{-1}$	1.36E+02	1.31E+02	1.41E+02	5.18E+01
$-\Delta S^0_{TTL,\sigma} J \ (mol \ K)^{-1}$	1.20E+02	9.53E+01	1.44E+02	9.69E+00
$-\Delta S^{0}{}_{NP,\pi} J \ (mol \ K)^{-1}$	1.24E+02	1.22E+02	1.26E+02	1.52E+02
$-\Delta S^0_{TTL,\pi} J \pmod{K}^{-1}$	7.97E+01	7.68E+01	8.25E+01	5.51E+01
$-\Delta H^0_{NP,\sigma} kJ mol^{-1}$	5.39E+01	4.21E+01	6.56E+01	9.04E+00
-ΔH ⁰ TTL,σ kJ mol ⁻¹	5.88E+01	4.33E+01	7.44E+01	7.43E+00
$-\Delta H^0_{NP,\pi} \text{ kJ mol}^{-1}$	6.80E+01	6.40E+01	7.20E+01	3.31E+01
-ΔH ⁰ ttl,π kJ mol ⁻¹	7.03E+01	6.48E+01	7.59E+01	2.49E+01

Note: F-value = 15286. F-value_{tab} = 2.79, *t*-value_{tab} = 1.97 at $1-\alpha = 0.95$ and 380 degrees of freedom.

Table 9. Kinetic parameters values and corresponding 95% probability confidence intervalsfor the kinetic model DBTFL used to describe the HDS of DBT and hydrogenation of FL.

Parameter	Estimated value	Lower limit	Upper limit	<i>t</i> -value
A _{FL,π} mmol (g h) ⁻¹	7.80E-02	7.73E-02	7.87E-02	2.33E+02
Ea FL,π kJ mol ⁻¹	7.80E+01	7.73E+01	7.87E+01	1.80E+02
$-\Delta S^{0}_{FL,\sigma} J \ (mol \ K)^{-1}$	8.98E+01	8.97E+01	8.99E+01	1.51E+03
$-\Delta S^0_{HHFL,\sigma} J \ (mol \ K)^{-1}$	1.08E+02	1.05E+02	1.11E+02	7.59E+01
$-\Delta S^{0}_{FL,\pi} J \ (mol \ K)^{-1}$	1.28E+02	1.27E+02	1.29E+02	2.71E+02
$-\Delta S^0_{\text{HHFL},\pi} J \ (mol \ K)^{-1}$	4.20E+01	4.17E+01	4.23E+01	3.08E+02
$-\Delta H^{0}_{FL,\sigma} kJ mol^{-1}$	8.98E+01	8.90E+01	9.06E+01	2.37E+02
-ΔH ⁰ hhfl,σ kJ mol ⁻¹	4.95E+01	4.78E+01	5.13E+01	4.30E+01
-ΔH ⁰ _{FL,π} kJ mol ⁻¹	7.01E+01	6.96E+01	7.06E+01	3.46E+02
-ΔH ⁰ hhfl,π kJ mol ⁻¹	5.60E+01	5.54E+01	5.65E+01	2.66E+02

Note: F-value = 252995. F-value_{tab} = 2.85, *t*-value_{tab} = 1.97 at $1-\alpha = 0.95$ and 386 degrees of freedom.

Table 1	10.	Ki	netic	param	eters v	alues	and	corres	pon	ding 95%	6 pr	obabil	ity	confid	ence
interval	s f	for	the	kinetic	model	DBT	ГРНЕ	used	to	describe	the	HDS	of	DBT	and
hydroge	ena	tion	of P	HE.											

Parameter	Estimated value	Lower limit	Upper limit	<i>t</i> -value
Aphe-thphe,π mmol (g h) ⁻¹	1.28E+00	1.23E+00	1.32E+00	5.74E+01
Aphe-dhphe, π mmol (g h) ⁻¹	4.31E-01	3.48E-01	5.13E-01	1.02E+01
Adhphe, π mmol (g h) ⁻¹	1.00E-02	-9.63E+01	9.63E+01	2.04E-04
Athphe, π mmol (g h) ⁻¹	4.30E+00	3.75E+00	4.84E+00	1.55E+01
Ea phe-thphe, <i>a</i> kJ mol ⁻¹	3.00E+01	2.95E+01	3.05E+01	1.16E+02
$E_{a PHE-DHPHE,\pi} kJ mol^{-1}$	7.99E+01	7.64E+01	8.33E+01	4.54E+01
Ea dhphe, <i>m</i> kJ mol ⁻¹	2.00E+02	-2.40E+04	2.44E+04	1.62E-02
Ea THPHE, <i>a</i> kJ mol ⁻¹	2.10E+02	8.98E+01	3.30E+02	3.43E+00
$-\Delta S^{0}_{PHE,\sigma} J \ (mol \ K)^{-1}$	9.04E+01	8.86E+01	1.02E+02	1.01E+02
$-\Delta S^0_{DHPHE,\sigma} J \ (mol \ K)^{-1}$	6.48E+01	4.95E+01	6.46E+01	8.31E+00
$-\Delta S^0_{OHPHE,\sigma} J \pmod{K}^{-1}$	2.00E+02	-3.02E+07	3.02E+07	1.30E-05
$-\Delta S^{0}_{THPHE,\sigma} J \text{ (mol K)}^{-1}$	7.46E+01	5.67E+01	9.25E+01	8.19E+00
$-\Delta S^{0}_{PHE,\pi} J \ (mol \ K)^{-1}$	8.17E+01	7.80E+01	8.54E+01	4.33E+01
- $\Delta S^0_{DHPHE,\pi} J \ (mol \ K)^{-1}$	5.87E+01	5.54E+01	6.20E+01	3.51E+01
- ΔS^0 ohphe, π J (mol K) ⁻¹	1.31E+02	-1.09E+05	1.09E+05	2.36E-03
-ΔS ⁰ THPHE,π J (mol K) ⁻¹	5.23E+01	5.05E+01	5.41E+01	5.79E+01
-ΔH ⁰ PHE,σ kJ mol ⁻¹	9.32E+01	8.21E+01	1.04E+02	1.64E+01
-ΔH ⁰ dhphe,σ kJ mol ⁻¹	4.22E+01	3.54E+01	4.91E+01	1.22E+01
-ΔH ⁰ OHPHE,σ kJ mol ⁻¹	1.00E-02	-5.63E-03	5.63E+03	3.49E-06
-ΔH ⁰ THPHE,σ kJ mol ⁻¹	3.30E+01	2.97E+01	3.62E+01	1.98E+01
-ΔH ⁰ PHE,π kJ mol ⁻¹	9.16E+01	8.94E+01	9.39E+01	8.04E+01
-ΔH ⁰ dhphe,π kJ mol ⁻¹	7.69E+01	6.65E+01	8.72E+01	1.46E+01
-ΔH ⁰ OHPHE,π kJ mol ⁻¹	1.00E-02	-4.21E+02	4.21E+02	4.66E-05
-ΔH ⁰ THPHE,π kJ mol ⁻¹	9.95E+01	9.64E+01	1.03E+02	6.30E+01

Note: F-value = 161765. F-value_{tab} = 2.79, *t*-value_{tab} = 1.97 at $1-\alpha = 0.95$ and 504 degrees of freedom.

Table 11. Kinetic expressions for dibenzothiophene hydrodesulfurization based on Langmuir-Hinshelwood-Hougen-Watson approach.

	Catalytic Sites			_	Activation		
Catalysts	DDS Route	HID Route	\mathbf{H}_{2}	Rate Expression	Energy (kJ mol ⁻¹)	Reference	
CoMo/v ALO	v	-	v	$r_{DBT} = \frac{kK_{DBT}P_{DBT}}{1 + K_{DBT}P_{DBT} + K_{PROD}P_{PROD}} \cdot \frac{K_{H_2}P_{H_2}}{1 + K_{H_2}P_{H_2}}$	163.3	Simple 1 of al ¹⁴	
C01010/ γ-AI ₂ O ₃	Χ		Λ	$r_{BP} = \frac{kK_{BP}P_{BP}}{1 + K_{BP}P_{BP} + K_{CHB}P_{CHB}} \cdot \frac{K_{H_2}P_{H_2}}{1 + K_{H_2}P_{H_2}}$	210.6	Singhal et al.	
CoMo/γ-Al ₂ O ₃	Х		x	$r_{DBT} = \frac{k K_{DBT} P_{DBT}}{1 + K_{DBT} P_{DBT} + K_{H_2S} P_{H_2S}} \cdot \frac{K_{H_2} P_{H_2}}{1 + K_{H_2} P_{H_2}}$	96.3	Vrinat ¹⁸	
				$r_{DBT_{\sigma}} = \frac{k_{DBT,\sigma} K_{H,\sigma} K_{DBT,\sigma} C_{H_2} C_{DBT}}{\left(1 + \left(K_{H,\sigma} C_{H_2}\right)^{0.5} + K_{DBT,\sigma} C_{DBT} + K_{BP,\sigma} C_{BP} + K_{H_2S,\sigma} C_{H_2S}\right)^3}$	122		
CoMo/γ-Al ₂ O ₃	Х	Х		$r_{DBT_{\pi}} = \frac{k_{DBT,\pi} K_{H,\pi} K_{DBT,\pi} C_{H_2} C_{DBT}}{\left(1 + \left(K_{H,\pi} C_{H_2}\right)^{0.5} + K_{DBT,\pi} C_{DBT} + K_{BP,\pi} C_{BP}\right)^3}$	186	Vanrysselberghe et al. ²⁷	
				$r_{BP_{\pi}} = \frac{k_{BP,\pi} K_{H,\pi} K_{BP,\pi} C_{H_2} C_{BP}}{\left(1 + \left(K_{H,\pi} C_{H_2}\right)^{0.5} + K_{DBT,\pi} C_{DBT} + K_{BP,\pi} C_{BP}\right)^3}$	255.7		
CoMo/v-AbO2	X	X	x	$r_{DBT_{\sigma}} = \frac{k_{DBT,\sigma}K_{DBT,\sigma}C_{DBT}}{\left(1 + K_{DBT,\sigma}C_{DBT} + K_{H_2S,\sigma}C_{H_2S}\right)^2} \cdot \frac{K_{H_2}C_{H_2}}{1 + K_{H_2}C_{H_2}}$	125.6	Broderick et al ²⁶	
		24	23	$r_{DBT_{\pi}} = \frac{k_{DBT,\pi} K_{DBT,\pi} K_{H_2} C_{DBT} C_{H_2}}{1 + K_{DBT,\pi} C_{DBT}}$	117.2	Dioucies et al.	

Scheme and Figure Captions

Scheme 1. Reaction network for the hydrodesulfurization of dibenzothiophene.

Scheme 2. Reaction network for the hydrogenation of polyaromatic compounds: a) Naphthalene,b) Fluorene, and c) Phenanthrene.

Scheme 3. Illustration of the adsorption of DBT on the two routes of HDS on NiMoS/ γ -Al₂O₃. The rectangular box represents brim regions, and the oval marks the CUS-like sites. Color scheme: green, nickel; blue, molybdenum; yellow, sulfur.

Figure 1. Parity diagram for comparing experimental with calculated conversion of DBT and the yields of BP and CHB, for the three kinetic models the HDS of DBT: a) DBT1S, b) DBT2S, and c) DBTBP2S.

Figure 2. Parity diagram for comparing experimental with calculated conversion of DBT and the yields of BP and CHB. The simulated values were calculated from the model DBTNP that describe the simultaneous HDS of DBT and hydrogenation of NP.

Figure 3. Parity diagram for comparing experimental with calculated conversion of DBT and the yields of BP and CHB. The simulated values were calculated from the model DBTFL that describe the simultaneous HDS of DBT and hydrogenation of FL.

Figure 4. Parity diagram for comparing experimental with calculated conversion of DBT and the yields of BP and CHB. The simulated values were calculated from the model DBTPHE that describe the simultaneous HDS of DBT and hydrogenation of PHE.

Figure 5. Parity diagrams for comparing experimental with calculated conversion of NP, FL, and PHE, fitting for the kinetic models DBTNP, DBTFL and DBTPHE, respectively.



Scheme 1. Reaction network for the hydrodesulfurization of dibenzothiophene.

a) Naphthalene



b) Fluorene



Fluorene (FL)

1,2,3,4,4a,9a-hexahydro-fluorene (HHFL)



Scheme 2. Reaction network for the hydrogenation of polyaromatic compounds: a) Naphthalene,b) Fluorene, and c) Phenanthrene.



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Figure 3. Parity diagram for comparing experimental with calculated conversion of DBT and the yields of BP and CHB. The simulated values were calculated from the model DBTFL that describe the simultaneous HDS of DBT and hydrogenation of FL.



Figure 4. Parity diagram for comparing experimental with calculated conversion of DBT and the yields of BP and CHB. The simulated values were calculated from the model DBTPHE that describe the simultaneous HDS of DBT and hydrogenation of PHE.



Figure 5. Parity diagrams for comparing experimental with calculated conversion of NP, FL, and PHE, fitting for the kinetic models DBTNP, DBTFL and DBTPHE, respectively.

Graphical Abstract

