

Multiscale kinetic analysis of the direct desulfurization pathway of dibenzothiophene on CoMoS
phase model

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To:

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Resumen

Título: Análisis cinético multiescala de la vía de desulfuración directa del dibenzotiofeno en la fase modelo CoMoS.

Autor: Michael Leonardo Ariza Gómez**

Palabras claves: Teoría del funcional de densidad (TFD), Hidrodesulfuración (HDS), Dibenzotiofeno (DBT), Transferencia de hidrógeno.

Descripción

La reacción de hidrodesulfuración (HDS) de moléculas como el dibenzotiofeno (DBT) es un elemento clave para reducir las emisiones de gases tóxicos. Generalmente, estas reacciones se llevan a cabo con un catalizador de disulfuro de molibdeno promovido por cobalto o níquel, lo que permite una mejor actividad catalítica del sistema. En general, se realizan experimentos y cálculos teóricos para comprender el fenómeno de la reacción de hidrodesulfuración, sin embargo, la dinámica del proceso se descuida y no se considera hasta la fecha. Hemos implementado diferentes metodologías para tener una noción de la evolución temporal de las especies en HDS. En este trabajo, realizamos un estudio teórico sobre la ruta de desulfuración directa del dibenzotiofeno en vacantes de azufre pertenecientes a la fase activa del modelo CoMoS. Usamos cálculos DFT estáticos para comprender el estado electrónico del sistema, luego estimamos las propiedades termodinámicas en condiciones de operación para estudiar el efecto de las contribuciones de la entropía y la entalpía de la reacción. Luego, desarrollamos un modelo microcinético (MK) que permite comprender la interacción de todos los pasos elementales. Finalmente, realizamos simulaciones cinéticas de Monte Carlo (KMC) para conocer la distribución espacial y la frecuencia con la que ocurren las reacciones en el borde de CoMoS.

En conjunto, estos hallazgos sugieren que: i) la monohidrogenación de la molécula dibenzotiofeno es el paso limitante de velocidad en la reacción para cualquier tipo de técnica utilizada en este estudio, lo cual fue verificado por medio de un grado de control de velocidad; ii) considerar adsorber hidrógeno molecular en el plano de la reacción, ayudo a comprender las altas condiciones de presión y temperatura que requieren las refinerías para remover estos heteroátomos de azufre iii) el escalado que se realizó en estudio, permitió comprobar que mediante la implementación exclusiva de los cálculos teóricos es posible describir la tendencia de los datos experimentales.

*Tesis de Maestría

** Facultad de Ingenierías Físicoquímica. Escuela de Ingeniería Química. Director: Profe. Víctor Gabriel Baldovino Medrano. Codirectores: Prof. Franziska Hess y Dr. Edgar Mauricio Morales Valencia.

Abstract

Title: Multiscale kinetic analysis of the direct desulfurization pathway of dibenzothiophene on CoMoS phase model.

Author: Michael Leonardo Ariza Gómez**

Keywords: Density functional theory (DFT), Hydrodesulfuration, Dibenzothiophene (DBT), Hydrogen transfer.

Description:

The hydrodesulfurization (HDS) reaction of molecules such as dibenzothiophene (DBT) is a key element in reducing toxic gas emissions. Generally, these reactions are carried out with a molybdenum disulfide catalyst promoted by cobalt or nickel, which allows a better catalytic activity of the system. In general, experiments and theoretical calculations are performed to understand the phenomenon of the hydrodesulfurization reaction, however, the dynamics of the process are neglected and not considered to date. We have implemented different methodologies to have a notion of the time evolution of species in HDS. In this work, we perform a theoretical study on the direct desulfurization pathway of dibenzothiophene in sulfur vacancies belonging to the active phase of the CoMoS model. We use static DFT calculations to understand the electronic state of the system, then we estimate the thermodynamic properties at operating conditions to study the effect of entropy and enthalpy contributions to the reaction. Then, we developed a microkinetic model (MK) that allows to understand the interaction of all elementary steps. Finally, we performed kinetic Monte Carlo (KMC) simulations to gain insight into the spatial distribution and frequency with which reactions occur at the catalyst surface.

Taken together, these findings suggest that: (i) monohydrogenation of the dibenzothiophene molecule is the rate limiting step in the reaction for any type of technique used in this study, which was verified by a degree of rate control; ii) considering adsorbing molecular hydrogen in the reaction plane helped to understand the high pressure and temperature conditions required by the refineries to remove these sulfur heteroatoms iii) the scaling performed in the study allowed to verify that by implementing only the theoretical calculations it is possible to describe the trend of the experimental data.

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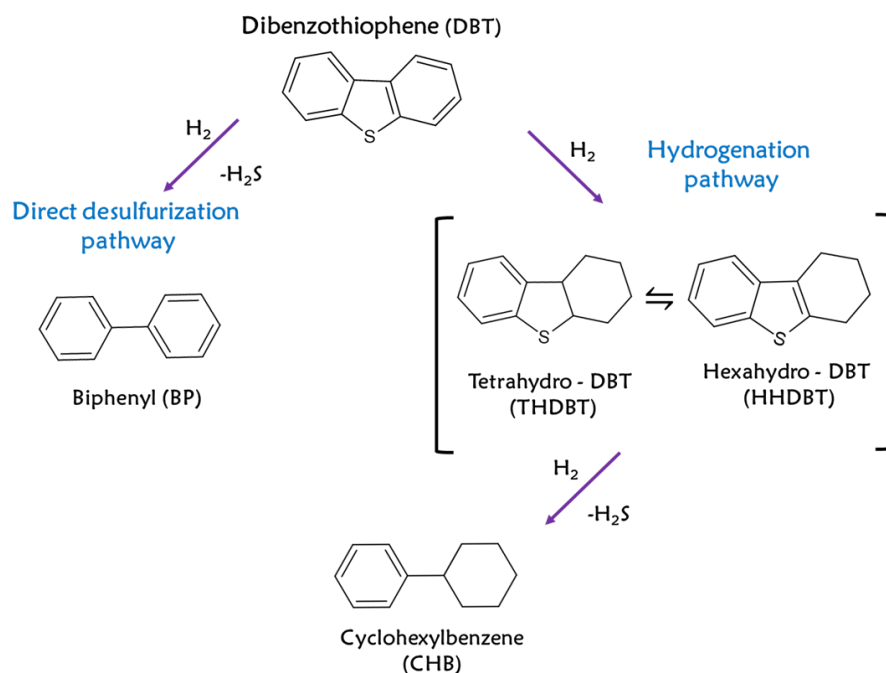
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Introduction

The legislative requirements with respect to the permissible sulfur content in diesel fuel has led to continuous improvement in hydrodesulfurization (HDS) processes. This is because the presence of sulfur in fuels can generate the emission of toxic gases that contribute to air pollution, harming human health and the environment. Therefore, it is crucial to have a comprehensive insight into the reaction mechanism behind HDS to achieve an efficient sulfur removal and thus produce cleaner fuels.(Alabdullah et al., 2020; Weng et al., 2020) In this regard, refractory S-heteroarenes compounds such as dibenzothiophene (DBT) and its methyl derivatives are study targets because their steric hindrance and low reactivity on the catalyst surface. (Low et al., 2019; Shafiq et al., 2022) The sulfur removal from DBT over transition metal sulfides, mainly molybdenum disulfide (MoS_x) promoted with cobalt (CoMoS) or nickel (NiMoS), comprise two reaction routes: (1) hydrogenation (HYD) of the aromatic ring via hydrogen addition to produce cyclohexylbenzene (CHB) with intermediates such as tetradibenzothiophene (THDBT) and hexadibenzothiophene (HHDBT) and (2) direct desulfurization (DDS) via C-S bond cleavage to generate biphenyl (BP) (**Figure 1**). (Egorova & Prins, 2004a; Landau, 1997; Morales-Valencia et al., 2021; Shafi & Hutchings, 2000; Singhal, Espino, & Sobel, 1981) The selectivity of these routes depends on the type of the catalyst, in specific, the HYD route is favored on MoS_2 phase, while the DDS route is prevalent on CoMoS and NiMoS phases.

Figure 1.

Reaction scheme for the hydrodesulfurization (HDS) of dibenzothiophene (DBT).



The atomic scale understanding of DBT hydrodesulfuration over CoMoS catalyst have significantly advanced in recent years thanks to the application of sophisticated characterization methods such as transmission electron microscopy (TEM) and scanning tunneling microscopy (STM). (Grønborg et al., 2016; Lauritsen & Besenbacher, 2015; Tuxen et al., 2012) Such methods have allowed the identification of two types of active sites, which are located at the edge of the hexagonal CoMoS structure: (1) the coordinatively unsaturated sites (CUS) that are sulfur vacancies generated during the HDS conditions and promote mainly the DDS route, since the sulfur atom of dibenzothiophene can bind to this vacancy, and (2) Brim sites are sulfur saturated borders where the dibenzothiophene adsorbs in planar mode on the metal and favors the HYD route. (Garcia de Castro et al., 2021; Girgis et al., 1991; Grønborg et al., 2016; Kazakova et al., 2021; Lauritsen & Besenbacher, 2015) Researchers have implemented different strategies to

elucidate the mechanism, including Langmuir-Hinshelwood formalisms where hydrogen and dibenzothiophene compete to adsorb on the same site. This assumption leads to hydrogenation of the sulfur molecule having a common intermediate called dihydro-dibenzothiophene (DHDBT); however, this compound has not been observed in HDS reactions. (Ferdous et al., 2006; Mijoin et al., 2001a; Vrinat, 1983) Vanrysselberghe and Froment, (Froment, 1996) postulate that direct desulfurization and hydrogenation reactions occur at two distinct active sites, and furthermore, that there is competition between adsorbed reactants and hydrogen atoms on the catalyst surface, thus influencing the rate determination of the reaction. This is based on a mathematical model that allows the calculation of the kinetic parameters of the reaction.

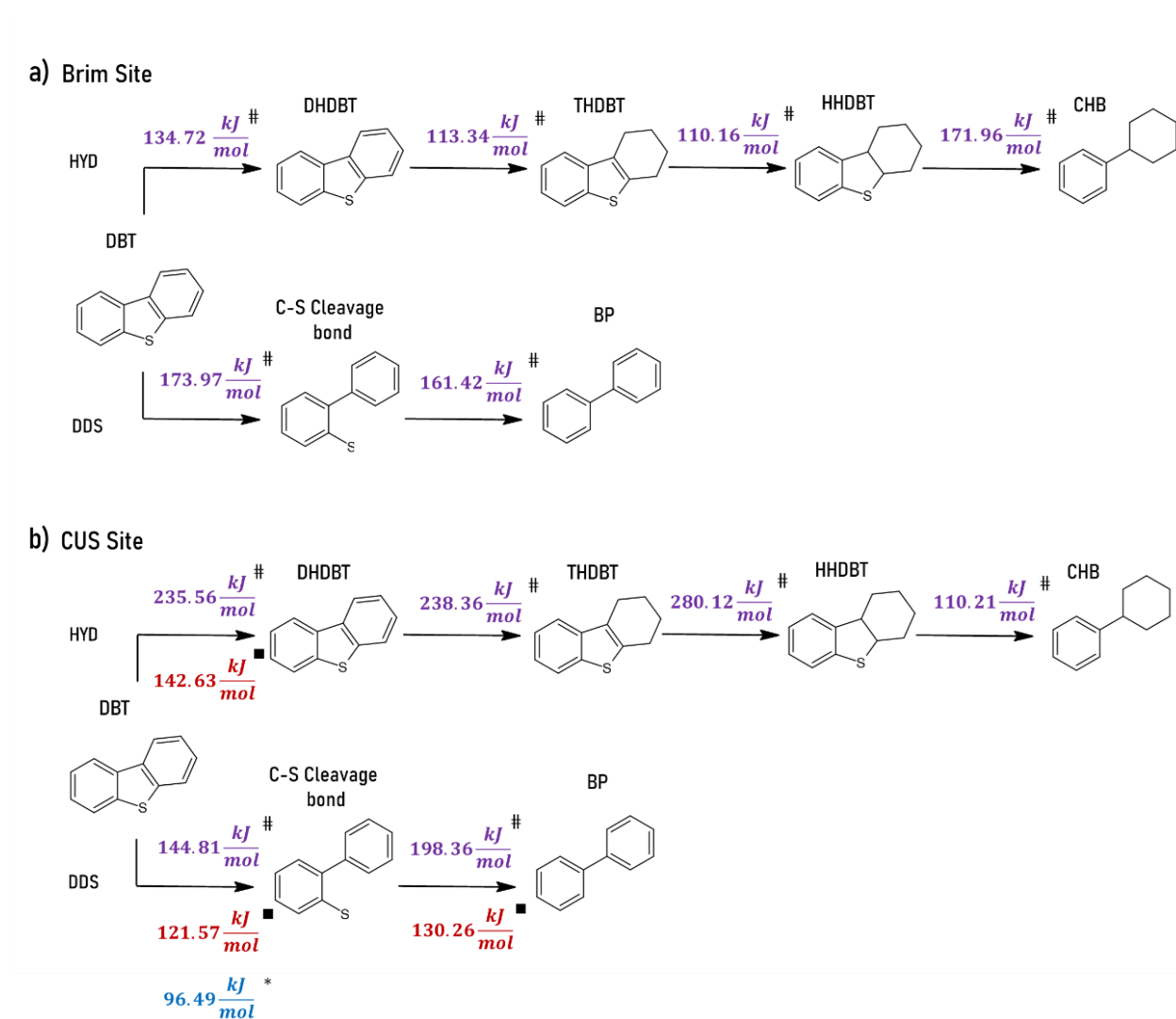
However, a kinetic model does not imply knowledge of the microscopic events occurring at the catalyst surface, since the determination of the kinetic parameters depends on the experimental conditions used to describe the kinetics of the reaction. Therefore, a combination of analytical techniques and theoretical calculations are constantly used to unravel the phenomena occurring at the catalyst surface. In the last decades, theoretical studies of the hydrodesulfurization reaction have been carried out for various organosulfur molecules. In the case of dibenzothiophene there have been few publications reporting in detail the mechanism for both reaction routes over the CoMoS catalyst. The literature has reported the possible energy barriers to obtain the desulfurized molecules, in the case of the hydrogenation route at the Brim site (**Figure 2a**), forming the cyclohexylbenzene molecule requires the formation of intermediates such as dihydrodibenzothiophene, tetradibenzothiophene and hexahydrodibenzothiophene, therefore the energies reported to form these species are $134.72 \text{ kJ mol}^{-1}$, $113.34 \text{ kJ mol}^{-1}$ and $110.16 \text{ kJ mol}^{-1}$, respectively. Instead, the direct desulfurization route for this same site must overcome a barrier of $173.97 \text{ kJ mol}^{-1}$, being this route less favorable for the reaction. On the other hand, **Figure 2b**

shows the hydrodesulfurization route for the CUS site, the values reported by the authors show that the kinetics of the reaction favor the direct desulfurization route over hydrogenation.

At the molecular level, theoretical calculations provide detailed insight into transition and intermediate states that are not observable at the macroscopic scale. However, these calculations have a limitation of not being able to describe the complete dynamics of a reaction. To understand the behavior of species at the surface and relate it to the macroscale, it is necessary to have a level of theory that considers the interaction of the proposed elementary events. Recently, Sandoval et al. (Sandoval-Bohórquez et al., 2021) implemented a strategy to reduce the number of parameters to be estimated in kinetic modeling. Using transition state theory together with statistical thermodynamics, they determined the adsorption energies of the species, as well as the standard and reaction entropies. These data, combined with experimental information, allowed describing the kinetics of the methane dry reforming reaction. It should be noted that this approach has been successfully applied in several research areas. (Dickens et al., 2019; Jørgensen, 2017; Z. Li et al., 2021; Smith, 2021; Xie et al., 2022) In general, microkinetics focuses on representing the kinetics of reactions by differential equations, which usually provides information on reaction rates and concentrations of species in a chemical system; however, it does not allow studying the time evolution of a microscopic system. Moreover, kinetic parameters alone are not sufficient to describe the evolution of dynamics in catalytic reactions. (Savva & Stamatakis, 2020) A key aspect to address this problem is the occurrence of individual elementary and statistical processes that involve the generation of time trajectories describing the highly active nature of the reaction mechanisms, which allows a better predictive quality of the events. (Andersen et al., 2019; Brenner et al., 2008; Hess & Over, 2017; Prats et al., 2018)

Figure 2.

Corresponding reaction energies for each of the steps involved in the direct desulfurization (DDS) and hydrogenation (HYD) reactions of dibenzothiophene over a) Brim and b) CUS sites. Data reported (#) by Zheng et al., (Zheng et al., 2021) (■) by Dumon et al., (Dumon et al., 2021) and (*) by Saric et al. (Šarić et al., 2018)



Kinetics Monte Carlo (KMC) is a technique used to simulate and analyze the kinetics of chemical reactions. Unlike deterministic approaches, it is based on stochastic principles and uses

random simulations to study reaction processes. Through these simulations, multiple reaction trajectories are generated that follow the rules of probability and statistics. Each trajectory represents a sequence of individual events, such as adsorption, desorption, chemical reactions, and diffusion on the catalyst surface.(Andersen et al., 2019; Reuter, 2011) These events are selected according to their reaction rates and associated probabilities. By simulating a large number of reaction trajectories, kinetics Monte Carlo provides information on the statistical distributions of reaction times, populations of different chemical species, rates of product formation and consumption, among other kinetic aspects.(Reuter, 2016; Michail Stamatakis, 2015) In recent years, this technique has been prioritized because of its success in describing catalytic systems. It has been used in branches such as WGSR,(Chutia et al., 2020; Michail Stamatakis et al., 2011; Yang et al., 2013a) NO oxidation,(Papanikolaou et al., 2018) HCL oxidation,(C. Li et al., 2018) and among others.(Réocreux et al., 2019; Saul et al., 1994; Van Veenendaal et al., 2000) To date, the dynamics of the direct desulfurization of dibenzothiophene in an active phase of the CoMoS catalyst by means of kinetic Monte Carlo simulation has not been reported in the literature, therefore it is essential to combine techniques such as DFT, microkinetic models and stochastic simulation that allow us to have a notion of the intrinsic events that govern the dibenzothiophene desulfurization reaction, that will allow us initially to know the distribution of the species on the surface, as well as to know the coverages, the rate determining steps (RDS) and most abundant surface intermediate (MASI). We have implemented different methodologies to have a notion of the temporal evolution of species in HDS. Initially, we studied the direct hydrodesulfurization reaction of dibenzothiophene on an unsaturated site, for which we used static DFT calculations to understand the electronic state of the system, then we estimated the thermodynamic properties under operating conditions to study the effect of the contributions of entropy and enthalpy of the

reaction. Subsequently, we developed a microkinetic model (MK) that allows understanding of the interaction of all elementary steps. Finally, we performed kinetic Monte Carlo (KMC) simulations to understand the spatial distribution and frequency at which reactions occur on the CUS edge of CoMoS.

2. Computational Methods

2.1 DFT Methods

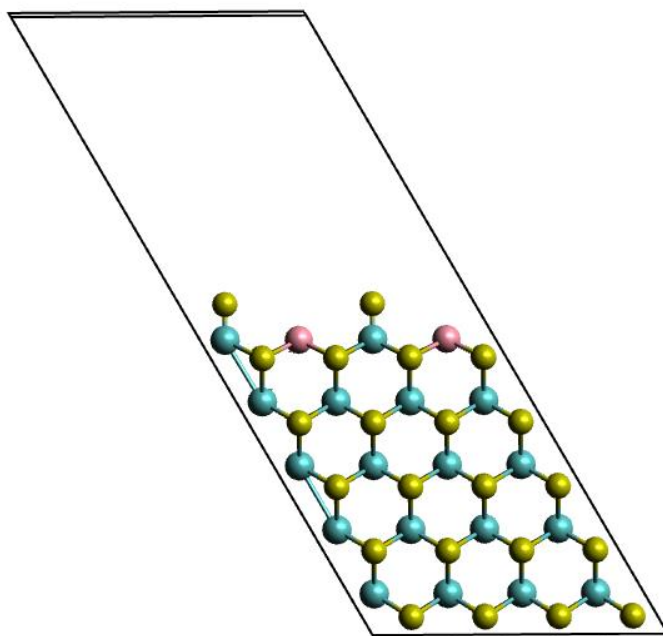
The calculations were carried out according to density functional theory with the Vienna ab initio simulation package (VASP),(Jung et al., 2006; Kresse & Furthmüller, 1996) within the generalized gradient approximation (GGA). The Perdew Burke and Ernzerhof (PBE) functional was used for the calculation of the exchange correlation energies(Perdew et al., 1996) and the potentials and the projector augmented waves (PAW)(Blöchl, 1994) method to treat the ionic–electronic interaction. The Becke-Jonson damping scheme (DFT-D3) was applied for including van der Waals interaction. (Grimme et al., 2010, 2012)

The electronic density was calculated up to a 500-eV cutoff energy and a 3x3x1 k-point mesh was used for the 3D Brillouin zone integration in all calculations.(Hu et al., 2019; Methfessel & Paxton, 1989) According to the calculations shown by Kresse et al.(Kresse & Hafner, 2000; Zhu et al., 2007) the magnetic properties are fundamental for an accurate quantitative description of the adsorption energy. Due to the participation of magnetic elements (Co) in the system, the spin polarization effect is considered. Structural optimizations had a convergence criterion corresponding to the SCF tolerance that was 10^{-6} eV while the maximum force on each relaxed atom was converged to 0.02 eV/Å.

Transition states were found using a combination of the climbing nudged elastic band method (CI-NEB) (Henkelman et al., 2000; Henkelman & Jónsson, 2000) followed by the dimer method.(Henkelman & Jónsson, 1999) This was done with the aim of finding a saddle point of the first order, which was verified by the reaction coordinate corresponding to the imaginary frequency. The structure was based on the proposal made by Dumon et al.(Krebs et al., 2008) In particular, these authors propose a 5-layer structure of CoMoS, having in its molybdenum edge an alternation of sites where molybdenum is replaced by cobalt atoms. The parameters of the supercell, correspond to (12.59 Å, 12.11Å, 30.74Å) as exhibited in Fig 2. The three lower layers of the structure were fixed in bulk, while the other upper layers were relaxed.

Figure 3.

Periodic slab model for CoMoS at the M-edge. Legend: turquoise sphere (molybdenum atoms), yellow sphere (sulfur atoms) and pink sphere (cobalt atoms).



The energy of adsorption (E_{ads}) and the energy barrier were defined by the following equations:

$$E_{ads} = E_{(slab/gas)} - E_{gas} - E_{slab} \quad \text{Eq (1)}$$

$$E_a = E_{TST} - E_{IS} \quad \text{Eq (2)}$$

Where $E_{slab/gas}$ corresponds to the total energy of the CoMoS surface with adsorbate, E_{gas} is the gas phase species, E_{slab} is the bare surface, respectively. On the other hand, E_a is the activation energy which is determined by the difference between the transition state (E_{TST}) and its initial state (E_{IS}).

2.2 Estimation of thermochemical parameters

Thermodynamic estimates such as enthalpies, entropies, and Gibbs free energy were calculated under typical conditions for the hydrodesulfurization reaction, i.e., $P = 5 \text{ MPa}$ and $T = 573.15 \text{ K}$.

2.2.1 Gas phase species

The transformation of electronic calculations into thermodynamic properties was carried out by implementing the ideal gas limit, (McQuarrie, 1975; Ochterski & Ph, 2000) which takes into account the degrees of freedom (DOF) of translational, rotational, and vibrational motion of the molecules. Therefore, to calculate the Gibbs free energy of the species in the gas-phase, the following equations were used.

$$G(T, P) = H(T) - TS(T, P) \quad \text{Eq (3)}$$

$$H(T) = E_{elec} + E_{ZPE} + \int_0^T C_p dT \quad \text{Eq (4)}$$

Where E_{elec} is the electronic energy obtained by DFT, E_{zpe} is the zero-point energy, and C_p is the contribution of heat capacity at constant pressure. On the other hand, to determine the entropy of an ideal gas as a function of temperature and pressure, we used:

$$S(T, P) = S_{trans} + S_{rot} + S_{vib} - k_B \left(\frac{P}{P_0} \right) \quad \text{Eq (5)}$$

The theoretical calculations of molar entropy of the gas-phase and adsorbed species as well as the transition states were carried out via the Sackur-Tetrode equation:

$$S_x^0 = R \ln(q_x) + RT \left[\frac{\partial \ln(q_x)}{\partial T} \right] \quad \text{Eq (6)}$$

where R is the universal gas constant and q_x the partition function describing translational, vibrational, and rotational degrees of freedom (DOF), and which are given by the following expressions:

$$S_{trans} = k_B \left\{ \ln \left[\left(\frac{2\pi M k_B T}{h^2} \right)^{\frac{3}{2}} \frac{k_B T}{P_0} \right] + \frac{5}{2} \right\} \quad \text{Eq (7)}$$

$$S_{rot} = \begin{cases} 0 & , \text{if monatomic} \\ k_B \left[\ln \left(\frac{8\pi^2 I k_B T}{\sigma h^2} \right) + 1 \right] & , \text{if Linear} \\ k_B \left\{ \ln \left[\frac{\sqrt{\pi I_A I_B I_C}}{\sigma} \left(\frac{8\pi^2 I k_B T}{h^2} \right)^{\frac{3}{2}} \right] + \frac{3}{2} \right\} & , \text{if nonlinear} \end{cases} \quad \text{Eq (8)}$$

$$S_{vib} = k_B \sum_i^{vib \text{ DOF}} \left[\frac{\frac{1}{T_i}}{e^{\frac{1}{T_i}} - 1} - \ln \left(1 - e^{-\left(\frac{1}{T_i}\right)} \right) \right], \quad T_i = \frac{k_B T}{h \nu_i} \quad \text{Eq (9)}$$

Where k_B is the Boltzmann constant, M is the molecular mass, h is the Planck constant, P_0 is the standard pressure (1 bar), σ is the symmetry number of the molecule, I is the moment of inertia (3 moments of inertia if the molecule is not linear, 1 if it is), ν_i is the number of vibrational frequencies of the molecule, and T is the temperature of the system.

2.2.2 Adsorbed species

The Gibbs free energy for a strongly adsorbed species is given by the harmonic limit, (McQuarrie, 1975; Ochterski & Ph, 2000) which implies that contributions such as translation and rotation are hindered on the surface and become modes of vibration. Thus, the degrees of freedom (DOF) for these species are treated as $3N$ (N , number of vibrational modes). In this way, entropy and internal energy are given by:

$$G(T) = H(T) - TS(T) \quad \text{Eq (10)}$$

$$H(T) = U(T) + PV \quad \text{Eq (11)}$$

$$U(T) = E_{elec} + E_{ZPE} + \sum_i^{vib\ DOF} \frac{\frac{1}{T_i}}{e^{\frac{1}{T_i}} - 1}, \quad T_i = \frac{k_B T}{h\nu_i} \quad \text{Eq (12)}$$

For the case the entropy is equal to:

$$S_{vib} = k_B \sum_I^{vib\ DOF} \left[\frac{\frac{1}{T_I}}{e^{\frac{1}{T_I}} - 1} - \ln \left(1 - e^{-\left(\frac{1}{T_I}\right)} \right) \right] \quad \text{Eq (13)}$$

2.3 Microkinetic Modeling

Microkinetic modeling was done using the VODE subroutine that was used to solve the corresponding set of ordinary differential equations (ODE). (Brown et al., 1989) To calculate the adsorption and desorption constants, it is taken into account an entropy reduction that occurs during the transition from the gas phase to the adsorption of the molecule, which is called an early 2D gas transition state, which will involve the vibrational, translational and rotational components of the molecule. The estimate of the rate constant is given by: (Nørskov et al., 2014; Michail Stamatakis & Vlachos, 2012)

$$k_{ads}^{fwd} = \frac{p_x * A_{st}}{\sqrt{2 * \pi * m_x * k_B * T}} \quad \text{Eq (14)}$$

$$k_{ads}^{rev} = \frac{q_{vib,i(g)} * q_{transl,2D,i(g)} * q_{rot,i(g)}}{q_{vib,x}} * \frac{k_B T}{h} * \exp\left(\frac{\Delta E_{ij}}{k_B * T}\right) \quad \text{Eq (15)}$$

Where A_{st} is the effective area of the site, $1.26 \cdot 10^{-19}$ for the cobalt site and $1.02 \cdot 10^{-19}$ for the sulfur site m_x is the mass of the molecule (i.e. molecular weight / Avogadro number), P_i is the partial pressure of the molecule, ΔE_{ij} is the activation barrier of process and Q are partition functions for the rotational, translational, and vibrational degrees of freedom. Consequently, the partition functions for the surface reactions are approximate to unity, (Zhang et al., 2018) this is because only the vibrational modes contribute to the partition functions, thus, the following expressions are given.

$$k_{surf}^{fwd} = \frac{q_{vib}^{\ddagger}}{q_{vib,i}} * \frac{k_B T}{h} * e^{\left(-\frac{\Delta E_i^{\ddagger}}{k_B * T}\right)} \approx k_{surf}^{fwd} = \frac{k_B T}{h} * e^{\left(-\frac{\Delta E_i^{\ddagger}}{k_B * T}\right)} \quad \text{Eq (16)}$$

And the reverse constant:

$$k_{surf}^{rev} = \frac{k_B T}{h} * e^{\left(-\frac{\Delta E_j^{\ddagger}}{k_B * T}\right)} \quad \text{Eq (17)}$$

2.4 Kinetic Monte Carlo

For the implementation of the Kinetic Monte Carlo simulation, Zacros 2.0 (M Stamatakis, n.d.) was used. For calculations, a set of reference species must be chosen to calculate the formation energies, which are used for fitting the cluster expansions (CE). The species are chosen according to the number of chemical elements participating in the reaction. In our case, we chose dibenzothiophene ($C_{12}H_8S$), hydrogen, (H_2) and biphenyl ($C_{12}H_{10}$). This choice of species must be linearly independent, meaning that in the moment of performing a stoichiometric balance,

the reference components cannot produce another reference species. (Michail Stamatakis & Vlachos, 2011a)

The inputs to the Monte Carlo kinetic simulation for Zacros are described in 4 steps (**Figure 5**): (1) the input to perform the simulation consist of specifying pressure, temperature, mole fraction of the gas phase and the simulation time, this is dispensable since it is necessary to ensure that the system reaches the steady state, our simulations took 10 days to reach this state. (2) the specification of the lattice that represents the catalytic surface, it specifies the number of participating sites and the bonds between the atoms to form the surface (**Figure 4**). On the other hand, (3) it is possible to add the adsorbate-adsorbate lateral interactions, in the case of this work this file was not considered. The pairwise interaction energy of the microscopic processes was omitted because the electronic energy of the elementary processes contains these repulsion and attraction interactions within its value, therefore, if the interaction energy between species were added, it would give a double energy count in the simulation. Finally, (4) a reaction mechanism must be specified within the simulation, where for each elementary event considered, the pre-exponential factor, the activation energy and the pe ratio which is a ratio between the direct and inverse rate constant of the process must be specified. The KMC simulation considers the probability distribution by means of the rate constants, i.e., events with a very high value of the velocity constant will have a higher probability of being selected. To have a purely stochastic effect, a random number is cast, which will correspond to an elementary event within the distribution and will be executed, the algorithm (**Figure 5**) will store the frequency with which the microscopic event is occurring as well as storing information regarding the state of the lattice and the energy contribution. The lattice state is updated, undoing the last configuration, however, it takes the species that participated in the previous configuration as reactants to update the list of

events with respect to that species and thus generate a new probability distribution that will allow to see the progress of the reaction. This process is repeated until the simulation reaches the stipulated time.

Figure 4.

Lattice used for the CoMoS surface in the KMC simulation, considering 2 sites for the reaction:

∇ , blue triangles for cobalt site and, $\odot$ purple circles for sulfur sites.

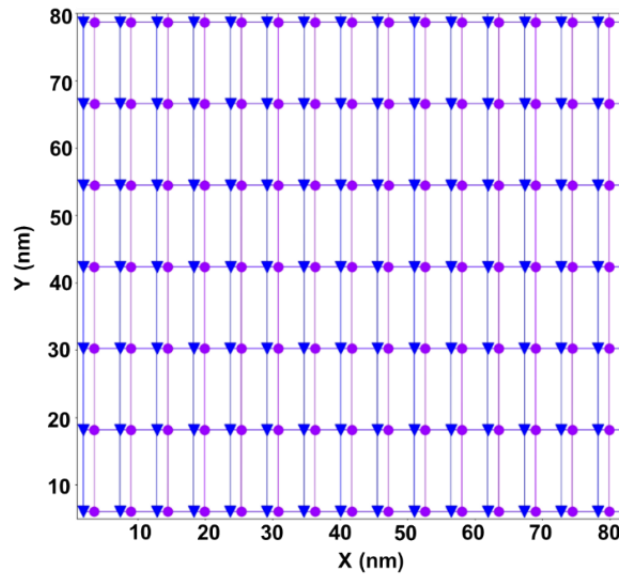
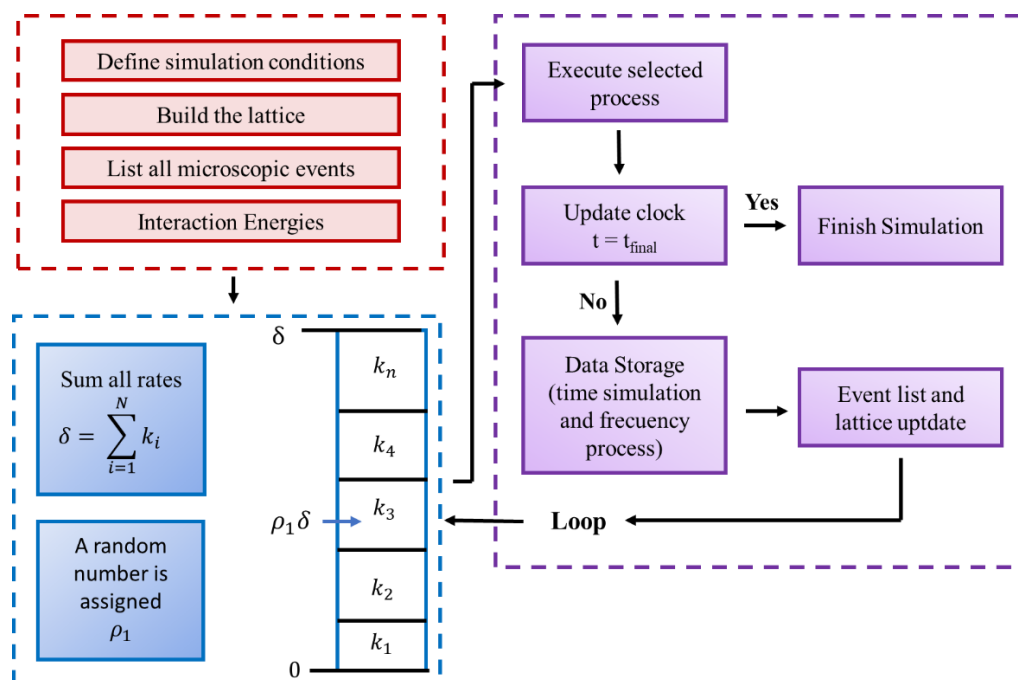


Figure 5.

Flowchart of the Kinetic Monte Carlo simulation implemented in Zacros



3. Results and discussion

3.1 Mechanism reaction

Based on the previous work of other research groups, (Dumon et al., 2021; Mijoin et al., 2001b; Zheng et al., 2017, 2021) the mechanism presented **Figure 6** and table 1 was proposed for this reaction. At first glance, the proposed mechanism does not satisfy the stoichiometry of the hydrodesulfurization reaction. This is because we assume that there are two modes of hydrogen adsorption leading to the same pathway. The first consideration is the adsorption of molecular hydrogen, which is strongly activated on the metal site; the distance between both adsorbed hydrogen atoms on the cobalt site is around $0.84\text{\AA}$, which should be compared to $0.75\text{\AA}$ when the molecule is in the gas phase, this indicates that there is an effect of the metal on this species. Therefore, to consider this elementary event, step 3 must be omitted to comply with the catalytic cycle. Consequently, the second adsorption that has been considered is the dissociative adsorption of hydrogen, in which Co-H and S-H species with bond lengths of $1.48\text{\AA}$ and $1.36\text{\AA}$ are formed,

respectively. To satisfy the reaction mechanism, we must omit the microscopic steps of molecular adsorption and the involvement of hydrogen diffusion to the sulfur site (Step 1-2). Once the stoichiometry of the system has been clarified from the point of view of hydrogen adsorption, the following sections will give a description of the microscopic events considered to desulfurize the dibenzothiophene molecule, in which different techniques are deployed to have a better idea of what possible events occur on the catalyst surface.

Figure 6.

Catalytic cycle of dibenzothiophene hydrodesulfurization by direct desulfurization pathway.

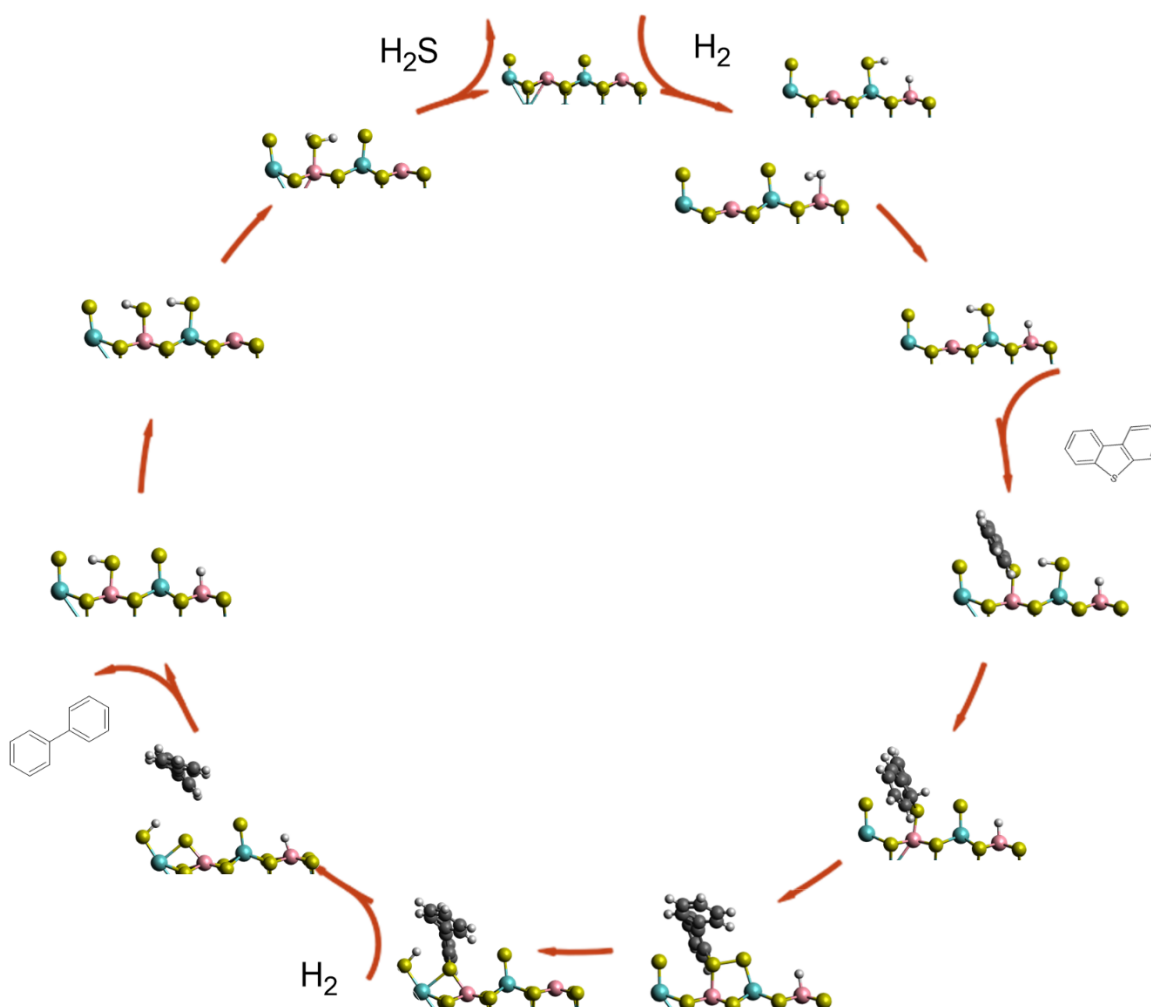


Table 1.

Reaction mechanism and catalytic cycle for direct desulfurization via hydrogenolysis by considering two steps of hydrogenation.

Step	Process	Elementary Step	σ
1	H ₂ Molecular Adsorption	$H_2 + \# \rightleftharpoons H_2^\#$	1
2	Surface dissociation hydrogen	$H_2^\# + * \rightleftharpoons H^\# + H^*$	1
3	Dissociative heterolytic Adsorption	$H_2 + \# + * \rightleftharpoons H^\# + H^*$	1
4	DBT Adsorption	$C_{12}H_8S + \# \rightleftharpoons C_{12}H_8S^\#$	1
5	Monohydrogenation	$C_{12}H_8S^\# + H^* \rightleftharpoons C_{12}H_9S^\# + *$	1
6	Breaking C-S bond	$C_{12}H_9S^\# + * \rightleftharpoons {}^*C_{12}H_9S^\#$	1
7	H diffusion	$H^\# + {}^*C_{12}H_9S^\# + * \rightleftharpoons H^* + C_{12}H_9S^\# + * + \#$	1
8	H ₂ Adsorption	$H_2 + \# + * \rightleftharpoons H^\# + H^*$	1
9	Hydrogenation and desorption	$C_{12}H_9S^\# + H^* \rightleftharpoons BP + S^\# + *$	1
10	HS Formation	$H^* + S^\# \rightleftharpoons SH^\# + *$	1
11	H diffusion	$H^\# + * \rightleftharpoons H^* + \#$	1
12	H ₂ S Formation	$HS^\# + H^* \rightleftharpoons H_2S^\# + *$	1
13	H ₂ S Desorption	$H_2S^\# + \# \rightleftharpoons H_2S^\#$	1
Global reaction			
$C_{12}H_8S + 2H_2 \rightleftharpoons C_{12}H_{10} + H_2S$			

Nota* Key to symbols: # (Co), an unoccupied metal site; * (S), an unoccupied sulfur site and σ is stoichiometric number.

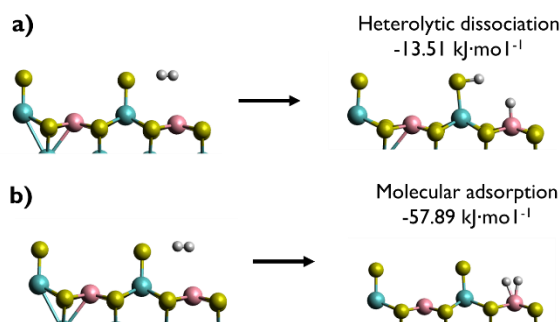
3.2 Hydrogen activation on the CoMoS surface

Hydrogen activation involves two types of adsorptions, the first being molecular adsorption, where hydrogen atoms are adsorbed onto the metal site with an electronic energy (-57.89 kJ·mol⁻¹), and a second consideration, where hydrogen undergoes a cleavage in the gas-phase, to then chemisorb as S-H and Co-H species, exhibiting an energy (-13.51 kJ·mol⁻¹), as illustrated in **Figure 7**. Hydrogen adsorption is often overlooked by most researchers, who assume that hydrogen is already in a dissociated form on the catalyst surface, thereby triggering the

reaction mechanism (Zheng et al., 2021) and, on the other hand, that is type of reaction is endothermic and weakly activated. (Anderson et al., 1988; Travert et al., 2002) However, one of the objectives of our research is to evaluate the possible events that can lead to the desulfurization of dibenzothiophene, so the consideration of this step is important to assess the dynamics of the reaction.

Figure 7.

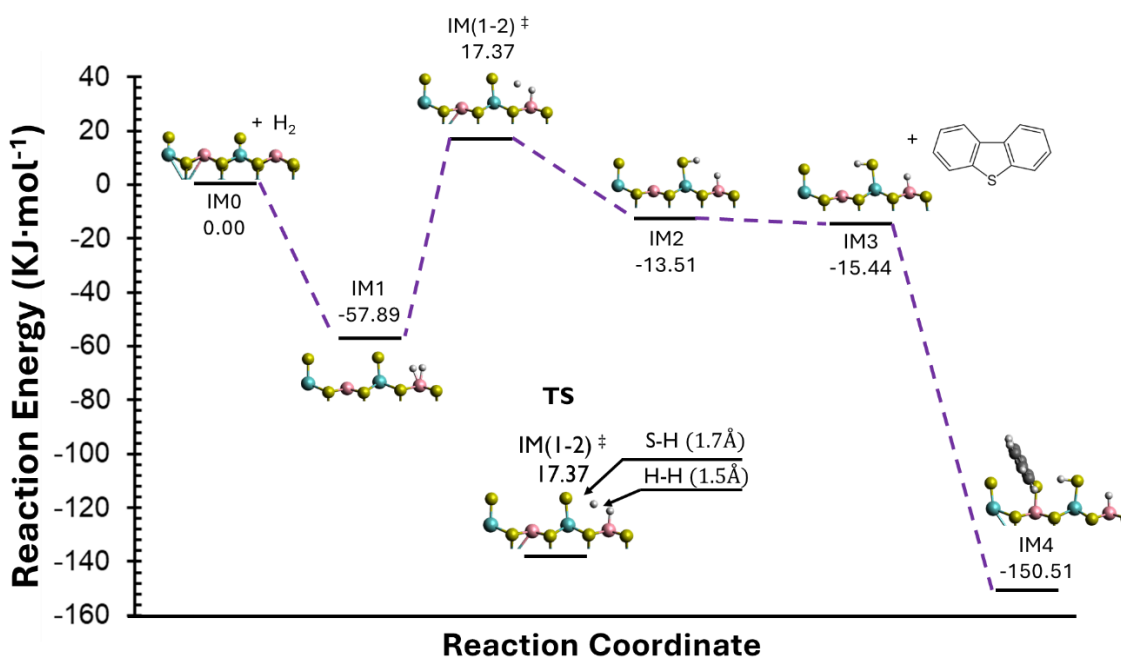
Hydrogen adsorption on CoMoS surface through a) heterolytic dissociation and b) molecular adsorption



Molecular adsorption is electronically more favorable than dissociative adsorption, which can be attributed to the strong affinity that exists on the metal site. However, the surface must be covered with atomic hydrogen to carry out hydrogen transfers to the sulfur-containing organic molecules of the system, and thus achieve sulfur removal. Therefore, we calculated the energy barrier required for molecular adsorption and then calculated the H-H bond cleavage, as shown in **Figure 8**. This process requires overcoming an energy barrier of $75.26 \text{ kJ}\cdot\text{mol}^{-1}$. This may be one of the limits for hydrogen diffusion on the catalyst surface, because electronically molecular adsorption is more likely.

Figure 8.

Potential energy diagram of the hydrogenation of the catalytic surface



3.3 DBT Direct Desulfurization

The potential energy surface diagram presented in **Figure 9** shows the process of obtaining the desulfurized product, biphenyl, as shown in Table 1. After obtaining dissociative adsorption of hydrogen, dibenzothiophene is adsorbed on the cobalt metal site through its sulfur atom, with an electronic energy of approximately -150.52 kJ·mol⁻¹. After dibenzothiophene adsorption on the vacancy, the first hydrogenation occurs towards the aromatic ring of the dibenzothiophene molecule, which has an energetic cost of 179.46 kJ·mol⁻¹, (see **Figure 9**, process between IM4-IM5) which is the highest energy point in the whole catalytic cycle and is assumed to be the rate-determining step.

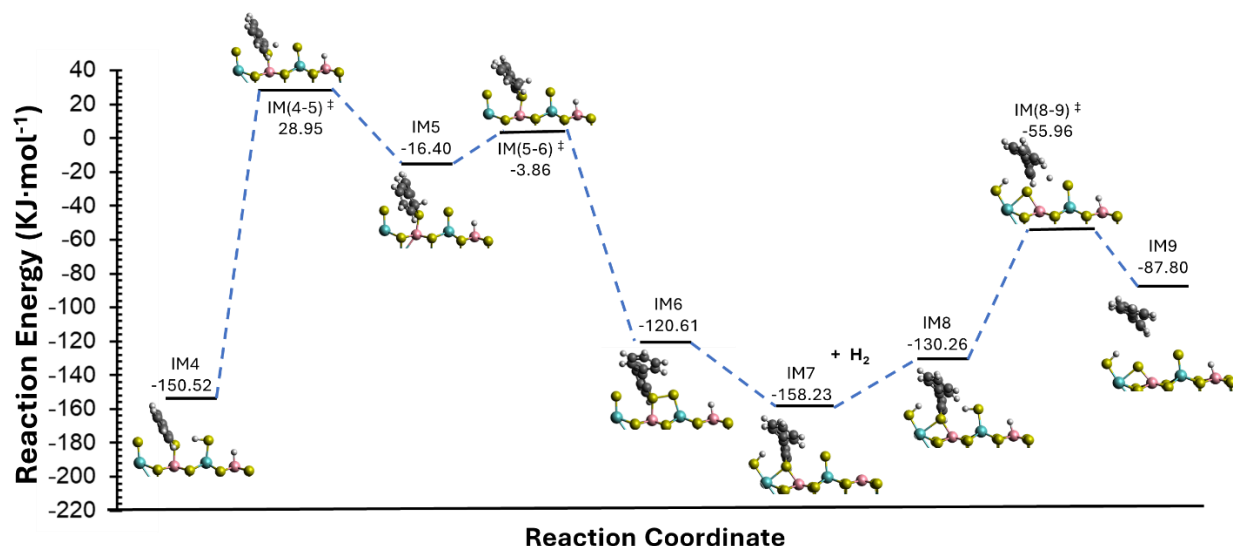
Since dibenzothiophene is found in such a low potential, it can be assumed that large amounts of this component could poison the catalyst surface, hindering the adsorption of different molecules, and in turn, the monohydrogenation, i.e., first hydrogenation toward dibenzothiophene, this would impede the progress of the reaction because it has a very high energy barrier.

Once this energy barrier is overcome, it results in the formation of the monohydrogenated intermediate IM5. This type of intermediate has not been detected in experiments, but according to the energy profile, it can be attributed to the slight energy barrier surrounding this intermediate, which is around $12.54 \text{ kJ}\cdot\text{mol}^{-1}$. This could imply that once the molecule is hydrogenated, it subsequently transforms into the thiophenolate intermediate IM6. The reaction coordinate for this elementary event is the cleavage of the C-S bond, which occurs due to a slight rotation that occurs in the aromatic ring of this species and is stabilized by the formation of a sulfur dimer having a bond length of $2.14 \text{ \AA}$ (S-S) at the catalytic surface. These sulfur dimers have been experimentally observed using the scanning tunneling microscopy technique (Grønborg et al., 2016; Hinnemann et al., 2008; Lauritsen & Besenbacher, 2015; Tuxen et al., 2012) so these types of processes that resemble the IM6 image can limit the coverage of other species. (Morales-Valencia et al., 2021)

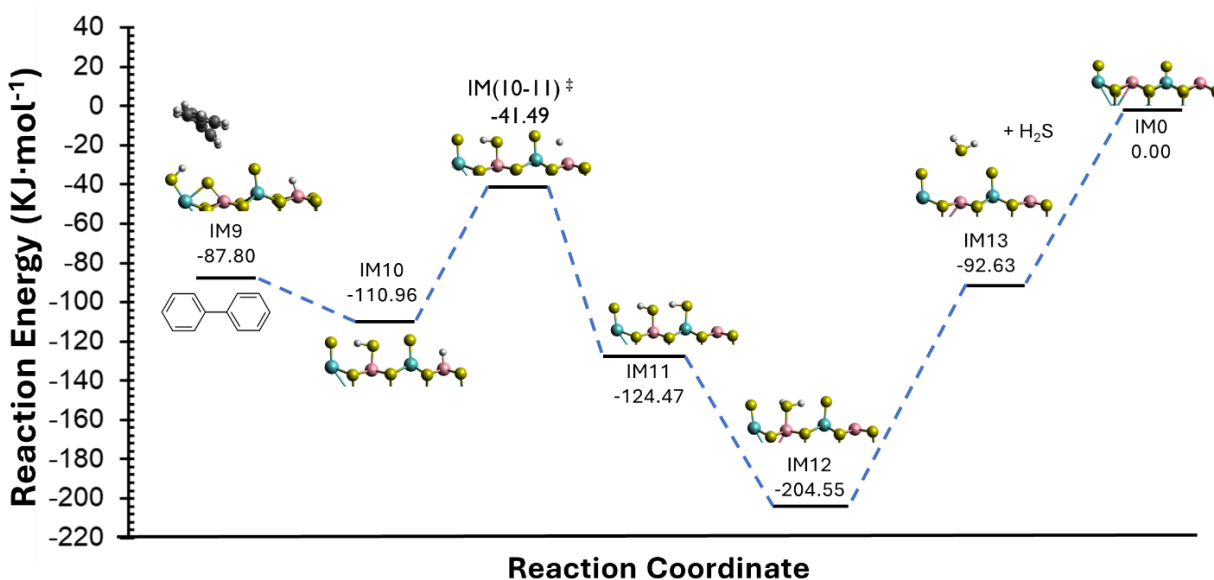
Starting from the formation of thiolate (IM7), it is assumed that the next elementary event requires the second hydrogenation for the desorption of the desulfurized molecule called biphenyl, thus fulfilling the stoichiometry of the reaction, in which two molecules of hydrogen are required to remove the sulfur atom from dibenzothiophene as illustrated in **Figure 9**. For this, the second hydrogenation toward the organosulfur molecule shows an energy barrier exposure of $74.29 \text{ kJ}\cdot\text{mol}^{-1}$, which is very low compared to the first hydrogenation of the dibenzothiophene molecule. This could indicate that the progress of prehydrogenations reduces the energy required for the cleavage of the C-S bond.

Figure 9.

Potential energy diagram of the direct desulfurization pathway for the dibenzothiophene molecule.



Finally, **Figure 10** shows the reaction mechanism aims to unravel the way in which H₂S desorbs and the catalytic cycle of the reaction can be completed. Thus, the diffusion step (step 10, table 1) of hydrogen over the active sites of the catalyst reaches an energy close to 69.47 kJ·mol⁻¹. This energy is probably achieved because, as mentioned above, hydrogen is closely bound to the metallic site. Lastly, the desorption of H₂S shows a significant barrier to have the molecule in the gas phase, which is 111.92 kJ mol⁻¹ (**Figure 10**). The literature lacks a comprehensive description of this desorption process, as several authors assume that the formation of H₂S occurs through the remaining surface atoms of the catalyst. Consequently, their proposed mechanisms do not account for the energies required to form the H₂S molecule, and their diagrams only illustrate the desorption of biphenyl.

Figure 10.*H₂S* desorption from the hydrodesulfurization reaction mechanism of dibenzothiophene

4. Gibbs free energy estimate at reaction conditions

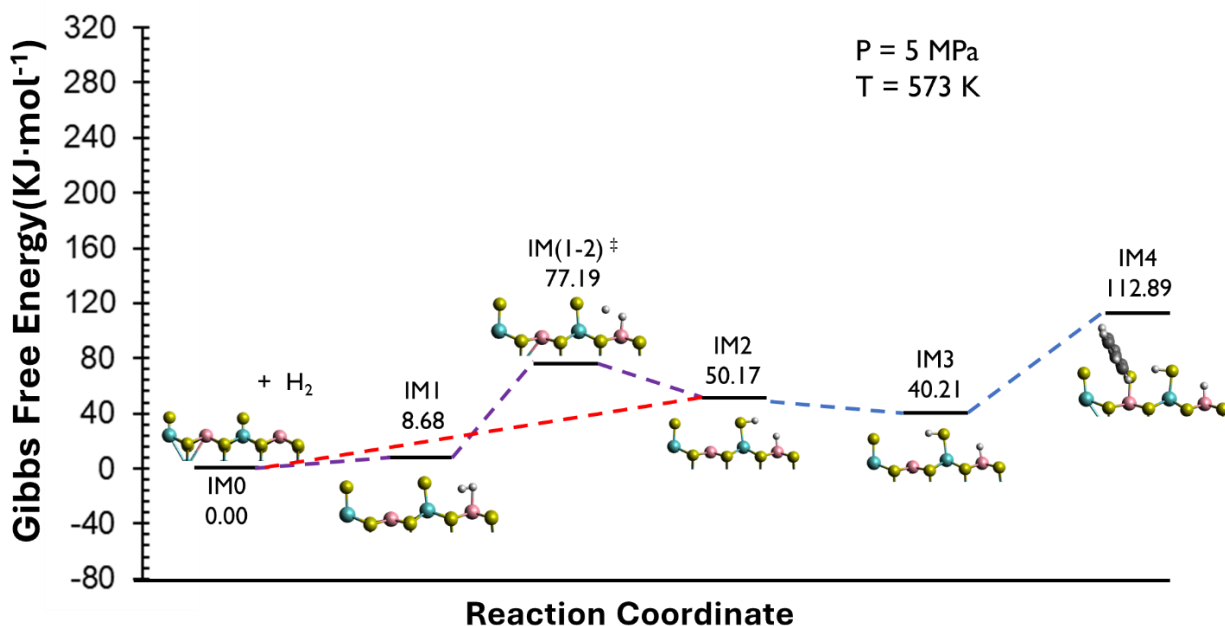
From the transformation of the electronic profile to thermodynamic properties by means of statistical mechanics, its great impact is observed when evaluated under reaction conditions ($P=5\text{Mpa}$ and $T=573\text{ K}$). Entropy and enthalpy calculations are shown in the supplementary information (**Table S2**), as a large part of the system is in an endergonic state, this type of results have been reflected in the work of Zheng et al. (Zheng et al., 2021)

In the **Figure 11**, molecular adsorption continues to have an even higher probability compared to dissociative adsorption. This could indicate a high coverage of hydrogen molecules on the surface. An effective solution to address this problem would be to increase the temperature of the system to accelerate the diffusion of hydrogen atoms on the surface and achieve a stronger

interaction with dibenzothiophene. However, implementing this type of process would involve significant energy costs for the refinery industry.

Figure 11.

Gibbs free energy profile of hydrogen molecule adsorption and dissociative adsorption on a molybdenum disulfide surface promoted by cobalt on sulfur vacancy.

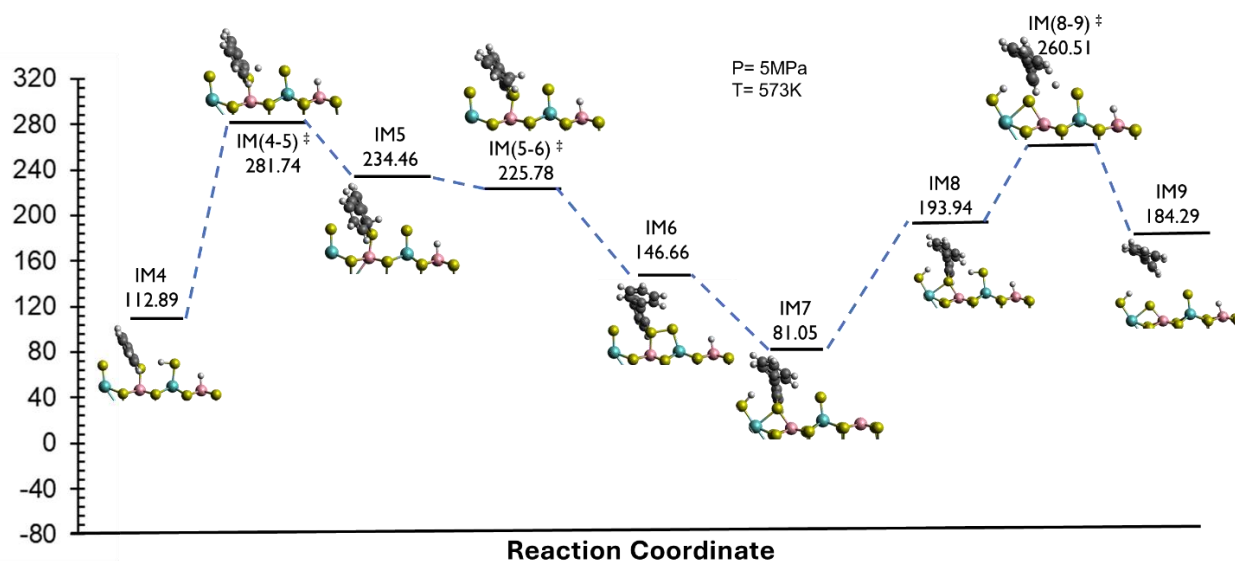


Meanwhile, monohydrogenation (**Figure 12**, IM4 to IM5) remains a bottleneck in the process, although it is affected by enthalpic and entropic contributions from the reaction conditions, it is still the rate-limiting step, suggesting that the dominance of the reaction could be directly related to this elementary step. To overcome the energy barrier of this step, 168.85 kJ mol⁻¹ is required in this work. However, an unexpected factor was the reduction of the energy barrier for step 6, where the cleavage of the C-S bond of the monohydrogenated intermediate (IM5-IM6) occurs. Based on the electronic profile, this intermediate was expected to be stable on the surface (**Figure 9**). However, under thermodynamic effect, hydrogenation apparently destabilizes the

structure of the dibenzothiophene molecule, leading to an immediate cleavage of the C-S bond. This may explain why this monohydrogenated structure has never been observed experimentally. On the other hand, the C-S bond cleavage presents different values in the literature, this is due to the methodology used to perform the electronic calculations and to the estimation of thermodynamic properties. In the work of Zheng et al. (Zheng et al., 2021) they obtained an energy of $173.97 \text{ kJ mol}^{-1}$ did not use the magnetic properties of cobalt in their calculations, which are fundamental for a description of the adsorption energy and consequently, a possible deviation of the energy barrier. Valencia et al. (Valencia et al., 2012) obtained an energy of $318.73 \text{ kJ mol}^{-1}$, they did not consider the presence of the catalyst in their theoretical calculations, so their reactions occur in the gas phase. On the other hand, Weber et al. (Weber & Rob van Veen, 2008) (Weber & Rob van Veen, 2008) calculated this bond cleavage for dibenzothiophene on a NiMoS catalyst and found that it required an energy of $131.38 \text{ kJ mol}^{-1}$ to overcome this energy barrier.

Figure 12.

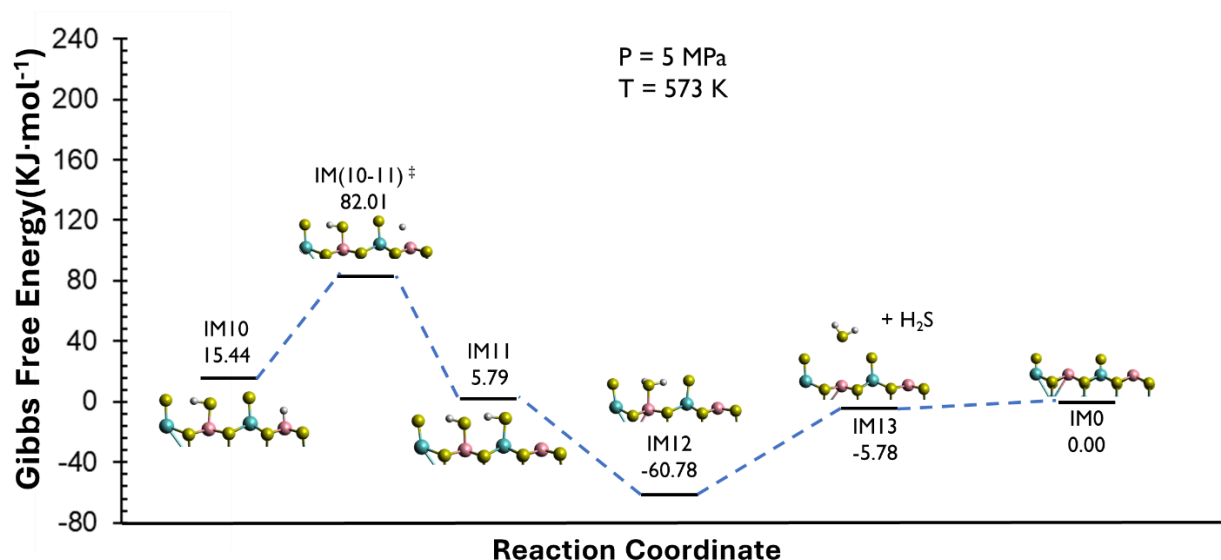
Gibbs free energy profile of dibenzothiophene to biphenyl desulfurization at sulfur vacancy



Finally, the formation of the H_2S molecule occurs as a spontaneous reaction (**Figure 13**). This result shows that at long reaction times, the catalyst surface possibly remains saturated and causes a deactivation of the catalyst. Initially, this inhibition effect of H_2S on the surface has been observed in experimental work, which would imply that this molecule enters to compete for the sites on the surface of the catalyst, preventing the adsorption of other species.

Figure 13.

Gibbs free energy profile for hydrogen sulfide formation in sulfur vacancy.



These exhaustive and systematic calculations allow us to gain insight into this type of hydrodesulfurization processes, as the electronic profile only shows us a stable form of the species, and a thermodynamic profile allows us to see what possible implications the system has under typical conditions. However, these calculations do not consider the dynamics of the system or the interaction of elementary events, so it is necessary to have a clearer view of the reaction by applying other methodologies.

5. Microkinetic model

A microkinetic model will allow us to break the barrier between static calculations and an interaction between elementary events, so this tool gives a detailed understanding of the system through the dominant reaction steps limiting steps, coverages, among others, this from the reaction rates of microscopic events. From the estimations of the rate constants, the Langmuir-Hinshelwood formalism was applied for the reaction mechanism presented in Table 2, where the number of postulated elementary events was reduced. In this case, the monohydrogenation of dibenzothiophene until the formation of thiophenolate (step 5-7, Table 1) was taken as a single elementary event, due to the low energy barrier of the step 6 (12.54 kJ mol⁻¹) and the electronic stability of the intermediate IM7. On the other hand, two types of active sites were considered, (#) indicating the cobalt sites and (*) for the sulfur sites. The reaction rate constant of the n-th step was expressed by arithmetic substitution of the inverse reaction rate constant (k_n^{rev}) which is related by the direct reaction rate constant (k_n^{fwd}) and the reaction equilibrium coefficient (K_n).

$$k_n^{rev} = \frac{k_n^{fwd}}{K_n} = \frac{k_n}{K_n} \quad \text{Eq (18)}$$

Table 2.

Calculation of the direct and inverse reaction constants at the reaction conditions of $P = 5\text{Mpa}$ and $T = 573\text{K}$

Step	Process	$k^{fwd} (\text{s}^{-1})$	$k^{rev} (\text{s}^{-1})$
1	H ₂ Molecular Adsorption	3.84E+07	5.38E+06
2	Surface dissociation hydrogen	9.74E+08	4.32E+10
3	Dissociative heterolytic dsorption	1.21E+07	5.38E+10
4	DBT Adsorption	9.74E+08	2.05E+15
5*	Monohydrogenation	2.26E-03	5.90E-05
6	hydrogenation and desorption	6.71E+05	2.37E+00
7	HS Formation	1.49E+07	1.66E+06
8	H diffusion	9.02E+11	9.25E+06

9	H ₂ S Formation	1.30E+07	2.37E+08
10	H ₂ S Desorption	3.84E+07	5.38E+06

Nota. 5* combination of steps 5-7 respect to Table 1.

The pseudo-steady state approximation was applied for the coverage of the intermediates in the system, implying that their net production rate is equal to zero, thus obtaining the differential algebraic equations (or DAE) presented below:

$$\frac{dF_{H_2}}{dw^*} = -k_1 \frac{P_{H_2}}{P_0} [\theta^\#] + \frac{k_1}{K_1} [\theta_{H_2^\#}] - k_3 P_{H_2} [\theta^\#] [\theta^*] + \frac{k_3}{K_3} [\theta_{H^*}] [\theta_{H^\#}] \quad \text{Eq (19)}$$

$$\frac{dF_{C_{12}H_8S}}{dw^*} = k_4 \frac{P_{C_{12}H_8S}}{P_0} [\theta^\#] - \frac{k_4}{K_4} [\theta_{C_{12}H_8S^\#}] \quad \text{Eq (20)}$$

$$\frac{dF_{H_2S}}{dw^*} = k_{10} [\theta_{H_2S^\#}] - \frac{k_{10}}{K_{10}} \frac{P_{H_2S}}{P_0} [\theta^\#] \quad \text{Eq (21)}$$

$$\frac{dF_{BP}}{dw^*} = k_6 [\theta_{C_{12}H_9S^\#}] [\theta_{H^*}] - \frac{k_6}{K_6} \frac{P_{BP}}{P_0} [\theta_{S^\#}] [\theta^*] \quad \text{Eq (22)}$$

$$\frac{d\theta_{C_{12}H_8S^\#}}{dt} = 0 = k_4 \frac{P_{C_{12}H_8S}}{P_0} [\theta^\#] - \frac{k_4}{K_4} [\theta_{C_{12}H_8S^\#}] \quad \text{Eq (23)}$$

$$\frac{d\theta_{H_2^\#}}{dt} = 0 = k_1 \frac{P_{H_2}}{P_0} [\theta^\#] - \frac{k_1}{K_1} [\theta_{H_2^\#}] \quad \text{Eq (24)}$$

$$\begin{aligned} \frac{d\theta_{C_{12}H_9S^\#}}{dt} = 0 = & k_5 [\theta_{C_{12}H_8S^\#}] [\theta_{H^*}] [\theta_{H^\#}] - \frac{k_5}{K_5} [\theta_{C_{12}H_9S^\#}] [\theta_{H^*}] [\theta^\#] \\ & - k_6 [\theta_{C_{12}H_9S^\#}] [\theta_{H^*}] + \frac{k_6}{K_6} \frac{P_{BP}}{P_0} [\theta_{S^\#}] [\theta^*] \end{aligned} \quad \text{Eq (25)}$$

$$\begin{aligned} \frac{d\theta_{S^\#}}{dt} = 0 = & k_6 [\theta_{C_{12}H_9S^\#}] [\theta_{H^*}] - \frac{k_6 P_{BP}}{K_6 P_0} [\theta_{S^\#}] [\theta^*] - k_7 [\theta_{H^*}] [\theta_{S^\#}] \\ & + \frac{k_7}{K_7} [\theta_{HS^\#}] [\theta^*] \end{aligned} \quad \text{Eq (26)}$$

$$\begin{aligned} \frac{d\theta_{HS^\#}}{dt} = 0 = & k_7 [\theta_{H^*}] [\theta_{S^\#}] - \frac{k_7}{K_7} [\theta_{HS^\#}] [\theta^*] - k_9 [\theta_{H^*}] [\theta_{HS^\#}] \\ & + \frac{k_9}{K_9} [\theta_{H_2S^\#}] [\theta_{H^*}] \end{aligned} \quad \text{Eq (27)}$$

$$\begin{aligned} \frac{d\theta_{H^*}}{dt} = 0 = & k_2 [\theta_{H_2^\#}] [\theta^*] - \frac{k_2}{K_2} [\theta_{H^*}] [\theta_{H^\#}] + k_3 \frac{P_{H_2}}{P_0} [\theta^\#] [\theta^*] - \frac{k_3}{K_3} [\theta_{H^*}] [\theta_{H^\#}] \\ & - k_5 [\theta_{C_{12}H_8S}] [\theta_{H^*}] [\theta_{H^\#}] + \frac{k_5}{K_5} [\theta_{C_{12}H_9S^\#}] [\theta_{H^*}] [\theta^\#] - k_8 [\theta_{H^\#}] [\theta^*] \\ & + \frac{k_8}{K_8} [\theta_{H^\#}] [\theta^\#] \end{aligned} \quad \text{Eq (28)}$$

$$\begin{aligned} \frac{d\theta_H^*}{dt} = 0 = & k_2 [\theta_{H_2^\#}] [\theta^*] - \frac{k_2}{K_2} [\theta_{H^*}] [\theta_{H^\#}] + k_3 \frac{P_{H_2}}{P_0} [\theta^\#] [\theta^*] - \frac{k_3}{K_3} [\theta_{H^*}] [\theta_{H^\#}] \\ & - k_6 [\theta_{C_{12}H_9S^\#}] [\theta_{H^*}] + \frac{k_6 P_{BP}}{K_6 P_0} [\theta_{S^\#}] [\theta^*] - k_7 [\theta_{S^\#}] [\theta_{H^*}] \\ & + \frac{k_7}{K_7} [\theta_{HS^\#}] [\theta^*] + k_8 [\theta_{H^\#}] [\theta^*] - \frac{k_8}{K_8} [\theta_{H^\#}] [\theta^\#] - k_9 [\theta_{H^*}] [\theta_{HS^\#}] \\ & + \frac{k_9}{K_9} [\theta_{H_2S^\#}] [\theta_{H^*}] \end{aligned} \quad \text{Eq (29)}$$

$$\frac{d\theta_{H_2S^\#}}{dt} = 0 = k_9 [\theta_{H^*}] [\theta_{HS^\#}] + \frac{k_9}{K_9} [\theta_{H_2S^\#}] [\theta_{H^*}] - k_{10} [\theta_{H_2S^\#}] - \frac{k_{10} P_{H_2S}}{K_{10} P_0} [\theta^\#] \quad \text{Eq (30)}$$

Where F_i is the molar flow of i-th gas-phase species, $\theta_{i^\#}$ and θ_{i^*} are coverages the i-th surface species over the cobalt sites (#) and the sulfur sites (*), respectively, and w^* is the mass of catalyst multiplied by concentration of active sites. The concentration of active sites in CoMoS-

based catalysts generally refers to the surface concentration of the CoMoS phase which value range between 50-150 $\mu\text{mol g}^{-1}$ as determined through surface characterization techniques such as XPS and STM. Therefore, a value of 50 $\mu\text{mol g}^{-1}$ was deemed suitable for the microkinetic analysis. The reaction rate constants and equilibrium constant were defined as a function of temperature through the Arrhenius and van't Hoff equations, respectively:

$$k_n = A_n e^{-\left(\frac{E_{a,n}}{RT}\right)} \quad \text{Eq (31)}$$

$$K_n = e^{-\left(\frac{\Delta H_n^\circ}{RT}\right)} e^{\left(\frac{\Delta S_n^\circ}{R}\right)} \quad \text{Eq (32)}$$

where for the n-th reaction, A_n is the pre-exponential factor, $E_{a,n}$ is the activation energy, ΔS_n° is the standard reaction or adsorption entropy, ΔH_n° is the standard reaction or adsorption enthalpy, T is the reaction temperature, and R is the universal gas constant.

5.1 Evaluation of the microkinetic model

In the simulation of the direct desulfurization reaction, the system pressure, the temperature and concentration of the reactants and products were varied in order to observe the influence on the reaction kinetics. However, the large energy barrier that represents the monohydrogenation step ($179.46 \text{ kJ}\cdot\text{mol}^{-1}$) limited the execution of the simulation. As presented in Table 2, this step has a reaction rate constant of 10^8 - 10^{14} s^{-1} lower compared to the other microscopic events. Therefore, it was necessary to reduce the activation energy barrier of this step to perform the microkinetic simulation. The reduction of the energy barrier was done according to the experimental values reported in the literature, which are between 60 and 163 kJ mol^{-1} . (Doukeh et al., 2019; Gachet et al., 1982; Lamure-Meille et al., 1995; O'Brien et al., 1986; Rolf Edvinsson, 1993; Singhal, Espino, Sobel, et al., 1981; Vrinat, 1983) The reduction of the energy barrier may imply that another elementary reaction step takes priority over the mechanism. To avoid this issue,

the following strategies was employed: The first one consisted in performing a variation of the activation energy at isoconversion, i.e., the conversion was kept constant in about 2% in the differential kinetic regime, in order to alleviate the thermodynamic effects that impact the reaction mechanism, then the degree of rate control calculation (DRC) was performed. This method consists of determining the influence of the kinetic constants of the elementary steps on the global reaction rate (r), in this way it is possible to define what the rate determining steps would be, through the following expression (Campbell, 2017; Stegelmann et al., 2009):

$$X_{RC,n} = \frac{k_i}{r} \left(\frac{\partial r}{\partial k_n} \right)_{k_{m \neq n}, K_i} = \left(\frac{\partial \ln r}{\partial \ln k_n} \right)_{k_{m \neq n}, K_n} \quad \text{Eq (33)}$$

$$X_{RC,n} = \left(\frac{\partial \ln r}{\partial \ln k_n} \right)_{k_{m \neq n}, K_n} \approx \left[\frac{\ln \left(\frac{r}{r_o} \right)}{\ln \left(\frac{k_n}{k_{n,o}} \right)} \right]_{k_{m \neq n}, K_n} \quad \text{Eq (34)}$$

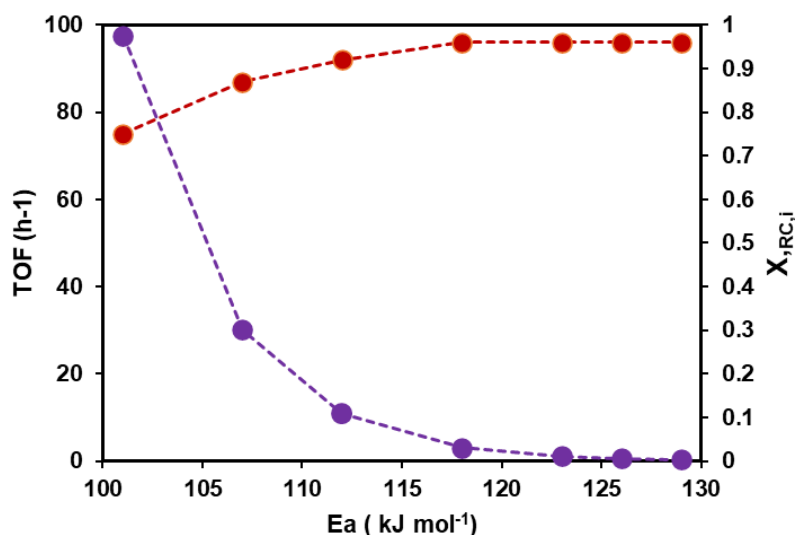
Where, k_m ($n \neq m$) indicates the other rate constants which together the equilibrium constants K_n must remain constant, implying that when adjusting the forward reaction constant of any elementary step, its inverse constant must be affected by the same value, so that the ratio between constants remains equivalent. In this case, the original rate constants ($k_{n,o}$) were increased by 10%, resulting in a new rate constant value (k_n) and consequently, the original global reaction rate ($r_{n,o}$) changes to a new value (r_n). The values that $X_{RC,i}$ can take are between -1 and 1. A positive value indicates that by increasing k_n , the reaction rate r_n will increase and the steps are called rate determining steps, while a negative value indicates the opposite, and are called inhibition steps, if the value of $X_{RC,i}$ becomes zero, it means that the evaluated event has no significant effect on the reaction.

Figure 14 shows the results of this procedure, as observed an activation energy greater than or equal to 118.0 kJ mol⁻¹ is required to ensure that the monohydrogenation step remains the

rate-limiting step, thus there is no repercussion on the nature of the reaction mechanism. Therefore, it was selected a value of $126.0 \text{ kJ mol}^{-1}$ to perform the simulation, this value is 30% lower than original value of $179.46 \text{ kJ mol}^{-1}$, values higher than this activation energy led to the TOF values to decay to zero.

Figure 14.

Degree of rate control analysis for determination of the new activation energy.



In this case, different reaction conditions were evaluated based on the values reported in the literature, where typically the temperature and total pressure range between 523-623K and 4-6 MPa, respectively. (Ali et al., 2012; Braggio et al., 2019; Dorneles de Mello et al., 2018; Dorneles De Mello et al., 2017; Morales-valencia et al., 2018) In **Figure 15**, the effect of the reactants partial pressure on the TOF is plotted. As can be seen, increasing the pressure of dibenzothiophene from 2.6 to 36 kPa (**Figure 15a**) increased the TOF value from 0.02 to 0.27 h^{-1} at 533 K, from 0.03 to 0.42 h^{-1} at 553K, from 0.04 to 0.59 h^{-1} at 573 K, from 0.05 to 0.74 h^{-1} at 593 K, from 0.06 to 0.87 h^{-1} at 613K. It is notable that an increase in temperature favors the kinetics of the reaction;

in agreement with the experimental evidence reported in the literature.(Broderick & Gates, 1981; Gachet et al., 1982) On the other hand, the effect of hydrogen pressure is also a key factor to understand how it influence over the overall reaction. To facilitate analysis, the results are presented in terms of the pseudo-first-order rate constant (k_{DBT}) in order to normalize the effect of dibenzothiophene pressure on turnover frequency, i.e., $TOF/P_{DBT} = k_{DBT}f(P_{H_2}, P_{H_2S}, P_{BP}, \dots)$. In this sense, **Figure 15b** shows the impact of H_2 partial pressure on the pseudo-first-order rate, as observed, increase the H_2 pressure from 3.0 to 3.6 MPa between 533-573K did not affect the value of k_{DBT} , in specific, the average values were $0.084 \text{ (h kPa)}^{-1}$, $0.013 \text{ (h kPa)}^{-1}$ and $0.017 \text{ (h kPa)}^{-1}$ at 533K, 553K and 573K, respectively. While the value of k_{DBT} increased from 0.019 to $0.022 \text{ (h kPa)}^{-1}$ and 0.022 to $0.026 \text{ (h kPa)}^{-1}$ at 593 and 613K, respectively.

Figure 15.

Effect of the partial pressure of the reactants on the pseudo-first-order rate constant for the temperature range from 533 to 613K. (a) Effect of dibenzothiophene pressure from 2.6 to 36 kPa at H_2 pressure of 3.6 MPa and (b) effect of hydrogen pressure from 3.0 to 3.6 MPa.

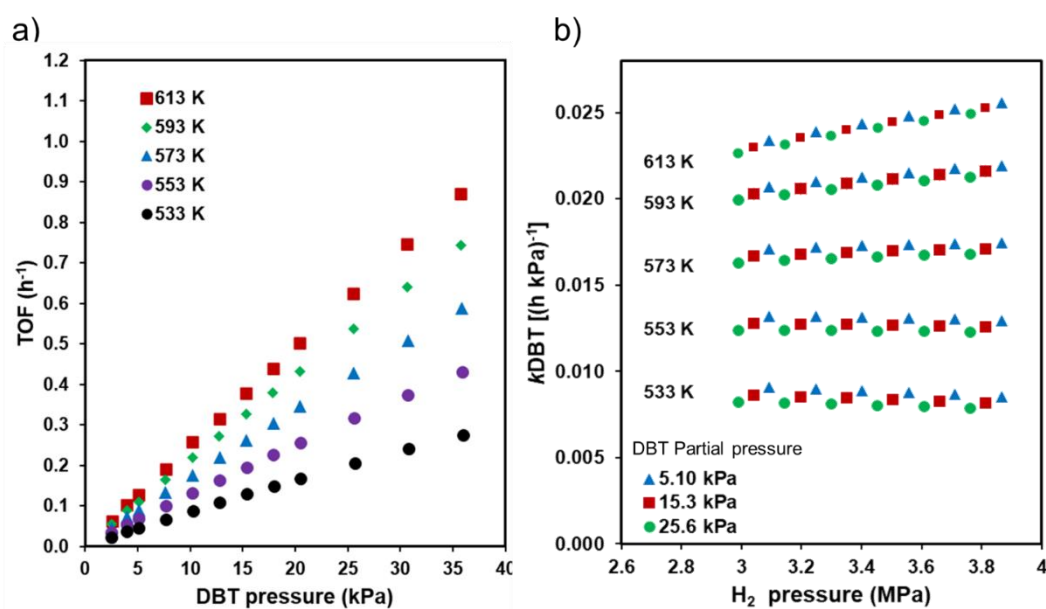


Figure 16 shows the influence of the products partial pressure on the k_{DBT} . Increasing the pressure of biphenyl from 0.35 to 7.8 kPa (**Figure 16a**), did not affect k_{DBT} values for all temperature evaluated, i.e., the pseudo-first-order rate constant is zero-order respect to biphenyl pressure. In agreement with other studies which have found that the hydrogenation pathway of DBT is not influenced by the presence of biphenyl.(Broderick et al., 1982; Sapre, 1998) On the contrary, when the partial pressure of H_2S was increased (**Figure 16b**), from 0.34 to 7.7 kPa, k_{DBT} decreased from 0.007 to 0.001 at 533K, from 0.011 to 0.003 at 553 K, from 0.016 to 0.006 at 573 K, from 0.021 to 0.011 at 593K and from 0.024 to 0.016 at 613 K, respectively, in close agreement with the reported the literature.(Doukeh et al., 2019; Egorova & Prins, 2004b; Kabe et al., 2001) This sulfur inhibition is due to two main factors: strong competitive adsorption on the cobalt active sites of the catalyst and the increase in the reverse reaction rate of the steps involved in the formation of the species H_2S , HS and S .

Figure 16.

Effect of partial pressure of the products on the pseudo-first-order rate constant for the temperature range 533 to 613K. (a) Effect of biphenyl pressure from 0.35 to 7.8 kPa and (b) effect of H_2S pressure from 0.34 to 7.7 kPa. For both cases the H_2 pressure were 3.6 MPa.

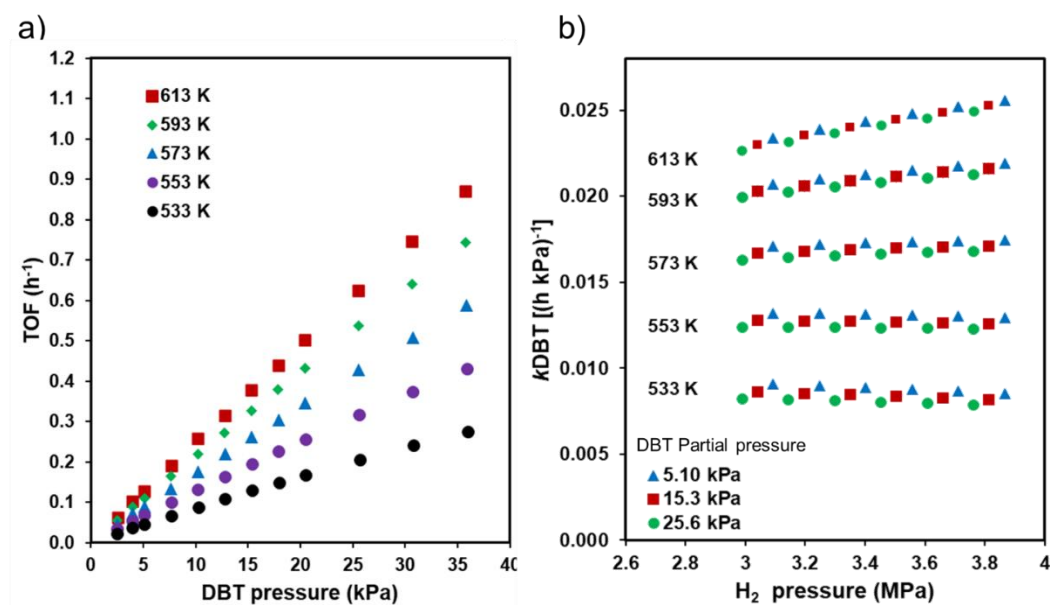
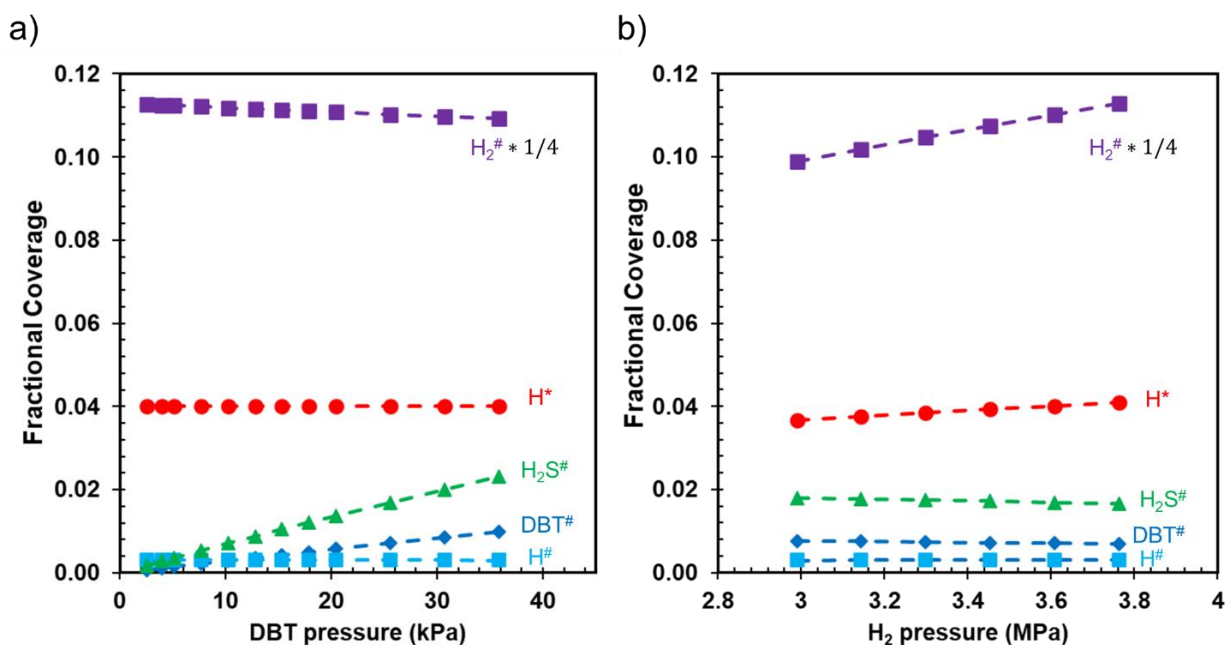


Figure 17 shows the surface coverages of the reaction intermediate species. In this case, it was necessary to reduce the value of the molecular hydrogen coverage by $\frac{1}{4}$ due to its high coverage in order to appreciate that of the other species. On the other hand, species such as thiophenolate, HS and S were not taken into account for the analysis because of they presented coverages lower than 10^{-4} . **Figure 17a** shows that by increasing the dibenzothiophene pressure from 2.6 to 36 kPa at 573K, there is an increase in the dibenzothiophene coverage from 0.001 to 0.010, and in the H_2S coverage from 0.002 to 0.023, while there is a slight decrease in the molecular hydrogen coverage from 0.111 to 0.109. In **Figure 17b**, the increase in H_2 pressure from 3.0 to 3.8 MPa lead to an increase in the molecular hydrogen surface coverage from 0.396 to 0.451.

Figure 17.

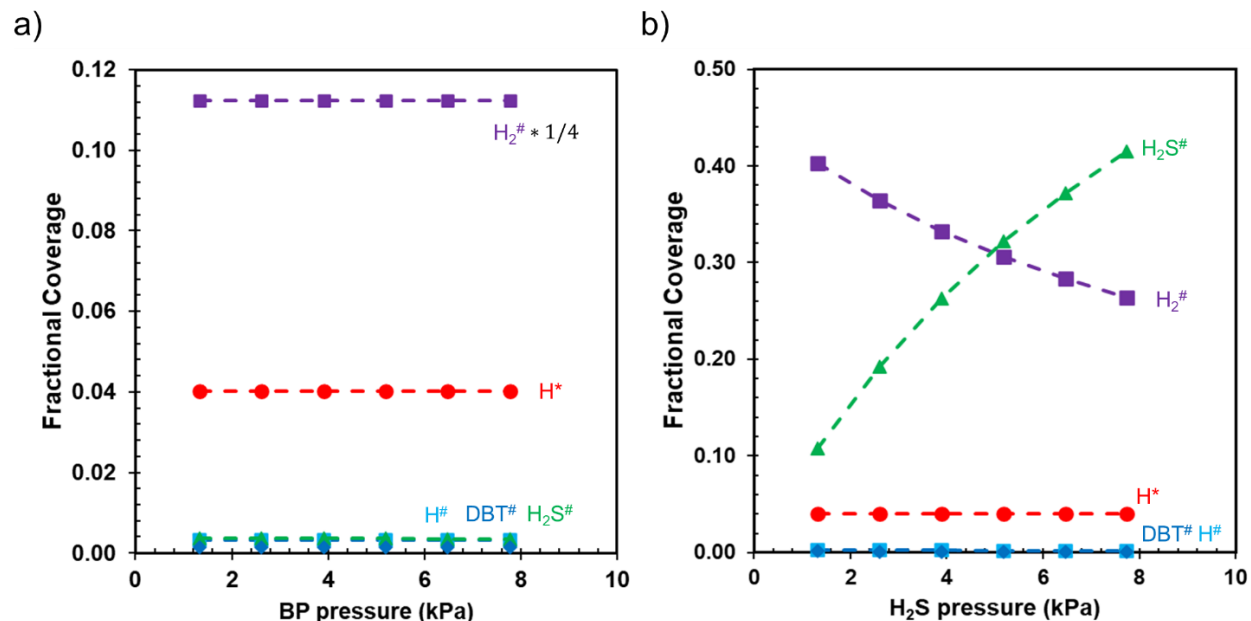
Calculated surface coverage at different reactant partial pressure and 573K. (a) Effect of dibenzothiophene pressure 2.6 to 36 kPa at 3.6 MPa H_2 and (b) effect of hydrogen pressure 3.0 to 3.6 MPa at 5.1 kPa DBT.



In **Figure 18**, the products participate as co-fed in the reaction. Increasing the biphenyl pressure from 0.35 to 7.8 kPa (**Figure 18a**), did not have a significant effect on the coverage of the other intermediate species, which explains why the first order constant is of order zero with respect to the partial pressure of this product (**Figure 16a**). On the contrary, when H_2S is co-feeding (**Figure 18b**) a significant effect on the catalytic surface is shown, the H_2S coverage increase from 0.108 to 0.415. while the molecular hydrogen coverage decreases from 0.402 to 0.263 due to this sulfur inhibition effect.

Figure 18.

Calculated surface coverage by partial pressure effect of products (a) effect of biphenyl pressure from 0.35 to 7.7 kPa, 3.6 Mpa H₂, 5.1kPa DBT b) effect of H₂S pressure from 0.34 to 7.7, Mpa H₂, 5.1kPa DBT, total pressure 5MPa and 573K.



In general, the microkinetic model provided us with a tool to analyze how the temperature and pressure of the system affect the surface coverage of the compounds in a steady state. Furthermore, we confirmed that the initial cleavage of the C-S bond is the determining rate step and that molecular adsorption is the most abundant intermediate on the catalytic surface. In the next section, we used kinetic Monte Carlo to visualize the spatial distribution of reactants at a specific time on the catalyst surface. This approach allowed us to generate a more complete and accurate representation of the catalyst surface.

6. Kinetic Monte Carlo Simulation

The hydrodesulfurization of dibenzothiophene was simulated in a lattice that considers the cobalt (topCo) and sulfur (topS) sites, as proposed in the DFT and microkinetic calculations, the lattice used in our simulations is shown in **Figure 4**. However, there is a disparity in the rate constants of the explored reactions pathway, in specific, the reaction rate constant of the monohydrogenation is between 10^8 - 10^{14} s⁻¹ lower than the other steps (Table 2). According to Monte Carlo kinetics, the higher the reaction constant, the higher the probability that reaction step will take place. Hence making these simulations require long computational hours to reach the steady state condition. There are events such as diffusion and in some cases adsorption/desorption steps take priority during the simulation because they are so fast and not allow for other steps occur.

6.1 Scale factor

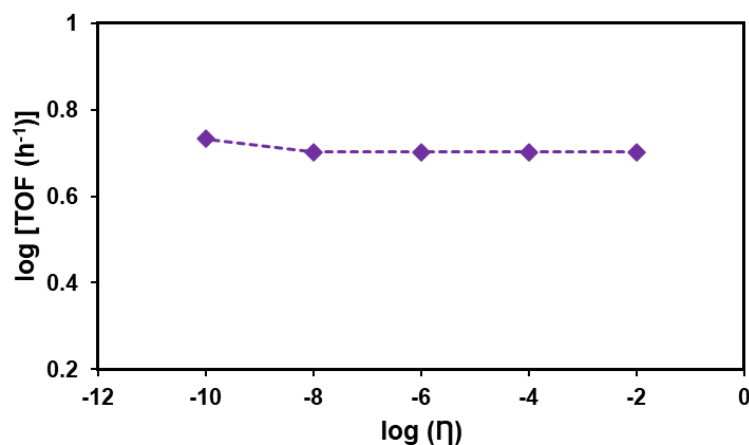
We have employed a manual scaling approach, where the rate constants of the fastest elementary events are multiplied by a scaling factor (Ω) to reduce simulation time and computational cost associated with executing the reaction mechanism.(Chatterjee & Voter, 2010; Dybeck et al., 2017) The rate constants should be lowered to an order of magnitude of the slowest processes, but it should remain in quasi-equilibrium and fast. These strategies have been developed to get algorithms to solve this issue of time disparity in algorithmic executions. (Piccinin & Stamatakis, 2014; Prats et al., 2018; Michail Stamatakis & Vlachos, 2011b; Yang et al., 2013b)

Considering the above, calculations were implemented to see the impact of the scale factor on the system (**Figure 19**). In this case, we reduced the rate constant of biphenyl desorption progressively to identify, which was the point where the model is not affected by these changes

and thus decrease the simulation time. Therefore, when we start to decrease the scale factor from 10^{-2} to 10^{-10} , there was only a change in the net reaction rate for the order of 10^{-10} this is equivalent to 5.40 h^{-1} , however for scales larger than this value the turnover frequency (TOF) remains constant at 5.04 h^{-1} . Therefore, it was selected a scaling factor of 10^{-8} for this elementary event without altering the result of the catalytic activity of the system, this behavior what observed for other reaction steps whose scaling factors range from 10^{-9} to 10^{-2} (Table 3).

Figure 19.

Biphenyl production as a function of scale factor (Γ). Simulations performed at $T = 573\text{K}$, $P_{DBT} = 36 \text{ kPa}$ and $P_{H_2} = 3.6 \text{ MPa}$.



The elementary events such as adsorptions, desorptions, and diffusions were modified by a scaling factor value lower than 10^{-8} , since higher values did not allow to system show any response. Indeed, when the simulation was carried out with the original values of the rate constants (Table 2), the system showed the first molecule of biphenyl or H_2S after one month of simulation.

Table 3.

Modification of the reaction constant for elementary events of the reaction mechanism.

Process	Log η
H ₂ Molecular Adsorption	-8
Surface dissociation hydrogen	-9
Dissociative heterolytic Adsorption	-9
DBT Adsorption	-9
hydrogenation and desorption	-2
H diffusion	-9

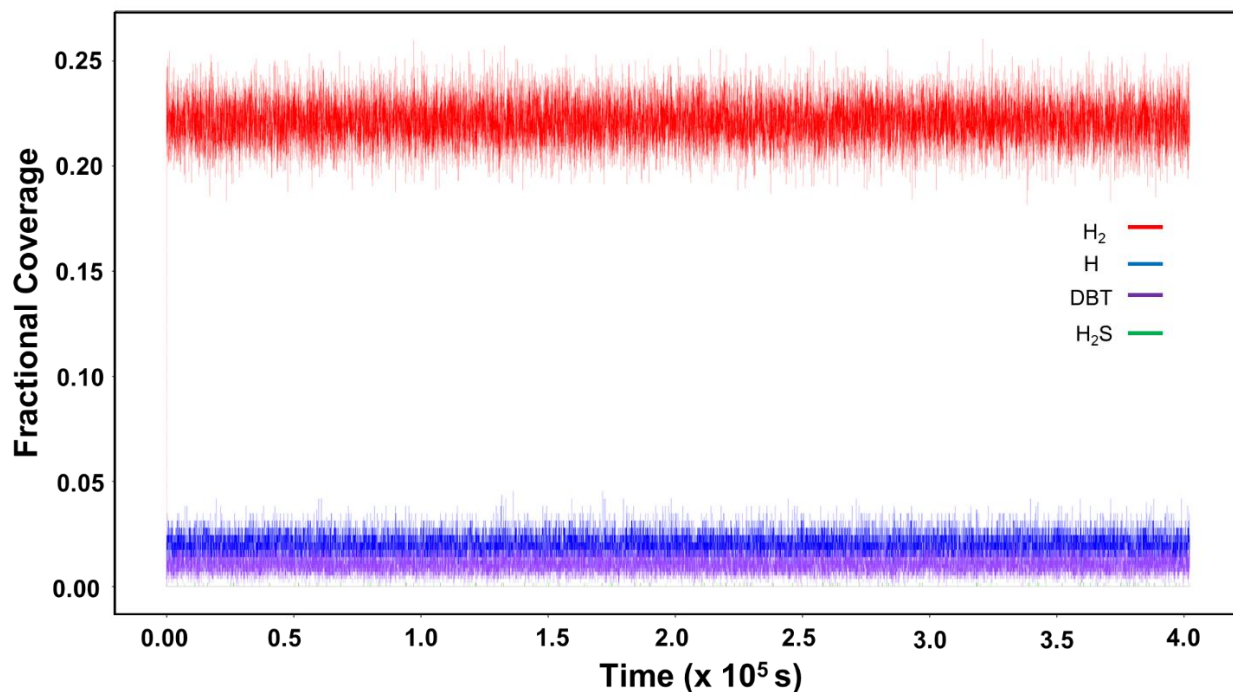
One way to verify if the manual scaling was effective is to have a point of comparison with another type of technique, in our case, we decided to make the comparison with the microkinetic evaluation, in this way we can know by means of trends if the effectiveness of the constant reduction in the KMC simulation shows the same behavior in both techniques. Each simulation point was performed in triplicate, and then the average of the replicates was taken, and a percentage error of the data set was performed.

6.2 Influence of partial pressure of reactants and products on simulation.

Figure 20 shows the time evolution of the surface coverages at $T=573$ K, $P_{\text{DBT}} = 36$ kPa, $P_{\text{H}_2} = 3.6$ Mpa, whose values are 0.22, 0.02, 0.01, 0.01 for H₂, H, DBT, H₂S, respectively. Hence, H₂ is the most abundant species on the surface, in agreement with the results obtained by microkinetics (**Figure 16**).

Figure 20.

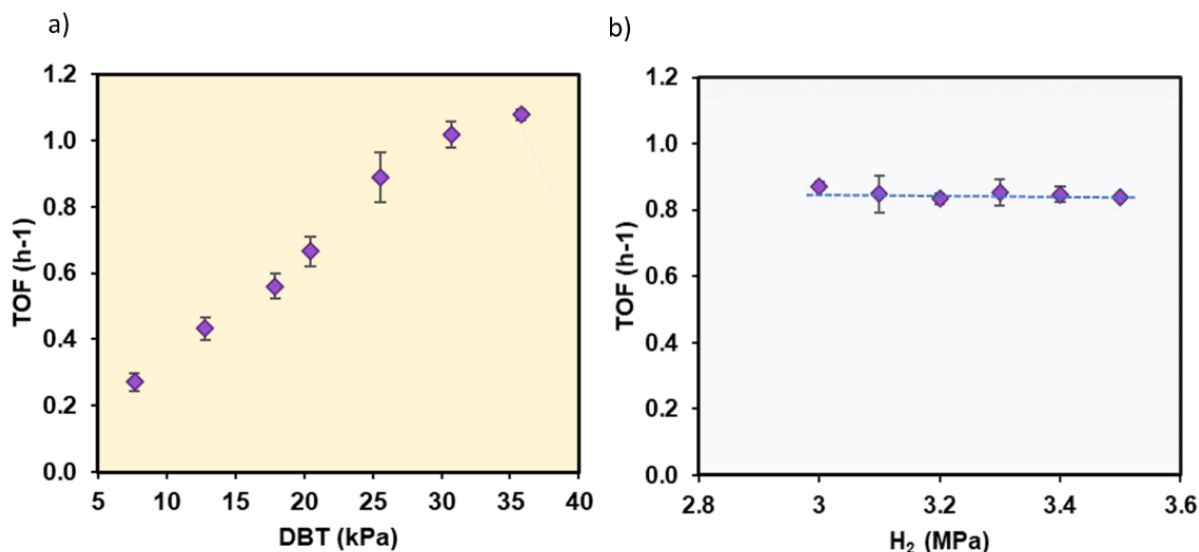
Temporal evolution of intermediate species coverage at a temperature of 573 K, $P_{DBT} = 25.6$ kPa and $P_{H_2} = 3.6$ MPa.



On the other hand, **Figure 21** presents the effect of the partial pressure of the reactants on the reaction rate at a temperature of 573 K. By increasing the DBT pressure, from 7.7 kPa 36 KPa, and setting the hydrogen pressure to 3.6 MPa (**Figure 21a**), increases TOF value, from 0.27 ± 0.03 to 1.08 ± 0.02 h^{-1} , the kinetic effect agrees directly with the simulations performed under the microkinetic model and the experimental data shown by Broderick (Broderick & Gates, 1981) On the other hand, by increasing the value of hydrogen pressure from 2.6 to 3.5 MPa (**Figure 21b**) at a constant 25.6 kPa pressure of dibenzothiophene, the TOF value remains constant at an average of 0.85 ± 0.03 h^{-1} , since the excess that exists of this species is too large to see a significant influence of this reactant.

Figure 21.

Effect of reactant pressure on net reaction rate at a temperature equal to 573K in kinetic Monte Carlo simulation a) effect of dibenzothiophene pressure from 7.7kPa to 36 kPa, 3.6 MPa H₂ b) effect of H₂ pressure from 3.0 to 3.5 MPa, 25.6 kPa DBT. All points in the simulations were done in triplicate.



One of the main advantages of the kinetic Monte Carlo simulation is to be able to visualize the distribution of the species, which allows to understand how the molecules are located on the surface. **Figure 22** illustrates the distributions of the species in steady state over the catalytic surface. According to the microkinetics and the electronic energy profile, the adsorption of molecular hydrogen could occur at high coverages, and the Monte Carlo simulation graphically represents this effect. However, not taking into account the interaction between adsorbate-adsorbate, does not allow having a more detailed kinetics of the surface events, so it is possible that the interaction between hydrogen molecules could make more sites available to adsorb other species involved in the process.

Figure 22.

Representation of the catalytic surface in steady state at reaction conditions of $P_{DBT} = 25.6$, $P_{H_2} = 3.6$ KPA and $T = 573$ K, gray circles indicate vacant sites, colored sites represent occupancy by some species, red sites occupied by H_2 , blue site occupied by H , pink site occupied by DBT, light blue site occupied by HS and green site occupied by H_2S .

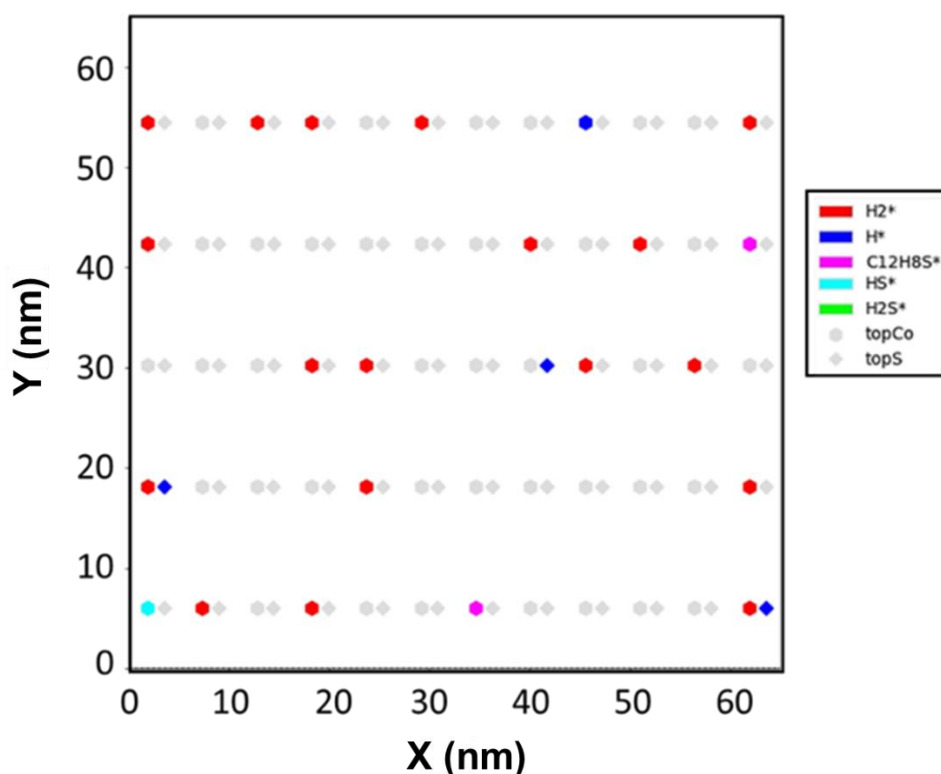


Figure 23 shows the increase of biphenyl pressure from 4.4 to 8.3 kPa, however, cofeeding this product does not contribute or affect the TOF value of the average of $6.1 \pm 0.02 \text{ h}^{-1}$. With respect to the pressure of H_2S (**Figure 24**), it was evaluated in pressure ranges of 4.3 kPa to 6.9 kPa, but no progress of the reaction was observed in the simulation, since this molecule saturated the surface of the catalyst preventing the generation of the products, in agreement with the

microkinetics analysis and the experimental data provided by Broderick et al.(Broderick & Gates, 1981; Houalla et al., 1980)

Figure 23.

Effect of biphenyl pressure on the net reaction rate at a temperature equal to 573K in kinetic Monte Carlo simulation at pressures from 4.4 to 8.3 kPa, 25.6 P_{DBT} and P_{H_2} 3.6 Mpa

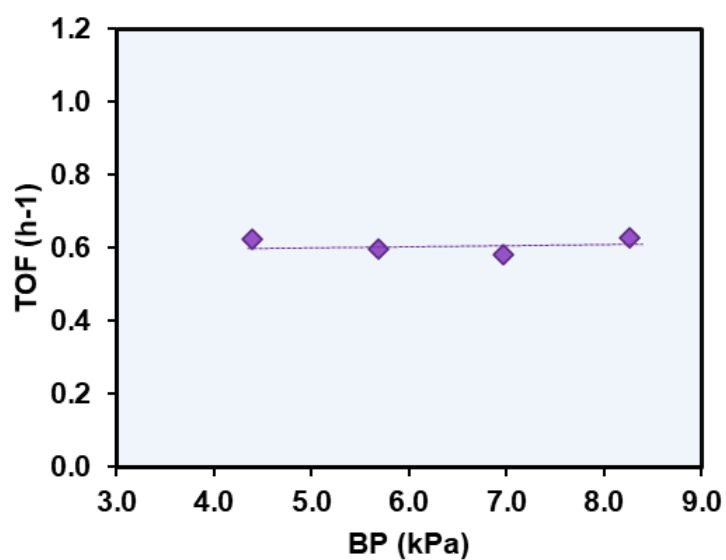
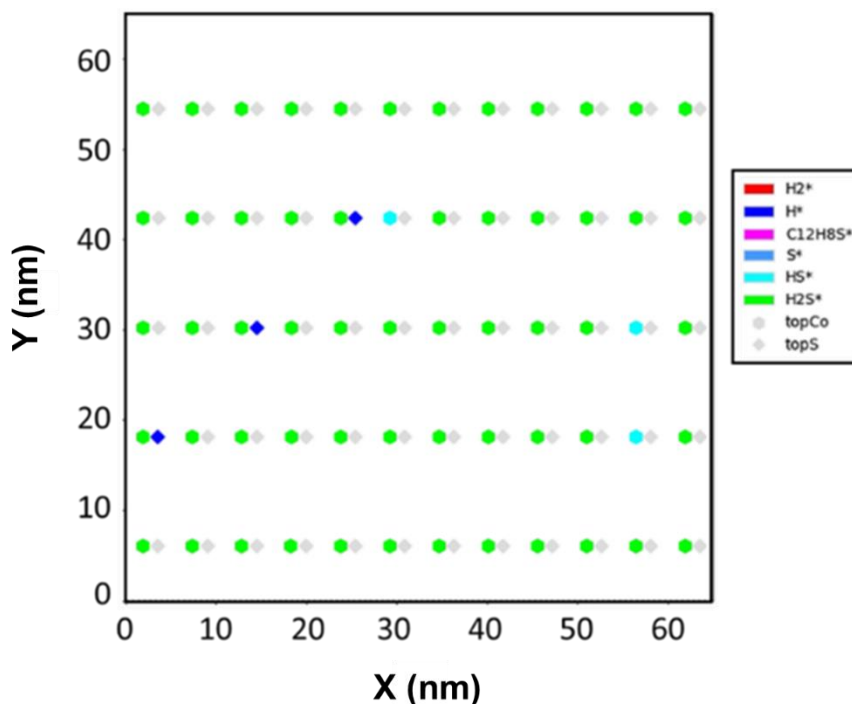


Figure 24.

Influence of H_2S on the reaction, gray circles indicate vacant sites, colored sites represent occupancy by some species, red sites occupied by H_2 , blue site occupied by H , pink site occupied by DBT , light blue site occupied by HS and green site occupied by H_2S .



Kinetic Monte Carlo simulation is undoubtedly a powerful computational tool that allowed us to evidence a trend similar to that reported by the microkinetic modeling part and the literature, through a transient state of the system. As mentioned above, this is the first approach through steady state and transient modeling that manages to capture the same phenomenon represented by using theoretical calculations in the dibenzothiophene desulfurization reaction. In principle, it is evident that molecular adsorption must be considered, since as it is seen, the coverage of this species may be impeding the adsorption of other molecules, and in the case of H_2S , may be poisoning the surface.

7. Conclusions

In this research, the hydrodesulfurization reaction of dibenzothiophene via direct desulfurization was studied on a cobalt-promoted molybdenum disulfide catalyst (CoMoS) where adsorption and reactions occurred on the CUS site, which exhibits cobalt and sulfur atoms. The reaction mechanism was postulated to evaluate hydrogen transfer and sulfur removal on the catalytic surface using different methods. The first hydrogenation step of DBT was found to be kinetically difficult due to an energy barrier of around $179.46 \text{ kJ mol}^{-1}$. However, statistical thermodynamics calculations suggested that the contributions of entropy and enthalpy played a fundamental role in the stability of the monohydrogenated intermediate, which showed a slight energy barrier for the C-S bond cleavage step. Nevertheless, thermodynamics revealed that there was no energy barrier between the hydrogenated intermediate and C-S, indicating that the reaction rate of this event is fast enough for this species not to remain on the surface. The influence of reactant and product partial pressures, as well as temperature, on the reaction rate was evaluated using microkinetic modeling, describing an inhibition of the H_2S reaction kinetics due to species saturation on the surface. A sensitivity analysis showed that the monohydrogenation step is the rate-determining step (RDS), which is significant in the possible inhibition of the direct desulfurization reaction.

KMC simulation, together with microkinetics, showed a high coverage of molecular hydrogen on the surface, as expected from the electronic energy of this type of adsorption. This could imply a decrease in dibenzothiophene adsorption due to competition for surface sites between H_2 , DBT y H_2S . The results of this study demonstrate that it is possible to explain the experimental data trend using different techniques based on robust theoretical foundations.

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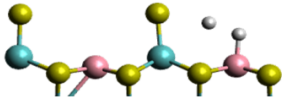
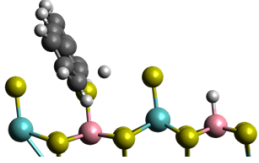
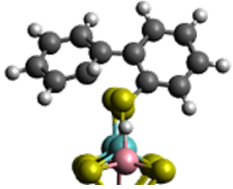
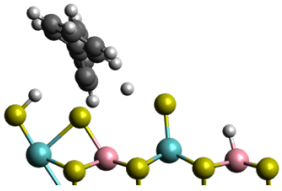
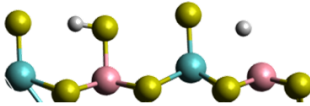
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Supplementary Information

Section A. Theoretical calculations.

Table S1.

Reaction coordinate of transition states in CoMoS.

<u>No.</u>	<u>Elementary reaction</u>	<u>TST</u>
<u>1M2</u>	$H_2^\# + * \rightleftharpoons H^\# + H^*$	
<u>IM5</u>	$C_{12}H_8S^\# + H^* \rightleftharpoons C_{12}H_9S^\#$	
<u>IM6</u>	$C_{12}H_9S^\# + * \rightleftharpoons {}^*C_{12}H_9S^\#$	
<u>IM9</u>	$C_{12}H_9S^\# + H^* \rightleftharpoons BP + S^\# + *$	
<u>IM11</u>	$H^\# + * \rightleftharpoons H^* + \#$	

Section B. Consistency of Kinetic Parameters

Generally, the calculation of thermodynamic properties is essential for understanding the process, so it is reasonable to seek an expression that represents the coherence of the parameters obtained through these calculations. The criteria proposed by Boudar & Djega-Mariadassou,

(Krebs et al., 2008; Spencer, 1988) allow the evaluation of the enthalpy and entropy of adsorption through a series of rules. First, adsorption is negative, i.e., it is regularly exothermic and, therefore, must satisfy the following inequality:

$$-\Delta H_{ad}^{\circ} > 0 \quad \text{Eq S1)}$$

The second criterion stipulates that the entropy of the species in the gas phase must be greater than the entropy of the adsorbed component, due to its change from three-dimensional to two-dimensional state, and lastly, a species cannot lose entropy before adsorption.

$$\Delta S_{ad}^{\circ} = S_{ad}^{\circ} - S_g^{\circ} < 0 \quad \text{Eq (S2)}$$

$$0 < -\Delta S_{ad}^{\circ} < S_g^{\circ} \quad \text{Eq (S3)}$$

To make a correlation between entropy and adsorption enthalpy, a pattern was postulated, where:

$$41.8 < -\Delta S_{ad}^{\circ} < 51.04 - 1.4 \Delta H_{ad}^{\circ} \quad (\text{in joule mole}^{-1}) \quad \text{Eq (S4)}$$

The physicochemical analysis of kinetic and adsorption parameters showed (Table 3) that all adsorption enthalpies and entropies exhibited thermodynamic consistency, and that the direct and reverse activation energies of the model fell within the thermodynamic consistency range proposed by Santacesaria, ranging from 20 a 210 kJ·mol⁻¹.(Santacesaria, 1997)

Table S2.

Estimation of kinetic parameters

Step	$A_n (s^{-1})$	ΔS^0 (J · mol ⁻¹ K ⁻¹)	ΔH^0 (kJ · mol ⁻¹)	Ea (kJ · mol ⁻¹)
IM1	9.74E+08	-85.1	-39.8	0.0
IM2	8.95E+13	1.7	40.7	75.3
IM3	9.74E+08	-83.3	0.8	0.0
IM4	1.02E+08	-209.7	-56.7	0.0
IM5	4.11E+13	16.2	130.5	178.4

IM6	2.98E+14	-18.1	-97.5	12.2
IM7	4.98E+14	35.6	-45.1	0.0
IM8	5.75E+08	-112.3	47.9	27.9
IM9	5.99E+13	49.6	28.9	73.7
IM10	6.71E+05	155.8	-88.9	0.0
IM11	3.12E+13	-5.9	-12.7	69.3
IM12	9.02E+11	-10.9	-72.9	0.0
IM13	1.85E+17	68.3	93.9	111.4
Pre-exponential factors for Langmuir–Hinshelwood (LH) reactions according to Dumesic et al. (Dumesic et al., 1993) $10^{11} \cdot s^{-1}$ for the mobile transition state with rotation; $10^{13} \cdot s^{-1}$ for the mobile transition state without rotation; and $10^{15} \cdot s^{-1}$ for the immobile transition state without rotation. Pre-exponential factor for adsorptions: $10^3 \cdot Pa^{-1}s^{-1}$ for mobile transition state. Pre-exponential factor for desorptions: $10^{16} \cdot s^{-1}$ for more rotational and translational freedom for transition state.				

Table S3.

Activation energies for elementary steps forward and backward from DFT calculations in eV.

Step	Elementary Step	Ea ^{fwd}	E ^{rev}
IM1	$H_2 + \# \rightleftharpoons H_2^\#$	0.00	0.60
IM2	$H_2^\# + * \rightleftharpoons H^\# + H^*$	0.78	0.33
IM3	$H_2 + \# + * \rightleftharpoons H^\# + H^*$	0.00	0.16
IM4	$C_{12}H_8S + \# \rightleftharpoons C_{12}H_8S^\#$	0.00	1.40
IM5	$C_{12}H_8S^\# + H^* \rightleftharpoons C_{12}H_9S^\# + *$	1.86	0.46
IM6	$C_{12}H_9S^\# + * \rightleftharpoons {}^*C_{12}H_9S^\#$	0.13	1.21
IM7	$H^\# + C_{12}H_9S^\# + * \rightleftharpoons H^* + C_{12}H_9S^\# + * + \#$	0.00	0.39
IM8	$H_2 + \# + * \rightleftharpoons H^\# + H^*$	0.29	0.00
IM9	$C_{12}H_9S^\# + H^* \rightleftharpoons BP + S^\# + *$	0.77	0.33
IM10	$H^* + S^\# \rightleftharpoons SH^\# + *$	0.00	0.24
IM11	$H^\# + * \rightleftharpoons H^* + \#$	0.72	0.86
IM12	$HS^\# + H^* \rightleftharpoons H_2S^\# + *$	0.00	0.83
IM13	$H_2S + \# \rightleftharpoons H_2S^\#$	1.16	0.00

Section C. Influence of partial pressure at different temperatures.

In the following images the surface coverage of the chemical species in the temperature range of the hydrodesulfurization reaction is represented, additionally, the effect of the reactant and product pressures is involved.

Figure S1

Calculated surface coverage by partial pressure effect of reactants and products (a) effect of dibenzothiophene pressure 2.6 to 36 kPa, 3.6 Mpa H₂ b) effect of hydrogen pressure 3.0 to 3.6 MPa, 5.1 KPa DBT. (c) effect of biphenyl pressure from 0.35 to 7.7 kPa, 3.6 Mpa H₂, 5.1kPa DBT d) effect of H₂S pressure from 0.34 to 7.7, Mpa H₂, 5.1kPa DBT, total pressure 5MPa and 533K.

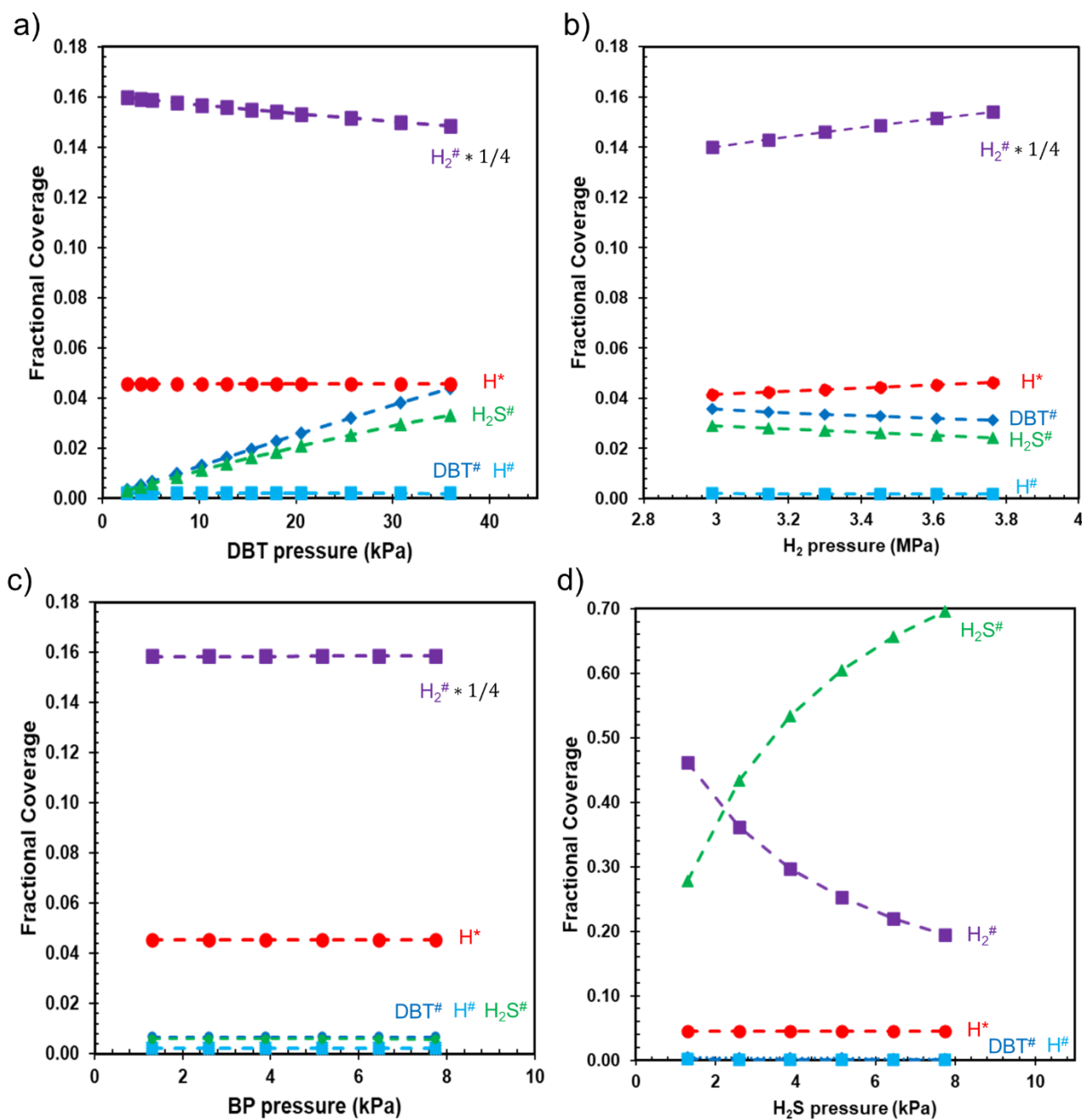


Figure S2.

Calculated surface coverage by partial pressure effect of reactants and products (a) effect of dibenzothiophene pressure 2.6 to 36 kPa, 3.6 Mpa H₂ b) effect of hydrogen pressure 3.0 to 3.6 MPa, 5.1 KPa DBT. (c) effect of biphenyl pressure from 0.35 to 7.7 kPa, 3.6 Mpa H₂, 5.1kPa DBT d) effect of H₂S pressure from 0.34 to 7.7, Mpa H₂, 5.1kPa DBT, total pressure 5MPa and 553K.

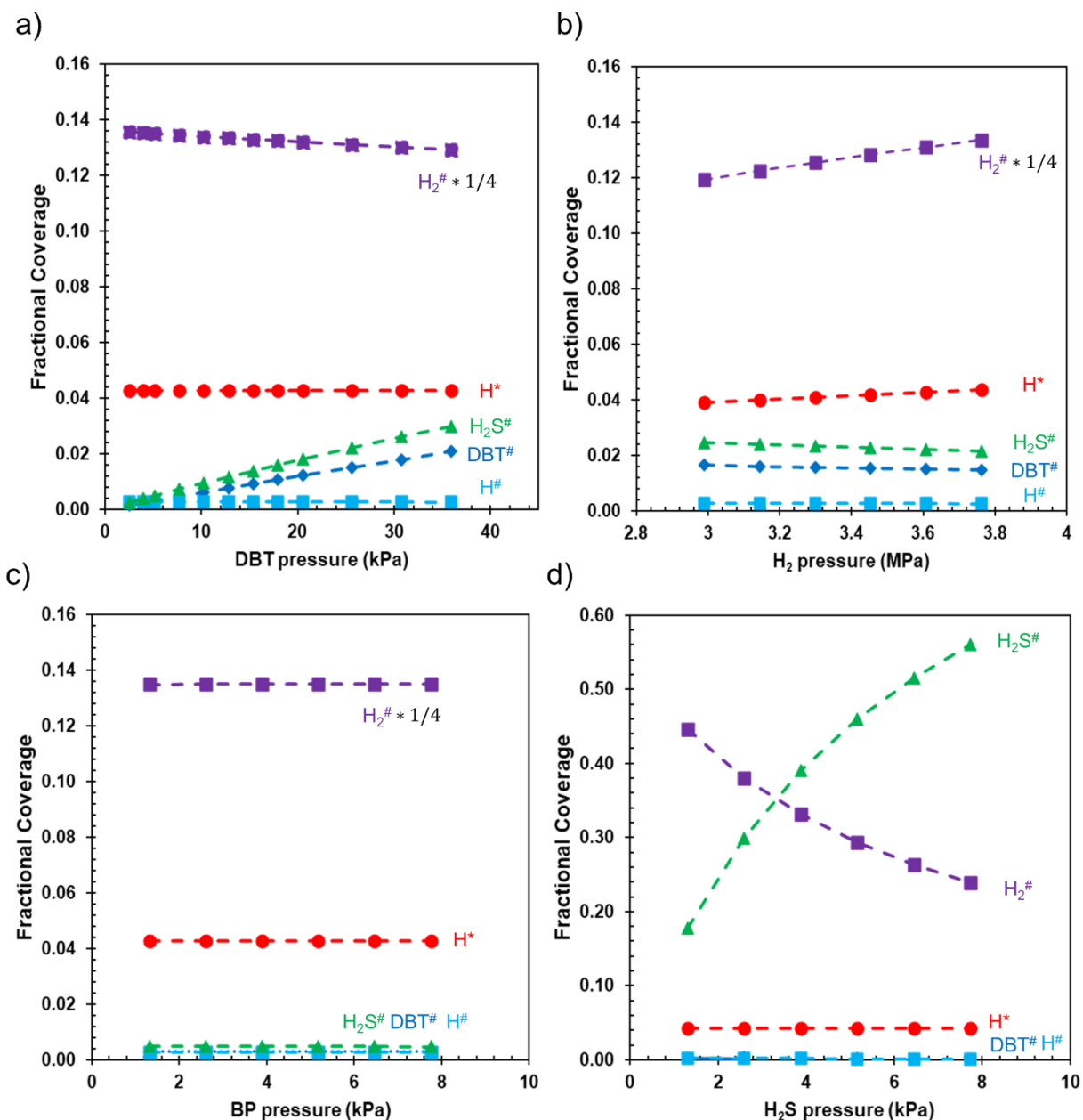


Figure S3.

Calculated surface coverage by partial pressure effect of reactants and products (a) effect of dibenzothiophene pressure 2.6 to 36 kPa, 3.6 Mpa H₂ b) effect of hydrogen pressure 3.0 to 3.6 MPa, 5.1 KPa DBT. (c) effect of biphenyl pressure from 0.35 to 7.7 kPa, 3.6 Mpa H₂, 5.1kPa DBT d) effect of H₂S pressure from 0.34 to 7.7, Mpa H₂, 5.1kPa DBT, total pressure 5MPa and 593K.

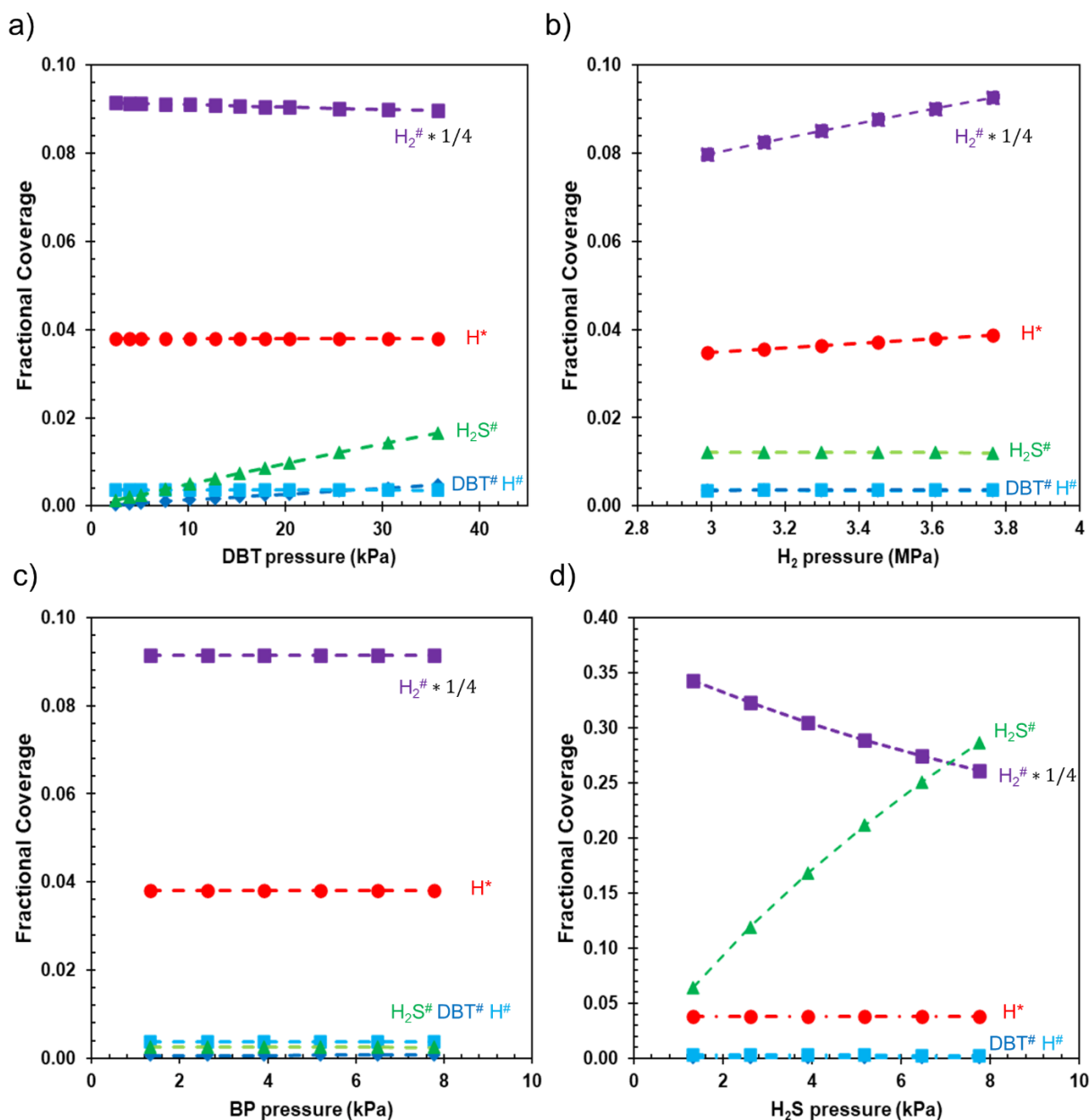


Figure S4.

Calculated surface coverage by partial pressure effect of reactants and products (a) effect of dibenzothiophene pressure 2.6 to 36 kPa, 3.6 Mpa H₂ b) effect of hydrogen pressure 3.0 to 3.6 MPa, 5.1 KPa DBT. (c) effect of biphenyl pressure from 0.35 to 7.7 kPa, 3.6 Mpa H₂, 5.1kPa DBT d) effect of H₂S pressure from 0.34 to 7.7, Mpa H₂, 5.1kPa DBT, total pressure 5MPa and 613K.

