Transition States And Modeling For Co9S8/MoS2 Catalysis

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TRANSITION STATES AND MODELING FOR Co$_9$S$_8$/MoS$_2$ CATALYSIS

GABRIEL ANGEL GONZALEZ

Materials Science and Engineering

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Dedication

Family-Friends

To my brother Jorge Gonzalez and his wife Anabel for their support from my high school education to my doctoral degree.

Gonzalez Family
Olivas Family
John T. Noel’s Family
Damian O. Maynard’s Family
Sergio A. Rivera’s Family
Hugo Lopez’s Family
Marco A. Olguin
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Jesus Adrian Ortiz
TRANSITION STATES VIA COMPUTATIONAL METHODS

GABRIEL ANGEL GONZALEZ

DISERTATION

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**Statement of the Problem**

The understanding of catalytic reactions usually occurs based on experimentation. A reaction model to test a catalytic material for sulfur removal or heterogeneous atoms is the so called hydrodesulfurization reaction (HDS), which means the removal of sulfur content during the fluid catalytic cracking (FCC) of crude oil. However, the actual mechanism is not fully understood for transitional metal catalyst, including promoted systems such as cobalt-molybdenum di-sulfide (Co/MoS₂), some mechanism talk about the reaction occurring at brim sites or edge sites usually occupied by molybdenum or sulfur atoms, as indicated by in-situ EXAFS techniques. In here, the problem is to use quantum mechanical systems by meaning of pseudopotentials to describe a HDS reaction as indicated by calculating transitional energies using computational numerical approaches. Data as produced during this particular study will be of high usage for experimental chemist, material scientist and physicist when designing new catalytic materials.

**Research Objectives**

The primary research objectives is to understand the hydrogen activation mechanism and the subsequent reactions between the activated hydrogen on the Co₉S₈/MoS₂ catalyst and the dibenzothiophene (DBT) molecule for sulfur removal at the sulfur-sulfur (S-S), Molybdenum-Molybdenum (Mo-Mo) and Molybdenum-Sulfur (Mo-S) sites as well as to determine the most efficient catalytic site and the catalytic effect of different stacking height on the Co₉S₈/MoS₂ catalyst.

The following steps are part of the research proposal plan:

1) Constructing a seed model of the Co₉S₈/MoS₂ interface using the “building interfaces” module in Materials Studio.

2) Proposing a reaction pathway mechanism for the hydrogen activation on the Co₉S₈/MoS₂ interface and the subsequent hydrodesulphurization reaction
mechanism of dibenzothiophene (DBT) on the hydrogen activated Co$_9$S$_8$/MoS$_2$ interface.

3) Using linear synchronous transit (LST) and linear quadratic transit (QST) methods to find the transition states energies via density functional theory (DFT).

4. Comparing the hydrogen activation and DBT transition state energies at the sulfur-sulfur (S-S), molybdenum-molybdenum (Mo-Mo), and molybdenum-sulfur (Mo-S) sites of the Co$_9$S$_8$/MoS$_2$ interface to determine the most efficient catalytic site for sulfur removal from DBT.

5) Building Co$_9$S$_8$/MoS$_2$ interface models with different stacking height to determine if the stacking height has an important effect in the activity of the catalyst.

6) Exploring Metal Organic Frameworks for sulfur removal of organo-sulfur compounds

Justification of Importance

Data produced during this particular study will be of high usage for designing new catalytic materials, this could be possible by determining the most efficient site for the catalytic activity. Based on this information a catalyst could be designed having the chemical structure of the established efficient site, or a crystal could be grown in the specific direction that contains the active site of the catalyst.
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Chapter 1 Transition state theory for chemical reaction rates

1.0 Introduction

Henry Eyring was a theoretical chemist (Fig. 1) [1] and he is known as the author of the transition state theory. Henry Eyring was born on February 20, 1902 in Colonia Juarez, Chihuahua, Mexico. Henry Eyring’s family moved to El Paso, Texas on July 1912 because of the Mexican revolution. His father was a rich cattle rancher who had to leave behind all that he owed when they moved to El Paso.

Figure 1. Henry Eyring

Henry Eyring’s family lived in El Paso for about a year and they were struggling due to financial issues. He also missed one year of school, he had completed 5th grade when he left Mexico. In 1913 Henry Eyring’s family relocated in Pima Arizona where he graduated from high school in
1919 and attended the University of Arizona obtaining a B.S in Mining Engineering in 1923 and a Masters in Metallurgy in 1924. Henry Eyring became a chemistry instructor from 1924-1925 at the University of Arizona then he left to the University of California at Berkeley to pursuit his doctoral degree in chemistry which he obtained in 1927 [2].

Henry Eyring wrote about 650 scientific papers that described how to determine the rates of chemical reactions. Henry Eyring’s transition state theory is recognized as the most important developments in chemistry in the 20th century. Transition state theory describes that the rate of a chemical reactions depends on the lifetime of an activated complex which controls the reaction rate [3].

1.1 The transition state theory: Background

A transition state relates the col or saddle point of potential energy surface also known as hypersurface which if formed from a plot of potential energy against interatomic distances. The transition state is considered a small region in the neighborhood of the maximum in the profile that corresponds to the saddle point in the potential energy surface (PES). John C. Polanyi detected the transition states for the first time for the following chemical reaction.

\[
\text{F + Na}_2 \rightarrow \text{F} - \text{Na} - \text{Na} \rightarrow \text{NaF} + \text{Na}^* \tag{1}
\]

on this reaction Na* is in an excited state that emits a yellow spectrum D-line, on each side of this yellow line there is faded yellow line attributed to a transition state [4]. Transition states provide information about the following:

a) The rates of a reaction

b) The quasi-equilibrium since the concentration of reactants to products will be unchanged
c) The motion of the system at the col or saddle point.

These features for chemical reactions were already known before transition state theory and they have its foundations in three main lines of development: thermodynamics, kinetic theory and statistical mechanics. The thermodynamic contributions of Welhelmy, Van’t Hoff, and Arrhenius, the kinetic theory treatments of Trautz and Lewis on the basis of collision theory and the statistical mechanics approach of Marcelin, Rice, and Tolman. The pioneer of transition state theory was Henry Eyring whose brilliance was to put together all the known transition state ideas in his time into a simple but general chemical rate equation as shown in equation 2. [5-6]

\[
k = \frac{kT}{h} e^{-\Delta H/R \cdot T} \times e^{-\Delta S/R}
\]

(2)

1.1.2 Transition state theory from thermodynamics: Reaction rates

The reaction rate theory origins from thermodynamics and can be traced back to 1777 when Karl Friedrich Wenzel (1740–1793) worked on the corrosion of metals by acids and he introduced the idea of the relationship between the acid concentration and the rate of attack of the metal, since then it was known that chemical reactions are functions of time, and they occur at a finite rate [7]. In 1850 Ludwig Ferdinand Wilhelmy (1812–1864) studied quantitatively the temperature dependence which was very important for the development of transition state theory in rates processes. Wilhelmy studied the inversion and the influence of concentration on the reaction rate of sucrose using a polarimeter in the reaction of hydrolysis of sucrose using various acids in aqueous solutions as shown in the chemical (Eq. 3).
Wilhelmy noticed that the sucrose rotates the plane or polarized light to the right and as the hydrolysis of sucrose progressed the rotation shifts to the left because the increase of fructose concentration rotates to the left. Wilhelmy realized that the concentration of sucrose decreases in an exponential way with time and that this reaction is of first order with respect to sucrose, Wilhelmy expressed this result in following mathematical (Eq. 4).

\[
\frac{dc}{dt} = k_1 c \\
\ln c = \ln c_0 - k_1 t \\
\ln\left(\frac{c}{c_0}\right) = -k_1 t \\
c = c_0
\]

In equation 4 the concentration of sucrose is represented by \(c\) at time \(t\) and \(k_1\) is the rate constant for the reactions. Wilhelmy is considered the pioneer of chemical kinetics because he was the first scientist who formulated the kinetic law of a first order reaction [8].

The initial systematic study of the kinetics of chemical reactions during the 19th century showed that reaction rates depended on the temperature. John J. Hood showed in 1878 that the rate constant \(k\) of a reaction changes with the absolute temperature \(T\), where \(A\) and \(B\) are constants for the reaction system (Eq. 5).

\[
\log k = \frac{B - A}{T}
\]
In 1884 Jacobus van’t Hoff (1852–1911) used thermodynamic approaches to reaction rate theory describing the concentration equilibrium constant $K_c$ for a reaction that fluctuates with temperature (Eq. 6).

$$\frac{d \ln K_c}{dT} = \frac{\Delta E}{RT^2}$$

In Eq. 6 $\Delta E$ is the standard change in internal energy, $T$ is the temperature, and $R$ the gas constant. The equilibrium constant for any reaction at equilibrium is the ratio of the rate constants $k_1$ and $k_{-1}$ in the forward and reverse directions respectively (Eq. 7).

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{\Delta U^*}{RT^2}$$

The application of Eq. 7 requires that the rate constants vary with temperature, van’t Hoff obtained from Eq. 7 the following equations 8 and 9 respectively.

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} - I$$

$$\frac{d \ln k_{-1}}{dT} = \frac{E_{-1}}{RT^2} - I$$

In equations 8 and 9, $E_1-E_{-1} = \Delta U$ (internal energy) and $I$ experimentally has been found to be equal to zero, therefore the rate constant is associated to temperature on Eq. 10 $E$ is temperature independent [9].
However on the days of Wilhelmy and van’t Hoff scientist with the aid of thermodynamics could just study the initial and final state of a reaction but they could not describe what really was happening between the initial and final state of the reaction. Scientist could not know the reaction mechanism and the relationship it could have with the reaction rate or the mechanism on the external conditions such as temperature, pressure, and the physical state of the reactants.

In 1889 Svante August Arrhenius (1859-1927) suggested that in a reacting system there are molecules in equilibrium proportion of ordinate molecules and active molecules where only the active molecules are able to react. By using van’t Hoff’s thermodynamic approach to temperature dependence Arrhenius proposed that the rate of a chemical reaction and rate constant $k$, Eq. 11

$$k = Ae^{-\Delta E/kT}$$ (11)

This equation is useful for analyzing the temperature dependence of the rates of many reactions over limited temperature ranges. In the Arrhenius equation $\Delta E$ is the activation energy, $A$ is the frequency factor (collision number), $k$ represents the Boltzmann’s constant, and $T$ is the absolute temperature [10]. Chemical thermodynamics could not answer many question about a chemical reaction, it could not tell what was the rate of the reaction, how the rate could change with temperature, pressure, composition of the reaction mixture. Chemical thermodynamics could not explain the nature of the chemical process by which the reaction proceeds, therefore the search for the answer gave origin and development of the transition state theory [11-12]
1.1.3 Transition state theory from kinetic theory: Reaction rates

Before the transition state theory proposed by Henry Eyring the reaction rates in a chemical reaction were calculated by estimating the number of collisions between reacting molecules by using measurements on the momentum transfer between the collisions of the atoms or molecules using a Ramsauer apparatus. This method had no reasonable relationship when molecules collide taking in account that each collision among the molecules had a different order of magnitude resulting in not momentum transfer due to the wrong orientation of the atoms and molecules at the time of the collision.

Henry Eyring proposed a new method to calculate the reaction rates in a chemical reaction based on the calculations via quantum mechanics of the forces of the atoms due to the motion and rearrangement of the electrons and where the nuclei moves according the influence of the forces found. In a system of atoms if the electrons of lowest quantum state are plotted against the nuclei distances a potential energy surface (PES) is obtained which directs the motion of the nuclei. The system of atoms on the PES will obtain kinetic energy having a specific energy and position on the surface. The regions on the PES with low valleys correspond to compounds if a low region is separated from other low valleys by a higher region or hill with more than 23 kcal the compound will be stable at room temperature and below. This is considered a description of a chemical reaction on a potential energy surface corresponding from a low region to another where at the point highest region called the transition state for more detail see (Fig 3, section 1.4.2) [13].

The transition state theory was developed by Henry Eyring in 1930s. An schematic plot of the potential energy of a chemical system as it proceeds from the reactants to products is used to follow
the progress of the reaction (Fig. 2). The reactants molecules have to rise above the activation energy barrier ($E_a$) to pass through the transition state complex to form products [14].

![Reaction rate diagram](image)

**Figure 2. Reaction rate diagram**

The transition state theory describes the details of the reactants to form products for reactions as shown in Eq. 12

$$AB + C \rightarrow BC + A \quad (12)$$

In order for a reaction to go to completion the transition state must pass through critical arrangement in a phase space which is the coordinate and momentum space for a system of atoms. The potential function is used to determine the energy of a system as a function of atomic positions, the system energy has a saddle point which lies lower in energy for a dissociated transition state arrangement Eq. 13.
or a highly compressed transition state arrangement Eq. 14

The main characteristic of transition state theory is that there is a concentration of atoms or molecules in transition state that is in equilibrium with the reactants and products. The Boltzmann distribution law directs the concentration of the transition state and the rate of the reaction is proportional to its concentration [15-16]

The energy of a transition state is higher that the energy of the reactants therefore the concentration of species in transition states is low this critical arrangement of the species that act as a controller of the rate flow of the reactants to products, but there is another factor that also is important the decomposition frequency into products, therefore the rate can be described as Eq. 15.

\[
\text{Rate} = (\text{Transition state concentration}) \times (\text{Decomposition frequency})
\]  

Bonds from transition state species must gain vibrational energy in order to separate into products when this separation occurs one of the vibrational degrees of freedom is lost and transformed into translational degrees of freedom of the products. The transition state theory describes the transition state species in equilibrium with the reactants Eq. 16.

\[
\text{A} + \text{B} \leftrightharpoons [\text{AB}]^\dagger \rightarrow \text{Product}
\]  

The equilibrium constant \(K^\dagger\) for the formation of the transition state \([\text{AB}]^\dagger\) is represented in Eq. 17.

\[
K^\dagger = \frac{[\text{AB}]^\dagger}{[\text{A}][\text{B}]}
\]
From the above expression the concentration of the species in transition state is shown in Eq. 18

\[ [AB]^\dagger = K^\dagger [A][B] \] (18)

The reaction rate can be expressed as the product of the concentration of the transition state and the frequency of its decomposition, it can be written as follows in Eq. 19.

\[
\text{Rate} = [AB]^\dagger \times (\text{frequency}) = (\text{frequency}) K^\dagger [A][B] \] (19)

where $K^\dagger$ is equivalent to the following expression Eq. 20.

\[ K^\dagger = e^{-\Delta G^\dagger / RT} \] (20)

and it is known that $\Delta G^\dagger$ is equivalent to Eq. 21.

\[ \Delta G^\dagger = \Delta H^\dagger - T\Delta S^\dagger \] (21)

Consequently, the equilibrium constant for the formation of the transition state can be written as follows in Eq. 22.

\[
K^\dagger = e^{-\Delta H^\dagger / RT} e^{\frac{-\Delta S^\dagger}{R}} x e^{-\frac{\Delta S^\dagger}{R}} \] (22)

using the expression in Eq. 23.

\[
\text{Rate} = [AB]^\dagger \times (\text{frequency}) = (\text{frequency}) K^\dagger [A][B] \] (23)

and substituting for Eq. 24 [17].

\[ K^\dagger = e^{\frac{-\Delta H^\dagger}{RT}} x e^{\frac{\Delta S^\dagger}{R}} \] (24)

the following expression is obtained in Eq. 25

\[
\text{Rate constant (k)} = (\text{frequency})[A][B] e^{\frac{-\Delta H^\dagger}{RT}} x e^{\frac{\Delta S^\dagger}{R}} \] (25)
The above expression Eq. 25 describes the transition state in terms of concentration and thermodynamic quantities, the frequency of decomposition of the transition state species can be described from this expression [18].

The vibration of transition state specie at the top of the potential energy barrier the vibrational mode of this specie can be described in Eq. 26.

\[
E_{\text{vib}} = kT \text{ (erg per molecule)}
\]  

(26)

where \( k \) is the Boltzmann’s constant and \( T \) is the temperature (K), it is equivalent to Eq. 27

\[
k = \frac{R}{N_o}
\]  

(27)

In the above expression, \( N_o \) is the Avogadro’s number therefore the vibrational mode is described in Eq. 28.

\[
E_{\text{vib}} = RT \text{ (Joules per molecule)}
\]  

(28)

If the frequency of the decomposition of the transition state is equal to the frequency of the vibration being lost due to the breaking a bond as products are formed, the energy can be expressed in Eq. 29.

\[
E = h\nu = kT
\]  

(29)

using Eq. 29 and solving for frequency yields Eq. 30.

\[
\nu = \frac{kT}{h}
\]  

(30)

which is also equivalent to the following Eq. 31.
Since the reaction rate can be expressed in terms of the concentration of the transition state in Eq. 32.

\[
\text{Rate} = k [AB]^\dagger
\]  

(32)

If the following expression is used Eq. 33.

\[
\text{Rate} = [AB]^\dagger \times (\text{frequency}) = (\text{frequency})K^\dagger[A][B]
\]  

(33)

and substituted (frequency) which is \( v = \frac{kT}{hN_0} \) into the expression Eq. 33 giving Eq. 34.

\[
\text{Rate} = [AB]^\dagger \times (\text{frequency}) = (\text{frequency})K^\dagger[A][B] = \frac{kT}{h} K^\dagger[A][B]
\]  

(34)

which is also equivalent to Eq. 35

\[
\text{Rate} = vK^\dagger[A][B]
\]  

(35)

and Eq. 35 is also equivalent to Eq. 36.

\[
\text{Rate} = \frac{kT}{h} K^\dagger[A][B]
\]  

(36)

Now the rate constant can be written as shown in Eq. 37 [19].

\[
k = \frac{kT}{h} K^\dagger = \frac{kT}{h} e^{-\Delta G^f/RT}
\]  

(37)
1.1.4 Transition state theory from statistical mechanics: Reaction rates

Using statistical mechanics a rate constant expression is obtained for the rate passage over the potential energy barrier where there is a distance, d, at the top of the barrier which is the distance where the transition state exists and where a vibrational mode of the complex is transformed from vibrational motion into translational motion of the products. Therefore the molecular velocity in one direction depends on the rate passage of the transition state through distance, d, where the mass of the transition state is described as \(m^+\), the average velocity Eq. 38.

\[
v = \left( \frac{2kT}{\pi m^+} \right)^{1/2}
\]  

Consequently, the time required for the transition state to pass through distance \(d\) is given in Eq. 39.

\[
\frac{d}{v} = d \left( \frac{\pi m^+}{2kT} \right)^{1/2}
\]

The number of complexes crossing the potential barrier through distance \(d\) per unit time is shown in Eq. 40

\[
\frac{d[\text{conc}]}{dt} = \frac{[\text{conc}]}{2} \left( \frac{\pi m^+}{2kT} \right)^{1/2} = \frac{[\text{conc}]}{dt} \left( \frac{2kT}{\pi m^+} \right)^{1/2}
\]

where [conc] represents the concentration of the transition state which can be calculated. If the difference between the zero-point energies of the reactants and the transition state is represented as \(E_o^\ddagger\), the equilibrium constant for the formation of the transition state is expressed in Eq. 41

\[
K^\ddagger = \frac{Q^\ddagger}{Q_A Q_B} e^{E_o^\ddagger / RT}
\]
where $Q_A$, $Q_B$ and $Q^\dagger$ represent the partition functions of reactants A and B and the transition state, respectively. The vibrational mode of the transition state is represented in Eq. 42

$$Q^\dagger = Q^{\dagger'} \times q^\dagger v$$  \hspace{1cm} (42)

where $q^\dagger v$ represents the vibrational mode of the bond being broken, and the vibrational mode is represented in Eq. 43.

$$q^{\dagger'}v = \frac{1}{1 - e^{-h\nu/kT}} = \frac{kT}{h\nu^\dagger}$$  \hspace{1cm} (43)

and the equilibrium constant $K^\dagger$ is represented is shown in Eq. 44

$$K^\dagger = \frac{kT^Q}{h\nu^\dagger Q_A Q_B e^{Eo'}/RT}$$  \hspace{1cm} (44)

This equation is of the same form found before with the rate constant, $k$, represented as follows in Eq. 45 [20-21]

$$k = \frac{kT}{h} \frac{Q^{\dagger'}}{Q_A Q_B} e^{Eo'}/RT$$  \hspace{1cm} (45)

This similarity to the Arrhenius equation, $k = Ae^{-\Delta E/kT}$ is evident when the pre-exponential factor, $A$, includes the frequency factor and the equilibrium factor equilibrium constant in terms of partition functions. The rate constant expression, $k$, in statistical mechanics is very similar to the rate constant expression obtained from the kinetic theory.

An exact rate constant is not possible but an approximate rate constant, $k_a$ is more likely to be calculated from probability that reactants in the distribution of quantum state will collide and react in agreement with the collision frequency. Usually the approximate rate constant $k_a$ is greater than the rate constant, $k$, calculated experimentally. The method to obtain an approximate rate constant

14
as close to the experimental rate constant is to change or alter the configuration of the transition state used in the energy calculations in order to affect a change in the approximate rate constant, \( k_a \). The calculations for a rate constant are done using the variation method in quantum mechanical calculations to obtain a minimum to get close to the real value of the experimental \( k \), this method is called the variational transition state theory.

The free energy of activation energy is expressed in Eq. 46

\[
\Delta G^\ddagger = -RT \ln K^\ddagger
\]  

(46)

The variational transition state theory optimizes the configuration to minimize \( K^\ddagger \) or maximize \( \Delta G^\ddagger \). In order to obtain an accurate minimization a series of transition states are considered for the calculations. In this way a reaction path is chosen with respect to the energy surface usually the path chosen is the path of steepest descent on either side of the saddle point. This path represents the path of minimum energy where the rate constant can now be represented as a function of a coordinate related to the parameter \( z \) as shown in Eq. 47.

\[
K(z)^{VT} = \frac{kT}{h} \frac{Q^{VT}}{Q_A Q_B} e^{-E(z)/RT}
\]  

(47)

The parameter \( z \) is related to the reaction path as a function of coordinates of the transition state expressed in Eq. 48.

\[
k(z)^{VT} = \frac{kT}{h} K^\ddagger e^{-\Delta G^\ddagger(z)/RT}
\]  

(48)
The value of \( k(z)^{VT} \) is minimized with respect to \( z \). The rate constant is minimized with respect to a parameter related to the configuration of the transition state in the same way that energy is minimized with respect of variables in a trial wave function.

1.2 Modern transition state theory background: reaction rates

The behavior of meta-stable states can be described by modern reaction rate theory to understand different physical, chemical, and biological processes. The origin of Brownian motion described by Einstein contributed indirectly to the development of modern reaction rate theory. Brownian motion is caused by thermal excitement of surrounding molecules that causes the motion of a small particle according to Einstein. In 1940 Kramers described the relationship between Einstein’s theory of Brownian motion and reaction rate theory, on his paper titled “Brownian Motion in a Field of Force and the Diffusion Model of Chemical Reactions” Kramers used a model in which a particle is moving under the influence of a field of force and a frictional force described by a damping coefficient \( \gamma \) deriving the Fokker-Planck equation in phase space for motion currently known as the Kramers’ equation.

Kramers used a flux over population method to explain the rate of passage over a barrier with three types of frictional forces: weak, intermediate and strong. Kramers realized that the range of intermediate frictional force is directly related to the transition state limit for the reaction rate which was derived by Henry Eyring, Pelzer and Wigner. Kramers considers his work published in 1940 as support for the transition state method developed and published in 1935 by Henry Eyring, although Kramers had already worked in the reaction rate theory in 1923 describing the activation energy as the minimum amount of energy needed before a reaction could occur. The rate theory developed by Kramers is known as the Kramers’ rate theory and it is used by the physics
community and Eyring’s rate theory is called the transition state theory used by the chemistry community.

Henry Eyring published in 1935 a paper titled “The Activated Complex in Chemical Reactions” it was already known by that time that the reaction rates (k) could be described by using the Eq. 49.

\[ k = v e^{-E/KB_T} \]  

(49)

the symbol v is considered a prefactor with dimensions of 1/s for unimolecular reactions and 1/(s*cm^3) for bimolecular reactions and KB is the Boltzmann constant. Eyring proposed a formula for the rate of reaction that could determine the prefactor v as shown on (Equations 30, 37 and 45), since previous works before Eyring the prefactor v, was not clearly stated and usually eliminated for a rate expression. Eyring described the prefactor by determining an equilibrium between the reactants and the activated complex which is defined as the group of atoms located at the saddle point of a potential energy surface. Eyring suggested that at the saddle point any quantum state perpendicular to the reaction coordinate reacts with the same universal time constant \( \frac{K_B T}{2\hbar} \). The reaction rate is obtained by the product of this universal time constant with the ratio of the partition function of the activated complex. This partition function approach allowed Eyring a rate constant formulation via quantum mechanical partition functions.

In 1932 a paper titled “Velocity coefficient of interchange reactions” by Pelzer and Wigner where they used transition state theory for the first time to estimate a reaction rate conversion of parahydrogen into normal hydrogen. They used Eyring-Polanyi idea from a paper titled “On Simple Gas Reactions” published in 1931 where Pelzer and Wigner used the ground Born-Oppenheimer potential energy surface for the motion of the nuclei having a fictional trajectory
from reactants to products showing negligible effects for the electronically nondiabetic interactions. To calculate the reaction rate they used thermal equilibrium distribution closely to the saddle point of the potential energy surface and estimated the unidirectional classical flux in the direction from reactants to products. The Pelzer and Wigner approach was used to calculate a reaction rate for the first time but it just applied to hydrogen exchange reactions, however Eyring’s 1935 paper “The Activated Complex in Chemical Reactions” provides general formulas that can be applied to different chemical reactions.

It is very clear that there was a scientific competition between Eyring and Wigner that even in 1938 they published simultaneously papers, Eyring’s paper was titled “The Theory of Absolute Reaction Rates” and Wigner’s paper was titled “The transition State Method”. Wigner approach is based on the classical mechanics since the uncertainty principle forbids the simultaneous determination of a dividing surface and the momentum across the surface. Wigner approach is also defined through a dividing surface or hyperplane which is constructed at right angles to the minimum energy path on a potential energy surface, however Wigner’s approach creates some uncertainties when using equilibrium thermodynamics as the basis for the theory. On other hand Eyring uses a thermodynamic approach within a quantum mechanical context, applying this method to the reaction of NO with $O_2$.[22].

1.3 Generalized transition state theory

Transition state theory as proposed by Eyring is very useful with many applications in chemical reactions but has some limitations therefore different alternatives have been proposed in order to correct these limitations. Transition state theory main limitations include the following:

a) The assumption that each intermediate has a long lasting time to obtain a Boltzmann distribution of energies also that intermediates have a very short lasting time to form products.
b) The supposition that atomic nuclei behave according to classic mechanics and that atoms and molecules required enough energy to form transition state structures.

c) Transition state theory does not take in account quantum tunneling where atoms or molecules can go through the energy barrier without the need of forming transition state structures and it is more remarkable when reactions have low energy barriers since quantum tunneling increases with decreasing energy barrier therefore the correct rate constant cannot be calculated exactly.

d) In the transition state theory at high temperatures molecules have higher energy vibrational modes therefore with complicated motion patterns and collisions may cause the location of transition states cannot to be found exactly at the saddle point but slightly away from it. The transition state theories or “generalized transition state theory” that have been used to correct the limitations of Eyring’s transition state theory especially when the transition state in not found at the saddle point include the following:

a. Canonical Variational Transition State Theory (CVTST)

b. Micro-canonical Transition State Theory (μCTST) also known as Rice-Ramsperger-Kassel-Marcus (RRKM) Theory when applied to unimolecular reactions

c. Microcanonical-Variational Transition State Theory (μVTST)

d. Improved Canonical Variational Transition State Theory (ICVTST).

There are other theories with similar names that have been used to tackle any specific limitation of the Eyring’s classical transition state theory, any form mentioned above of the transition state theory improved or optimized that will be mentioned later is considered as a generalized transition state theory.

In the CVTST the reactants are equilibrated in a canonical or fixed temperature. The CVSTS is represented by equation Eq. 50
\[ k^\dagger (T) = \frac{kT}{h} K^0 \exp(\Delta G^{1,0}(T)/RT) \]  

(50)

where \( K^0 \) is the reciprocal of the standard state concentration and \( \Delta G^{1,0} \) corresponds to the free energy of activation in standard state [23].

In the \( \mu \)CTST the reactants are equilibrated in a fixed total energy. The \( \mu \)CTST is employed to calculate analytical expressions of the excitation function of \( \sigma(E) \) of atom-diatomic exchange reactions which are constrained by the potential to near collisions. The reaction rate expressions obtained in a microcanonical treatment can be integrated over the energy taking into account the statistical distribution over energy states to give the canonical or thermal rates. The \( \mu \)CTST is expressed mathematically in the following form as shown in Eq. 51.

\[ K_{\mu\text{CTST}} (E) = \kappa (E) \frac{N^\dagger (E - V_i)}{hp(E)} \]  

(51)

In Eq. 51 \( h \) is the Planck’s constant and \( p(E) \) is the density of states of reactants per unit energy and volume. \( N^\dagger (E - V_i) \) represents the total number of internal states within the active modes with exception of the reaction coordinate, with energy less or equal \( N^\dagger (E - V_i) \) where \( V_i \) represents the potential energy of the transition state. The point of no return is identified with the maximum potential \( V(s) \) along the reaction coordinate pathway \( s \) where \( \kappa (E) \) is the transmission coefficient which is independent of energy and equal to unity.

Classical transition state theory overestimates the true rate constant leading to variational transition state theory (VTST) in this theory the dividing surface minimize the product flux in this way obtaining the correct reaction rate constant. Truhlar et al. used proposed the VTST where a dividing surface is taken to be a straight line in configuration space, intersecting the reaction
coordinate $s$ at right angles at the point $s^*$ obtaining in this way the microcanonical variational transition state $\mu$VTST theory [24], represented in Eq. 52.

\[
\begin{align*}
k_{\mu V} (E, s^*) &= k(E) \frac{N'[E - V'(s^*)]}{hp(E)} \\
\end{align*}
\]  

Both versions of the VTST such as $\mu$CTST and $\mu$VTST has been used to calculate bimolecular rate constants for association reactions without potential energy barriers, and for bimolecular reactions with small potentials barriers, in ion-molecule and radical-radical association reactions. [25].

ICVTST is a modification of canonical variational transition-state theory in which for energies below the threshold energy where the position of the dividing surface is taken to be that of the microcanonical threshold energy, this forces the contributions to rate constants to be zero below the threshold energy. A compromise dividing surface is then chosen so as to minimize the contributions to the rate constant made by reactants having higher energies. All transition state theories and new ones that will be mentioned from now on are also called “generalized transition state theory” and they are unified by the adiabatic theory of reactions where the rotations, vibrations and electronic motions are considered adiabatic as the system moves along the reaction coordinate, it has been shown that the adiabatic theory of reactions is very similar to the microcanonical variational transition state theory to determine the reactions rate constants. The improved canonical variational transition state theory ICVTST is represented in Eq. 53. [26].

\[
\begin{align*}
k \frac{IGT}{C} (T, s) &= kT \frac{QT}{h} \frac{IGT}{C} (T, s) e^{-\beta V^\ddagger} \\
\end{align*}
\]
In the 1960’s scientist started to use computers to calculate the classical motion of atoms and molecules on a single Born-Oppenheimer potential energy surface as well as comparing computational reaction rates calculations with Eyring’s transition state theory. The application of transition state theory in the quantum mechanical realm was computationally necessary, this consisted in the combination of classical transition state theory with quantum prescriptions for quantizing bound degrees of freedom as well as including tunneling and nonclassical reflection on the reaction coordinate in motion. In the 1960’s the goal was to merge classical and quantum concepts to take advantage of adiabatic connections since transition state theory is relevant to the total flux from reactants to products and only for modes with a well understood adiabatic or diabetic correlations between reactants and a transition state or between a transition state and products. Transition state theory was originally formulated by Eyring as a time-independent theory of stationary state reaction processes. Eyring’s transition state theory was a static picture of time-independent quasi-equilibrium between reactants and transition states, but we have to remember that Wigner was also working on the transition state theory in parallel with Eyring. Wigner’s transition state theory was based on the reactant trajectories passing through a dividing surface in the products direction and no returning back to the reactants this is called the no re-crossing assumption or dynamical bottleneck. However the time dependent approach to reactions rates was determined by a flux-flux time correlation function with a net flux through a dividing surface at time $t$ as proposed by Yamamoto who applied this formulation to classical transition state theory. Using a quantum mechanical methods Miller et al. calculated Yamamoto’s time-correlation function obtaining accurate reaction rates giving a short-time approximation considering this method as a quantum generalization of the transition state theory approximation. A very powerful method to determine reaction rates was developed by Day and Truhlar whom proposed the
variational short-time quantum transition state theory (V-ST-QTST) this method involved intrinsically global dynamics however it had some limitations for complex systems, which was improved to obtain exact rate constants based on the flux concept with transition state theory and extended global dynamics. The path-integral quantum transition state theory (PI-QTST) is based on the Feynman’s path integral, this method included quantum mechanical effects for all the modes of systems with equal balance and also includes anharmonic effects of the potential energy surface. The PI-QTST has some limitations for gas-phases reactions such as unimolecular and bimolecular reactions but it has great advantages for treating condensed phase systems an area where PI-QTST has been very useful. The PI-QTST has been found mathematically similar to the resonance state quantum state theory (RS-QTST) which can be used to describe unimolecular and bimolecular reactions. Interpolated variation transition state theory by mapping (IVTST-M) which is a method with efficient direct dynamics calculations and rate constants for chemical reactions based on a reaction path of energies, energy gradients and Hessians which are calculated with a small group of points along a reaction path with appropriate numeric function used for interpolating and mapping an independent variable that is not a linear function of the reaction coordinate. The IVTST-M minimizes the length of the path that must be calculated and also minimize the number of Hessians that have to be calculated. A similar method to (IVTST-M) is the variation transition state theory with interpolate corrections (VTST-IC) where the interpolation is assisted by the presence of an approximate potential energy function. The variational transition state theory with multidimensional tunneling (VTST/MT) describes a reaction path and a coordinate $s$ describing the progress along this path which considers a sequence of trial transition states with $s$ static various points along the path. VTST/MT has been very successful for a wide range of chemical reactions taking into account the quantum effects such as tunneling at energies below the effective barrier
height and nonclassical reflection by calculating an approximate probability of reaction associated with the ground state of the variational transition state. The VTST/MT was also formulated to treat condensed phase reactions in crystalline solids or surfaces of crystalline solids with applications that include adsorption/desorption reactions, these processes in solid-state system are considered simpler than the treatment of reactions in liquids since the rigidity of the solid systems simplifies the approximations. Ensemble averaged variational transition state theory with multidimensional tunneling (EA-VTST/MT) has been used for complex reactions in condensed phases such as liquids, amorphous material or enzymes where the reaction coordinates are very difficult to describe. Transition state theory has been evolving since Eyring’s transition state theory ideas, there is not just a single transition state theory that can be used to answer all the questions for all the chemical reactions but there is a group of transition theories also called generalized transition state theory that have been described very lightly above just give an insight of the development during these years of the original Eyring’s ideas about transition state theory [27].

1.4. Transition state theory via computational methods

1.4.1 Transition states and potential energy surfaces

Potential energy surfaces are very useful to describe the properties of a chemical reaction such as the structure, properties, reactivity, and spectra of molecules which can be determined in terms of potential energy surfaces. A potential energy surface forms when the Born-Oppenheimer approximation is used in the solution of the Schrodinger equation for a molecular system, where the electronic distribution of the molecule adjusts quickly to any movement of the nuclei. In the Born-Oppenheimer approximation a molecule can be expressed as a function of the positions of the nuclei this is called a potential energy surface. The features of a potential energy surface include a hilly landscape, valleys, mountain passes and peaks (Fig. 3) [28].
The transition state is described as a dividing surface or potential energy surface which separates the reactants from the products, where the transition state rate is proportional to the total flux of classical trajectories from reactant to product side of the potential energy surface [29]. Rene Marcelin (1885-1914) predicted that the progress of a chemical reaction could be described as a point in a potential energy surface where a plot of potential energy against inter atomic distances and angles. Potential energy surfaces were also very important in the development of transition state theory since the transition states of reaction are determined by the first order saddle points between reactants and products on a potential energy surface [30-31]. Potential energy surfaces are very useful for calculating the transition states, reaction pathways and reaction rates in reaction, chemical reactivity can be studied and simulated by using modern computational methods [32].
Modern computational molecular geometry optimization presents stationary point structures and energies on potential energy surfaces where the minima or the valleys represent the reactants, intermediates, and products giving rise to transition states (Fig. 3) [33-34].

1.4.2 Transition States locations via Linear Synchronous Transit (LST) and Quadratic Synchronous Transit (QST) methods.

Potential energy surfaces are very important to understand chemical reactivity. Finding the equilibrium geometries and transition states on the potential energy surfaces is very important to describe a chemical reaction. Optimization algorithms for minima and first order saddle points have been used to determine computationally the geometries and transition states of a reaction. Transition states are very difficult to locate in a potential energy surface and locating the minima are a slightly easier that transition states via computational algorithms. In order to find a transition state structure or (first order saddle point) on the potential energy surface a maximum must to be found in one direction and minima in all other directions [35]

The synchronous transit methods such as linear synchronous transit (LST) and quadratic synchronous transit (QST) algorithms search the transition state structure by starting from the reactant and product finding the maximum along a linear or quadratic path across the surface as shown in [Fig. 4].
This concept can be described with two structures instead of one used to start a transition state search. One structure is in the reactant valley and the other structure is in the product valley as seen in (Fig. 4) in this way a reaction path approximation is indicated and set the transition state. In the linear synchronous method (LST) sequences of single point energy are calculated on a set of linearly interpolated structures between the reactant and product. The maximum energy structure found along this path provides an approximation of the transition state structure. In the orthogonal direction to the LST path a single refinement is performed which is used as an intermediate to define a QST pathway. This process gives a further refined estimate for geometry optimization of the transition state structure [36].
1.4.3 Transition state locations for molecules

In the original linear synchronous transit (LST) method developed by Halgren and Lipscomb uses a model with a set of structures connected by reactants and products which is obtained by linear interpolated distances between reactants and products according to Eq. 54.

\[ r^i_{ab}(f) = (1 - f) r^{R}_{ab} - fr^{P}_{rab} \]  

(54)

On this equation \( r^{R}_{ab} \) and \( r^{P}_{ab} \) represent the inter-nuclear distances between atoms \( a \) and \( b \) in the reactant and product correspondingly and \( f \) is an interpolation parameter that varies between 0 and 1. The different number of inter-nuclear separations in a molecule with \( N \) atoms is \( N(N-1)/2 \) regularly greater than 3\( N \) Cartesian degrees of freedom of the system which provides a high optimization of the geometry of the system. The transition state pathway is defined by using the molecular geometry with inter-atomic distances to the optimal values obtained by minimizing the function \( S \) as shown in Eq. 55.

\[
S(f) = \frac{1}{2} \sum_{a \neq b}^{n} \frac{(r_{ab} - r^i_{ab}(f))^2}{(r^i_{ab}(f))^4} + 10^{-6} \sum_{\xi=x,y,z} \sum_{a} (\xi_a - \xi^i_a(f))^2 S(f) \\
= \frac{1}{2} \sum_{a \neq b}^{n} \frac{(r_{ab} - r^i_{ab}(f))^2}{(r^i_{ab}(f))^4} + 10^{-6} \sum_{\xi=x,y,z} \sum_{a} (\xi_a - \xi^i_a(f))^2 
\]

(55)

On Eq. 55 the \(-\xi^i_a \) is the interpolated Cartesian position of an atom and \( \xi_a \) is a coordinate, the function \( S \) is always greater than or equal to zero. The \( S \) function is minimized by the reactant and product geometries when \( f \) is 0 or 1. The transit path is formed on the basis of a geometrical analysis
and no energy calculations are required to obtain the transit path. The LST maximum estimate is refined by minimizing the geometric subject to constant $p$ as described on Eq. 56.

$$p = \frac{d_R}{d_R + d_p} \quad (56)$$

where $d_R$ represents the distance between the reactant and any other geometry of the molecule as stated on Eq. 57.

$$d^2_R = \frac{1}{N} \sum a (E_a - E^R_a)^2 \quad (57)$$

In the same way a similar expression can be written for $d_p$ and the resulting geometry may be taken as an optimized guess for the transition state or used to perform a QST calculation. In the QST a quadratic interpolation is performed through the reactant, the product, and $p_m$. The energy maximum along this quadratic path is the QST prediction of the transition state [37]

1.4.4 Transition state location in crystal structures

For crystal structures the calculation of the LST Eq. 55 is very difficult because the estimation of $S$ contains sums of an infinite number of atoms. A modified function $S$ for periodic systems is described on Eq. 58.
\[
S(f) = \frac{1}{2} \sum_{a,b,R}^{n} (r_{ab+R} - r_{ab+R}^i(f))^2 w(r_{ab+R}^i(f)) \\
+ 10^{-6} \sum_{a} (E_a - E_a^i(f))^2
\]

\[
w(r_{ab}^i) = 0: a=b
\]

\[
w(r_{ab}^i+R(f)) = \frac{1}{r_{ab+R}^i(f)} : a\neq b, R = 0
\]

\[
w(r_{ab+R}^i(f)) = \frac{1}{r_{ab+R}^i(f)} - \frac{1}{r_{cut}^4} : r_{ab+R}^i(f) < r_{cut}, a\neq b, R \neq 0
\]

\[
w(r_{ab+R}^i(f)) = 0: (r_{ab+R}^i(f)) > r_{cut}
\]

On Eq. 58 \(a\) and \(b\) run over the atoms in one unit cell and \(R\) runs over all real space lattice vectors. The finite range of the weight function \(w\) ensures that \(S\) can be easily evaluated for periodic systems. Note that \(w\) goes to zero smoothly at \(r_{cut}\). Typically \(r_{cut}\) is chosen such that \(R\) runs over a few unit cells [38].

1.4.5 Transition states and the conjugate gradient (CG) algorithms

The effectiveness of the LST/QST methods is improved by the conjugate gradient (CG) which is an algorithm to refine the saddle point geometry and for solving large scale nonlinear optimization problems. The CG methods are very useful to minimize functions and make intelligent use of the gradient information that is available at each cycle of the optimization process [39]. The CG method was developed by Sinclair and Fletcher proposing a gradient method for finding the saddle points based on the conjugate gradient optimization method, this method uses linear searches and as consequence the CG method does not generate search directions of zero curvature. The
The conjugate gradient method consists of maximum and minimum with a search for a maximum along the line joining two known minima, the linear synchronous transit LST. Minimization is performed in the direction orthogonal to the original directions followed by a maximum search along a parabolic path or quadratic synchronous transit QST which provides the two minima and the actual estimate of the saddle point. Convergence can be achieved through this process of minimum and maximum searches [40].

1.4.6 Transition states via LST/QST and CG algorithms integrated in Density Functional Theory (DFT).

The LST/QST transition state search methods and the CG method have been integrated to density functional theory (DFT) programs such as Dmol³ a localized basis set program based on the linear combination of atomic orbital (LCAO).

DFT seeks to find a solution to the Schrodinger equation by applying three basic simplifications, the Born-Oppenheimer approximation, Hartree-Fock approximation and the Linear Combination of Atomic Orbitals (LCAO).

First of all the electronic structure methods search for an approximation to the solution of the Schrodinger equation as in the case of the hydrogen atom described by Eq. 59.

\[ -\frac{\hbar^2}{8\pi^2 m} + V(x, y, z)\psi(x, y, z) = E\psi(x, y, z) \]  

(59)

The terms on the left represent the kinetic and potential energy respectively of an electron of mass \( m \) moving in the vicinity of a nuclear charge. The energy of the electron \( E \) and the wavefunction represented by \( \psi \) describe the motion of the electron as close as possible. The wavefunctions for the hydrogen atom are represented by the s, p, and d atomic orbital. The square
of the wavefunction times a small volume element provides the probability of finding the electron inside the volume element. The Schrodinger’s equation for hydrogen can be extended and generalized to a multilinear, multielectron system as described Eq. 60.

\[ \hat{H}\psi = E\psi \quad (60) \]

In this case \( \psi \) is a many-electron wavefunction and \( \hat{H} \) the Hamiltonian operator as shown in the Eq. 61.

\[ \hat{H} = -\frac{\hbar^2}{8\pi^2} \sum_A \frac{1}{M_A} \nabla^2_A + \frac{\hbar^2}{8\pi^2 m} \sum_a \nabla^2_a - e^2 \sum_{Aa} \frac{Z_A}{r_{Aa}} + e^2 \sum_{Ab} \frac{Z_A Z_B}{R_{AB}} + e^2 \sum_a \sum_b \frac{1}{r_{ab}} \quad (61) \]

The first two terms in Eq. 61 describe the kinetic energy of the nuclei represented with \( A \) and the kinetic energy of the electrons represented with \( a \) and the last three terms describe Coulombic interactions between particles. The nuclear masses are represented with \( M \), the electron mass \( m \), the nuclear charges \( Z \) (atomic numbers), the Plank’s constant \( h \) and the electron charge, \( R_{AB}, r_{ab} \) and \( r_{Aa} \) represent the distances separating nuclei, electrons, and electron and nuclei respectively.

As mentioned before DFT seeks to find a solution to the Schrodinger equation by applying three basic simplifications.

a) Born-Oppenheimer approximation: The Schrodinger equation can be simplified by assuming that the nuclei does not move, this is called the Born-Oppenheimer approximation and leads to an electronic Schrodinger equation as shown on Eq. 62.
The term in Eq. 63 which describes the nuclear kinetic energy from Eq. 61 is missing in equation Eq. 62 which equivalent to zero and the nuclear-nuclear Coulomb term is a constant which needs to be added to the electronic energy to yield a total energy for the system as shown in equation Eq. 62, even with the Born-Oppenheimer approximation, the Schrödinger equation is not easy to solve for more than a single electron therefore additional approximations are required.

b) Hartree-Fock approximation.

The self-consistent field describes the individual electron distribution with the correct potentials for one another’s motion. The self-consistent field method calculated with Pauli’s principle which has anti symmetric wavefunctions is called the Hartree-Fock method. The self-consistent field estimation is applied to antisymmetrized wavefunctions rather than to simple products of spin orbitals. The energy difference from the true energy from atoms and molecules of the solution of the Schrödinger equation and the solution obtained with the Hartree-Fock method is called the correlation energy which is caused by the interactions of electrons and the electrostatic field that electrons experience to differ from the averaged Hartree-Fock field. The Hartree-Fock method is not completely accurate because of the correlation energy problem, this energy error is produced.
from ignoring the instantaneous relative motion or correlation of the electrons. The correlation energy calculation error is very small but the problem of this error is that the molecular binding energies are also about the same magnitude and similar to the energy correlation error [41-43]

c) Linear combination of atomic orbitals (LCAO)

The Hartree-Fock approach has a spherical symmetry which is very direct to be used for atoms, but solutions for spinorbitals for molecular systems are computationally difficult that a modification of the Hartree-Fock method was implemented by C. C. J. Roothaan and G. G. Hall whom used a known set of basis function to expand the spinorbitals. The modification applied by C. C. J. Roothaan and G. G. Hall comes from the Hartree-Fock and Linear Combination of Atomic Orbitals (LCAO) approximations which were taken together and led to a set of equations which are known as the Roothann-Hall equations. In fact the Roothann-Hall equations needed a modification by adding a technique where an equation or system of equations needed an adjustment by adding an iterative technique which is used in a continuing way until the convergence is achieved, this is the called the self-consistent field (SFC) [44-45]

The ab initio methods start with the Hartree-Fock approximation and the Hartree-Fock equations are expected to find spinorbitals that can form configuration state functions. The ab initio methods although used by quantum chemist extensively they have limitations, mainly when large basis sets on molecules have so many atoms and electrons [46].

1.4.7 Transition states calculations and Dmol³ algorithm

Dmol³ algorithm is integrated in Materials Studio which has an efficient geometry optimization algorithm that determines the minimum energy structures. The transition states are calculated with the combination of the LST/QST algorithms which determine the evaluation of energy barriers.
Dmol³ algorithm uses numerical functions on an atom centered grid as its atomic basis functions which are calculated by the DFT equations for each individual atom achieving high accuracy and the high quality of Dmol³ basis set minimizes superposition effects. Dmol³ electron density is expanded in multipolar and atomic centered partial densities which gives an exact representation of the density even when the system increases in size therefore the Coulomb potential scales linearly with the size of the system. A numerical integration algorithm also scales linearly to calculate the Hamiltonian matrix elements. Dmol³ can determine all electron or pseudo-potential calculations as well as effective core potential (EPC) and DFT semi-local pseudo potentials (DSPP). Geometry and transition state optimizations are obtained using delocalized internal coordinates which allows Cartesian geometry constrains on molecules or periodic system while the running optimization in internal coordinates facilitating the quick location of transition states [47]

Dmol³ counts with the following computational features [48].

**Calculation Tasks**

- Restricted and unrestricted DFT calculations
- Geometry and energy predictions
- Transition state search using a combined LST/QST/Conjugate Gradient approach
- Transition state optimization using eigenvector following
- Graphical display of the reaction path with the reaction pre-viewer of the Materials Visualizer
- Optimization with robust delocalized internal coordinates
- Frequency calculations using full or partial Hessians
- Animation of normal modes using the Materials Visualizer
- Transition state confirmation using the NEB method

**Functionals**
Local DFT functionals: PWC, VWN
GGA-DFT functionals: PW91, BLYP, BP, BOP, PBE
VWN-BP, RPBE, and HCTH
Harris functional for fast calculations

Basis Sets

- Numerical AO basis sets: Minimal, DN, DND, DNP and TNP
- Relativistic effective core potentials and scalar relativistic all electron, effective core pseudo-potentials, all electron relativistic and DFT semi-core pseudo-potentials

Properties

- Band structure
- Bond order analysis
- Electron work function
- Electrostatic moments
- Fukui indices
- Heats of formation, free energy, enthalpy, entropy, heat capacity, ZPVE.
- Mulliken, Hirshfeld, and ESP charges
- Nuclear electric field gradients
- UV/Vis spectra, excited states, polarizability and hyperpolarizability

1.5 Theoretical transition states calculations on MoS$_2$ catalyst: background

Transition state structures are of high importance in order to understand and design chemical reactions, the transition state structures have been very difficult to locate, Govind et al proposed a generalized transition state location scheme (Eq. 58) where the molecular and crystal models can be treated within the same framework and generally applicable, this approach was based on the ideas of Halgren and Lipscomb for the linear (LST) and quadratic synchronous methods (QST) to locate the transition state structures, transition state energies and reaction pathways [49-50].

Theoretical studies on the catalytic properties of the edge structures of the active MoS$_2$ catalyst have applied the LST/QST methods and first principles density functional methods using pseudo-potentials that model the ionic cores of atoms to determine the chemical properties and catalytic
reactions of the MoS$_2$ catalyst. Todorova et al. using computational methods found the hydrogen activation energies of MoS$_2$ catalyst surfaces (Fig. 5) with a MoS$_2$ slab model.

Figure 5. Transition state calculations for the dissociation of H$_2$ on (100) 2H-MoS$_2$ surfaces [from ref. 51]. Molybdenum atoms (dark color), Sulfur atoms (gray color). a) Reactant side where the hydrogen molecule approaches the MoS$_2$ catalyst b) Hydrogen bond stretching when getting closer to the MoS$_2$ catalyst surface c) Considered the transition state structure where hydrogen bond is broken, but not yet bonded to the sulfur-sulfur site d) Hydrogen atoms have bonding to the sulfur atoms e) This is considered the final product of the hydrogen dissociation where the hydrogens have bonded completely to the sulfur-sulfur site.

The MoS$_2$ slab model (Fig 6) was first proposed by Raybaud where the (10\overline{1}0) surface of a MoS$_2$ single crystal is produced by cutting the (10\overline{1}0) MoS$_2$ layers to form a slab that is generated from three MoS$_6$ prisms stacked in the (10\overline{1}0) direction. This model consist of both sandwiches present in the unit cell and therefore the interlayer interactions are accounted for in the calculations, also this model has been used to investigate the active sites on the (10\overline{1}0) MoS$_2$ surface. On this model Todorova used LST/QST methods to calculate hydrogen dissociation. A H$_2$ molecule dissociates on the MoS$_2$ catalyst surface into two hydrogen atoms, which react further with the catalyst surface under formation of either one Mo-H or one S-H (heterolytic) or two S-H surface groups
(homolytic), Todorova’s results favored the heterolytic adsorption of hydrogen. Todorova also investigated the Ni and Co promoted MoS₂ effect on the H₂ dissociation observing a negative promotional effect on the H₂ dissociation in the case of Ni-promoter MoS₂, while Co was observed to have a positive effect [50-51].

![Structure of the MoS₂ (10̅10) plane](image)

Figure 6. Structure of the MoS₂ (10̅10) plane [from ref. 50] Molybdenum atoms (dark color), Sulfur atoms (gray color).

In a density functional theory study by Weber et al. proposed a reaction mechanism for the direct desulfurization (DDS) on a single-layer of a NiMoS cluster (Fig. 7) that consist of several individual steps where the dibenzothiophene (DBT) reacts with H₂ on the surface of the NiMoS₂ removing the sulfur from DBT and producing biphenyl (BP) and H₂S believing that the surface of the catalyst is completely covered with hydrogen when DBT molecule adsorbs [52]
Cristol et al. calculated the activation energy on a cobalt promoted catalyst (Fig. 8) for the direct desulfurization mechanism for sulfur removal of the dibenzothiophene (DBT) molecule which was found to be 1.0 eV (23 kcal mol\(^{-1}\)) this study proposed theoretical calculations useful to propose an active site and a reaction mechanism for the DDS pathway on a MoS\(_2\) catalyst [53].
Topsoe *et al.* found MoS$_2$ nanoclusters (Fig. 9) named brim sites were identified having using STM and DFT. The brim sites having a metallic character are very important for the hydrogenation and C-S bond scission. Topsoe observed that vacancies on the brim sites were not necessary for S-C scission to occur, an observation that was completely unexpected [54-55].
Figure 9. A) Structure of triangular MoS$_2$ nanoparticles. B) Model of MoS$_2$ triangular nanoparticles [from ref. 55]

Ramos et al. Co$_9$S$_8$/MoS$_2$ interface model (Fig. 10) proposed that the catalytic activity is directly connected with an increase of the contact surface area between the two sulfide phases, therefore the understanding and the nature of the possible interaction between the MoS$_2$ and Co$_9$S$_8$ in unsupported catalytic systems was important in order to understand the causes of the interface synergy.
Figure 10. A) High resolution transmission electron microscope (HRTEM) image of the Co₉S₈/MoS₂ bulk. Simulated image of Co₉S₈/MoS₂ bulk. B) Simulated image of Co₉S₈/MoS₂ bulk structure C) A representative ‘seed model’ from Co₉S₈/MoS₂ interface. Sulfur atoms (yellow color), molybdenum atoms (turquoise color) and cobalt atoms (purple color) [from ref. 56].

Ramos found that there is a strong electron donation from the Co to Mo which occurs through the intermediate sulfur atom bonded to both metals enhancing the metallic character, also changes in the coordination and electronic properties favored the synergetic effect between Co and Mo at the proposed interface region between the two bulk MoS₂ and Co₉S₈ phases [56]. The edges of MoS₂ are the active sites for the hydrodesulfurization reactions. The edges contain the surface sites for the catalytic activity of the MoS₂ due to its high surface energy, increasing the edge dimensions is very important to improve the catalytic properties. In order to design and develop more active and selective catalysts it is important to understand in specific detail the structure and nature of the sites for the HDS reaction [57-58].
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Chapter 2 Computational transition states calculations of the hydrodesulfurization (HDS) reaction occurring at the on Co₉S₈/MoS₂ interface

Problem: The Co₉S₈/MoS₂ interface has catalytic properties for removing sulfur from organo-sulfur compounds found in crude oil, this process in refinery industry is known as hydrodesulfurization (HDS) process. There have been different models to describe how the catalysis operates at the atomic level in order to understand the HDS process and to generate information to design new catalysts. In order to develop more efficient catalysts it is important to determine the reactivity and the localization characteristics of different catalytic sites present at the catalytically active interface between MoS₂ and Co₉S₈ bulk phases present on unsupported Co-promoted MoS₂ hydrodesulfurization catalysts.

Solution: The solution follows a first contribution in which we determined by using a combination of HRTEM simulation and modelling calculations the exact nanoscale structure of the interface formed by contacting bulk MoS₂ and Co₉S₈ phases of unsupported Co/MoS₂. The objective of the present contribution is to go forward by using DFT calculations in order to identify possible active sites for HDS present on the MoS₂ side of the interface created. Among the three different cases envisaged here, we were able to identify the most active site and to determine the causes for its higher reactivity (better product desorption efficiency, higher C-S bond rupture ability). Finally, some general conclusions about the role of the hydrogen activation were reached. This approach allows us to propose some clues to design more efficient catalysts based on bulk Co₉S₈/MoS₂ phases.

Abstract: We carried out transition state computational studies about sulfur removal from dibenzothiophene (DBT) considering a Co₉S₈/MoS₂ interface previously activated on its surface
with hydrogen. We also followed a reaction mechanism that describes sulfur removal on the surface of the Co$_9$S$_8$/MoS$_2$ at three different sites such as basal plane sulfur-sulfur (S-S), and edge sites such as the molybdenum-sulfur (Mo-S) and molybdenum-molybdenum (Mo-Mo) to determine the most effective catalytic site. This study revealed that the edge (Mo-Mo) site is the most catalytically active and efficient active site for the hydrodesulfurization (HDS) reaction, the edge (Mo-S) site was the second best site and basal plane (S-S) site showed the least catalytic activity for the HDS reaction. This information allows us to generate information to design new catalysts based on bulk Co$_9$S$_8$/MoS$_2$ phases with higher efficiency by increasing the proportion of (Mo-Mo) sites. The linear synchronous transit (LST) and quadratic synchronous transit (QST) methods integrated in a density functional theory (DFT) program such as Dmol$^3$ were used for the calculations of energy barriers of the transition state.
2.0 Introduction

MoS$_2$ is a transition metal sulfide catalyst used in the hydrodesulfurization process for sulfur removal in the refinery industry [1]. MoS$_2$ catalytic activity improves when Co or Ni is added which is considered a promotion effect that enhances the catalytic activity of the MoS$_2$ by a factor order of 1000 [2, 3]. Different models: intercalation, monolayer, decoration, synergy by contact, models have been used to explain the origin of the catalytic properties of MoS$_2$ [4-10]. Intensive studies have been done extensively about Co-promoted and unpromoted MoS$_2$, both experimentally and also with computational methods, to determine its catalytic properties [11-16]. Previously the Co$_9$S$_8$/MoS$_2$ interface model was used to explain the promotion effect and catalytic activity in sulfide phases, suggesting that activity is directly connected with an increase of the contact surface area between the two sulfide phases [10]. In contrast, no studies have been done using computational methods to determine the catalytic properties of the Co$_9$S$_8$/MoS$_2$ interface model. We determined the catalytic properties for the HDS reaction for this model based on a series of surface reactions via transition state computational calculations that includes the hydrogen activation, C-S bond scission, biphenyl (BP) formation and release of the hydrogen sulfide (H$_2$S) molecule from the surface of the Co$_9$S$_8$/MoS$_2$ interface model. The Co$_9$S$_8$/MoS$_2$ interface was obtained from HRTEM and computational modeling (Fig. 11) using this model we investigated the energy barrier required to start the hydrodesulfurization (HDS) reaction with organo-sulfur compounds such as dibenzothiophene (DBT) found in crude oil for following catalytic sites: basal plane (S-S) yellow atoms, edge sites (Mo-Mo) turquoise atoms and (Mo-S) turquoise-yellow atoms.
Figure 11. A) HRTEM image of the Co$_9$S$_8$/MoS$_2$ bulk structure. B) Simulated image of the Co$_9$S$_8$/MoS$_2$ bulk structure C) Basal plane top view image D) Edge sites front view of image E) Edge sites front tilted down image F) Edge sites front view of the representative “seed model” from the Co$_9$S$_8$/MoS$_2$ interface. G) Side view of a representative “seed model” from the Co$_9$S$_8$/MoS$_2$ interface. Sulfur atoms (yellow color), molybdenum atoms (turquoise color) and cobalt atoms (purple color).

The hydrotreating (HDT) process used for upgrading petroleum feeds to commercial fuels is used in the refinery industry to remove heteroelements (S, N, O) impurities. In this respect, the initial step in the activation of hydrogen on the MoS$_2$ is central for the following steps in the HDS process [18-19]. Performing computational transition state calculations on this case for the Co$_9$S$_8$/MoS$_2$ interface will be useful to understand its catalytic properties for the HDS process.

Transition state structures of Co$_9$S$_8$/MoS$_2$ used in this study are of high importance in order to understand the catalytic properties of the Co$_9$S$_8$/MoS$_2$ catalysis. The transition state structures have been very difficult to locate, Govind et al proposed a generalized transition state location scheme where the molecular and crystal models such as Co$_9$S$_8$/MoS$_2$ can be treated within the same
framework and generally applicable. This approach was based on the ideas of Halgren and Lipscomb algorithms for the linear (LST) and quadratic synchronous methods (QST) to locate the transition state structures, transition state energies and reaction pathways [20, 21]. Theoretical studies on the catalytic properties of the edge structures of the active MoS$_2$ catalyst have applied the LST/QST methods and first principles density functional methods using pseudo-potentials that model the ionic cores of atoms to determine the chemical properties and catalytic reactions of the MoS$_2$ catalyst [22, 23]. We are using these concepts to study the catalytic properties of Co$_9$S$_8$/MoS$_2$ catalyst. The Co$_9$S$_8$/MoS$_2$ interface model proposes that the catalytic activity increases due to the increase on the contact surface or interface between the two sulfide phases, but it does not mention which catalytic site is the most active one on the surface of Co$_9$S$_8$/MoS$_2$ [10].

In this study we use transition state computational calculations to determine the most active site out of three possible catalytic sites of Co$_9$S$_8$/MoS$_2$ catalysis such as basal plane (S-S) site, the edge site (Mo-S) and (Mo-Mo). This information is very valuable to design and grow crystals of Co$_9$S$_8$/MoS$_2$ with higher active sites on the surface of the crystallites.

### 2.1 Computational details

Dmol$^3$ code as provided by Material Studio 6.1 (Accelrys® Inc.) was implemented to perform all transition state calculations. The transition states (TS) were located by using the generalized LST/QST. First the LST maximization was run and subsequently an energy minimization was performed in directions conjugate to the associated reaction pathway. The resulting TS approximation was used to run the quadratic synchronous transit maximization. Afterward, another conjugate gradient minimization was performed. The cycle had to be repeated until a stationary point was located. The convergence criterion set for finding transition state calculations was that the tolerance for all root-mean-square forces on atoms was 0.25 eV/Å. The LST/QST methods at
the same level was used in searching for transition states. The vibrational frequency of possible TS was calculated, and each TS was identified to have one imaginary frequency [30-33].

The Co₉S₈/MoS₂ interface model was investigated. This model was treated as a crystal using a supercell with lattice parameters, \( a = 14.0 \) Å, \( b = 20.0 \) Å, and \( c = 6.0 \) Å and \( \alpha = \beta = \gamma = 90 \) (P1 non-symmetry) leaving sufficient empty space between adjacent neighboring atoms to reduce electron interactions in the periodic structure [10].

The effective core potentials were used for which the core electrons of S (1s², 2s²p⁶) and Mo (1s², 2s²p⁶, 3s²p⁶d¹⁰, 4s²p⁶) were represented by a weak pseudopotential [23, 34]. Double numerical basis sets comprising polarization functions on all atoms such as DNP are used in the calculations. The DNP basis set belongs to a double-\( \zeta \) quality basis set with a p-type polarization function which is added to hydrogen and d-polarization functions added to heavier atoms. In the Dmol³ code the basis sets is localized on atoms having different configurations giving different basis sets introducing an error in the calculations. This basis set superposition error (BSSE) can produce a false binding of the molecules, but this can be avoided when using DNP basis set the calculations. The DNP basis set is similar to 6-31G** Gaussian basis sets with a better accuracy for similar basis set size [35-37]. For each basis function the volume was restricted with a cutoff radius of 4.4 Å allowing efficient calculations without loss of accuracy to obtain high quality numerical results [38].

Local density approximation (LDA) functional combined with Vosko, Wilk and Nausair (VWN) functional was implemented to specify the exchange-correlation for the correlation effect between the electrons [24, 34]. The Brillouin-zone integrations were performed with a Monkhorst-Pack grid at a k-point set of (1 x 1 x 1) because of the large supercell. Spin polarization was used to all
calculations for the system containing Mo and Co [39-41]. Thermal smearing of 3 kJ/mol was applied in the calculations to accelerate the self-consistent field (SCF) convergence [35].

Geometry optimization convergence thresholds of 0.01 kcal/mol, 2.5 kcal/mol × Å and 0.005 Å were used between the optimization cycles for the energy change, maximum force, and maximum displacement, respectively. The charge density mixing used was 0.2 [23].

2.2 Results

We studied by means of computational transition state calculations the dissociation and activation of hydrogen and sulfur removal from dibenzothiophene on the catalytically active Co$_9$S$_8$/MoS$_2$ interface model. The energies of barrier for the hydrogen activation and the HDS reaction of the DBT on the surface of the Co$_9$S$_8$/MoS$_2$ interface were calculated. There are three possible activation sites for hydrogen and subsequent HDS reaction on the Co$_9$S$_8$/MoS$_2$ interface model surface, the basal plane (S-S) site, edge sites (Mo-Mo) and (Mo-S) as shown in (Fig. 12).

![Figure 12](image)

Figure 12. A) Front view of Co$_9$S$_8$/MoS$_2$ seed interface model. B) Side view of Co$_9$S$_8$/MoS$_2$ seed interface mode. Basal plane sulfur-sulfur (S-S) site yellow-atoms, edge sites molybdenum-molybdenum (Mo-Mo) turquoise-atoms and (Mo-S) turquoise-yellow atoms.
The hydrogen activation occurs on the basal plane (S-S) site and edge sites (Mo-Mo) and (Mo-S), these sites are used in the computational transition state calculations to calculate their energy barriers for the hydrogen activation followed by their reaction pathway for the sulfur removal from the HDS reaction [42].

In the direct desulfurization, DBT reacts with hydrogen activated on the surface of the catalyst to form biphenyl (BP) and H₂S. In contrast to the usual assumption that coordinated unsaturated (CUS) vacancies are required as proposed by Topsoe and Moses [26, 11], in this study we assume that such vacancies are not necessary for our computational calculations, but a study with CUS sites is left for future studies to compare the catalytic activities of the Co₉S₈/MoS₂ interface model with and without CUS sites.
2.3 Computational transition state calculations for Co$_9$S$_8$/MoS$_2$ catalyst for molybdenum-molybdenum (Mo-Mo) site.

For our reaction mechanism we selected the H$_2$ and DBT positions above basal plane (Mo-Mo) site on the Co$_9$S$_8$/MoS$_2$ catalysis that have the proper orientation on the surface of the catalyst on (Fig. 13 A-D) displays the electron density difference progress for the hydrogen activation on the Co$_9$S$_8$/MoS$_2$ at the (Mo-Mo) site, which is the rate determining step for the subsequent surface reactions to occur on the catalyst. The blue color represents the electron rich and the color red represents the electron poor areas respectively.

![Figure 13. Electron density difference progress for the Co$_9$S$_8$/MoS$_2$ catalyst at the (Mo-Mo) site. The blue color represents the electron rich areas and the red color represents the electron poor area.](image)

In the (Mo-Mo) site mechanism the hydrogen activation starts with a H$_2$ molecule in the gas phase above Co$_9$S$_8$/MoS$_2$ interface (Figure 14, state 1, first structure), followed by the direct desulfurization reaction of DBT on the activated hydrogen on the Co$_9$S$_8$/MoS$_2$ catalyst producing the biphenyl (BP) and hydrogen sulfide (H$_2$S) as byproducts (Fig. 14, states 2 to 10). The H$_2$ molecule above the catalyst is at a stable equilibrium distance on the Co$_9$S$_8$/MoS$_2$ catalyst, the H$_2$
molecule dissociates into two hydrogen atoms each one binding to the Mo-Mo site forming a homogenous Mo-H and Mo-H surface species (Fig. 14, state 1, first and second structures). The DBT molecule approaches in a gas phase to a stable equilibrium state above the two Mo-H species on the surface of the Co₉S₈/MoS₂ catalyst at this stage DBT undergoes the incision of the C-S bond (Fig. 14, state 2, second structure) more details on (section 2.3.2), then through a synchronized mechanism the BP is formed (Fig. 14, states 2 to 8) as well as the H₂S (Fig. 13, state 10, second structure).

Figure 14. Reaction pathway of the hydrogen activation and DBT sulfur removal at the (Mo-Mo) site.

The calculated energy profile for the (Mo-Mo) site and the values of this reaction sequence are shown in (Fig. 15). The energy profile shows that the overall reaction is endothermic.

2.3.1 Hydrogen activation of the H₂ molecule on the Co₉S₈/MoS₂ molybdenum-molybdenum (Mo-Mo) site
The hydrogen molecule above the Co$_9$S$_8$/MoS$_2$ catalyst was selected as the initial structure, then the geometries of the reactant structure were measured (Fig. 14, state 1, first structure), obtaining the following structure values bond length $d$(H-H) = 0.713 Å and distance on the z-axis = 2.60 Å. The structural values of the product state (Fig. 14, state 1, second structure) were calculated having the following structural values: $d$(Mo$_1$-H$_1$) = 1.68 Å, $\angle$S-Mo$_1$-H$_1$ = 103.455° and $d$(Mo$_2$-H$_2$) = 1.68 Å, $\angle$S-Mo$_2$-H$_2$ = 105.572°. For the calculations of the hydrogen dissociation an H$_2$ molecule was located above the (Mo-Mo) site of the Co$_9$S$_8$/MoS$_2$ catalyst at z-axis = 2.60 Å which is the sum of the van der Waals radii of hydrogen and Mo, r$_H$ = 1.20 Å, r$_{Mo}$ = 1.40 Å, after the relaxation the z-axis value changed from 2.60 Å to 3.028 Å. The linear and quadratic synchronous transient (LST/QST) methods were used to locate the transition state characterized by only one negative frequency of $\nu_{TS} = -2488.91$ cm$^{-1}$. The initial energy barrier for the edge (Mo-Mo) site (Fig. 15, state 1) has an initial energy barrier $\Delta E$= +91.22 kcal/mol (+3.95 eV).
Figure 15. Reaction pathway and transition states (1 to 10) of hydrogen activation and DBT sulfur removal for the edge (Mo-Mo) edge site.

2.3.2 The C-S bond breaking of DBT on the Co₉S₈/MoS₂ molybdenum-molybdenum (Mo-Mo) site.

In the initial step for the C-S bond incision the sequence of the adsorption of DBT from the gas phase to a stable equilibrium position above the active Mo-H and Mo-H sites of the Co₉S₈/MoS₂ catalyst (Fig. 14, state 2, second structure). The DBT ring is in an upright position a slightly leaned so the hydrogen pointing to the active site approximately to the C-S bond region. The C-S bond incision was found to have an energy barrier of $\Delta E = +530.373$ kcal/mol (+23 eV) (Fig 14, state 2, second structure). The S-Mo₂-H₂ site has adapted to the presence of the organic molecule by changing the Mo₂-H₂ distance from 1.68 Å to 1.73 Å and the $\angle$Mo₂-S₂-H₂ bonding angle from $\angle$105.226 Å to $\angle$104.878 Å. The first step of the desulfurization reaction occurs in a synchronized mechanism, which consist of three elementary processes, (a) breaking of one C-S bond, (b) the H transfer from the Mo₁-H₁ bond to the vacant position of the benzene ring and formation of the BP-S-Mo-H complex on the surface of Co₉S₈/MoS₂ catalyst as shown in (Fig 14, state 3, first and second structures) [11, 24].

2.3.3 The formation of the biphenyl (BP) molecule after the sulfur removal from the dibenzothiophene molecule on Co₉S₈/MoS₂ molybdenum-molybdenum (Mo-Mo) site.

The formation of the BP molecule consists of breaking the C-S bond followed by a concerted mechanism as shown on (Figure 14, states 2 through 8). Once the BP molecule is formed, it moves away from the surface, and then a new H₂ molecule splits into two hydrogen atoms which bind to the S atom forming Mo-S-H₂ bond (Fig 14, state 9, first structure). The breaking of the bond for the BP molecule formation has a barrier energy of $\Delta E = +574.782$ kcal/mol (+24.9 eV) (Fig. 14,
state 8, second structure), we omitted hydrogen on the rest of the carbon atoms on the BP molecule for visual clarity.

2.3.4 The release of the H$_2$S molecule from the Co$_9$S$_8$/MoS$_2$ catalyst (Mo-Mo) site.

The final step consisted of the desorption of the H$_2$S molecule from the Co$_9$S$_8$/MoS$_2$ catalyst. For this reaction to occur the BP molecule has to move into the gas phase and a new H$_2$ molecule must be adsorbed at a stable equilibrium position above the active site of the catalyst. The H$_2$ molecule finds a position above the Mo-Mo site then H$_2$ molecule splits into two hydrogen forming a Mo-S-H$_2$ species with d(S-H) = 1.41 Å (Fig 14, state 9, second structure), then the H$_2$S molecule is released from Co$_9$S$_8$/MoS$_2$ catalyst surface having an energy of barrier of $\Delta E = +8.806$ kcal/mol (+0.35 eV) (Fig 14, state 10, second structure). We performed similar calculations for the Co$_9$S$_8$/MoS$_2$ catalyst on the edge (Mo-S) site and the basal plane (S-S) site (sections 2.4-2.4.3 and 2.5-2.5.4) respectively. When compared to each other the edge (Mo-Mo) site reveals that it is the most effective and efficient catalytic site since the overall energy of barrier for hydrogen activation, C-S scission, BP formation and the release of H$_2$S molecule needs lower energy than the other two sites as shown on (Fig 16, states 1 to 10) although the initial energy of activation is lower for (Mo-S) than the (Mo-Mo site).
2.4 Computational transition state calculations for Co₉S₈/MoS₂ catalyst for (Mo-S) site.  
We selected the H₂ and DBT positions above the Co₉S₈/MoS₂ catalysis that have the most likely orientation for interaction and proper reaction on edge (Mo-S) site on the surface of the catalyst. (Fig. 17A-D) displays the electron density difference progress for the hydrogen activation on the Co₉S₈/MoS₂ at the (Mo-S) site, which is the rate determining step for the subsequent surface reactions to occur on the catalyst. The blue color represents the electron rich and the color red represents the electron poor areas respectively.
Figure 17. Electron density difference progress for the Co9S8/MoS2 catalyst at the (Mo-S) site. The blue color represents the electron rich areas and the red color represents the electron poor area.

The hydrogen molecule with bond length \(d(H-H) = 0.749 \, \text{Å}\) and the \(z\)-axis\(= 2.60 \, \text{Å}\) was set above the edge (Mo-S) site as the initial state, then the structure was measured (Fig 18, state 1, first structure) obtaining structural values of \(d(H-H) = 0.707 \, \text{Å}\) and \(z\)-axis\(= 2.60 \, \text{Å}\) and two Mo-H and S-H species with bond lengths \(d(\text{Mo-H}) = 1.680 \, \text{Å}\) and \(d(\text{S-H}) = 1.410 \, \text{Å}\) respectively.

Figure 18. Reaction pathway of the hydrogen activation and DBT sulfur removal at the edge (Mo-S) site on the Co9S8/MoS2. Blue color partial charges represent the electron rich areas and red color partial charges represent the electron poor areas.
The structure of the final state (Fig 16, state 1, second structure) was calculated having the following structural values: d(Mo-H) = 1.68 Å, \( \angle S_1-Mo_1-H_1 = 115.086^\circ \) and d(S-H) = 1.41 Å, \( \angle Mo_2-S_2-H_2 = 83.434^\circ \). For the calculations for the homolytic splitting \( \text{H}_2 \) molecule was located above the edge (Mo-S) site on the \( \text{Co}_9\text{S}_8/\text{MoS}_2 \) catalyst model at distance z-axis = 2.60 Å which is the sum of the van der Waals radii of hydrogen and Mo, \( r_H = 1.20 \) Å, \( r_{Mo} = 1.40 \) Å, after the relaxation the z-axis value changed from 2.60 Å to 3.00 Å.

The linear and quadratic synchronous transient (LST/QST) methods were used to locate the transition state characterized by only one negative frequency of \( \nu_{TS} = -704.03 \). The hydrogen activation on the edge (Mo-S) site (Fig 18, state 1, first and second structures) has an energy barrier \( \Delta E = +15.55 \) kcal/mol (0.67 eV) (Fig 19, state 1).

Figure 19. Reaction pathway and transition states (1 to 10) of hydrogen activation and DFT sulfur removal for the edge (Mo-S) site on the \( \text{Co}_9\text{S}_8/\text{MoS}_2 \).
2.4.1 The C-S bond incision of DBT on the Co₉S₈/MoS₂ sulfur-sulfur (Mo-S) site.

In the initial step for the C-S bond incision the sequence of DBT from the gas phase to a stable equilibrium position above the active Mo-H and Mo-S sites of the edge (Mo-S) site on the Co₉S₈/MoS₂ catalyst (Fig. 18, state 2, second structure). The DBT ring is in the upright position a slightly leaned so the hydrogen functions of the active site point approximately to the C-S bond region. The C-S bond incision was found to have an energy of barrier of $\Delta E = +312.911 \text{ kcal/mol} (+13.5 \text{ eV})$ (table 1 and Fig 18, state 2). The Mo-S-H site has adapted to the presence of the organic molecule by changing the S-H distance from 1.68 Å to 1.43 Å and the Mo-S-H bonding angles from $\angle 115.477^\circ$ to $\angle 129.393^\circ$ respectively. The first step of the desulfurization reaction on the edge (Mo-S) site occurs in a synchronized mechanism, which consist of three elementary processes, (a) breaking of one C-S bond, (b) the H transfer from the S-H bond to the vacant position of the benzene ring and formation of the BPS-Mo-H complex [11, 24] on the surface of Co₉S₈/MoS₂ the as shown in (Fig. 18, state 3, second structure).

2.4.2 The formation of the biphenyl (BP) molecule after the sulfur removal from the dibenzothiophene molecule on Co₉S₈/MoS₂ molybdenum-molybdenum (Mo-S) site.

The formation of the BP molecule consists of breaking the C-S bond followed by a concerted mechanism as shown on (Figure 18, states 2 to 8). Once the BP molecule is formed, it moves away from the surface, and then the H₂ molecule splits into two hydrogen atoms which bind to the S atom forming Mo-S-H₂ bond (Fig 18, state 9, first structure). The breaking of the bond for the BP molecule formation has a barrier energy of $\Delta E = +873.762 \text{ kcal/mol} (+37.8 \text{ eV})$ (Fig. 18, state 8, second structure and Fig. 19, state 8), we omitted hydrogen on the rest of the carbon atoms on the BP molecule for visual clarity.
2.4.3 *The release of the H$_2$S molecule from Co$_9$S$_8$/MoS$_2$ catalyst molybdenum-molybdenum (Mo-S) site.*

The final step consists of desorption of the H$_2$S molecule from the Co$_9$S$_8$/MoS$_2$ catalyst. For this reaction to occur the BP molecule has to move into the gas phase and an H$_2$ molecule must be adsorbed at a stable equilibrium position above the active site of the catalyst. The H$_2$ molecule finds a position above the Mo-S site with a distance of $z = 3.00$ Å moving towards the Mo-S site, the H$_2$ molecule splits into two hydrogens forming a Mo-S-H$_2$ species with $d$(S-H) = 1.41 Å (Fig 18, state 9, first structure) and the desorption of the H$_2$S molecule from Co$_9$S$_8$/MoS$_2$ catalyst with an energy barrier of $\Delta E = +8.378$ kcal/mol (+ 0.36 eV) (Fig 19, state 10).

2.5 *Computational transition state calculations for Co$_9$S$_8$/MoS$_2$ catalyst for (S-S) site.*

For our reaction mechanism we selected the H$_2$ and DBT positions above basal plane (S-S) site on the Co$_9$S$_8$/MoS$_2$ catalysis that have the proper orientation on the surface of the catalyst on (Fig. 20 A-D) displays the electron density difference progress for the hydrogen activation on the Co$_9$S$_8$/MoS$_2$ at the (S-S) site, which is the rate determining step for the subsequent surface reactions to occur on the catalyst. The blue color represents the electron rich and the color red represents the electron poor areas respectively.
Figure 20. Electron density difference progress for the Co$_9$S$_8$/MoS$_2$ catalyst, side and front view respectively. The blue color represents the electron rich areas and the red color represent the electron poor areas.

The catalytic series begins with a H$_2$ molecule in the gas phase above Co$_9$S$_8$/MoS$_2$ interface on the basal plane (S-S) site as shown on (Fig. 21, state 1, first structure) followed by the direct desulfurization reaction of DBT on the activated hydrogen on the basal plane (S-S) site on the Co$_9$S$_8$/MoS$_2$ catalyst producing biphenyl and H$_2$S as byproducts (Figure 21, states 2 to 10).
The calculated energy profile and its values of this reaction sequence on the basal plane (S-S) site are shown on (Fig. 22). The energy profile shows that the overall reaction is highly endothermic. The main steps in the hydrogen activation and DBT sulfur removal on the basal plane (S-S) site consist of (a) splitting the H₂ molecule (Fig. 21, state 1, first and second structures), (b) the C-S bond breaking of DBT (Fig. 21, state 2, second structure), (c) the formation of the BP molecule (Fig 21, state 8, second structure), and (d) the release of the H₂S molecule for the catalyst surface (Fig 21, state 10, second structure).

2.5.1 **Hydrogen activation of the H₂ molecule on the Co₉S₉/MoS₂ sulfur-sulfur (S-S) site.**

The H₂ molecule with a bond length d(H-H) = 0.74 Å and a distance along the z-axis = 3.0 Å above basal plane (S-S) site on the Co₉S₉/MoS₂ catalyst was selected as the initial step, then the
geometries of this initial structure was measured (Fig. 21, state 1, first structure), obtaining structural values of \(d(H-H) = 0.70\ \text{Å}\) and \(z = 3.0\ \text{Å}\), which is the sum of the van der Waals radii of hydrogen and sulfur, \(r_H = 1.20\ \text{Å}\), \(r_S = 1.80\ \text{Å}\), after the geometry optimization was run for this structure, the \(z\)-axis value changed from 3.0 Å to 2.9 Å. The structural values of the final state (Fig. 21, state 1, second structure) was calculated having the following structural values: \(d(S-H_1) = 1.41\ \text{Å}\), \(\angle Mo-S-H = 110.1^\circ\), \(d(S-H_2) = 1.41\ \text{Å}\), \(\angle Mo-S-H = 108.4^\circ\).

![Figure 22. Reaction pathway of the hydrogen activation and DBT for sulfur removal at the sulfur-sulfur (S-S) site on the CoSx/MoS2.](image)

Once the parameters for the first and second structures in (Fig 21, state 1) were measured we proceeded to find the transition state structure produced from first and second structures, via linear and quadratic synchronous transient methods which located the transition state energy characterized by only one negative frequency of \(\nu_{\text{TS}} = -331.23\). The energy barrier for the hydrogen activation (Fig 22, state 1) was found to be \(\Delta E = +430.46\ \text{kcal/mol or} \ (+18.66\ \text{eV})\) higher than the basal plane for MoS2 with value of \(+122.22\ \text{kcal/mol} \ (+5.30\ \text{eV})\) as published by Anderson et al.
The overall reaction on the basal plane (S-S) site is highly endothermic and unrealistic, however using Dmol³ code as provided by Material Studio 6.1 (Accelrys® Inc.) we can force any reaction to occur confirming that the basal plane (S-S) site for the reaction pathway is indeed inert for the HDS process as shown on (Figs. 21 and 22) respectively. According to Tanaka and Okuhara basal planes with (S-S) sites serve as hydrogen storage for hydrogen atoms that migrated from the edge and corner sites of MoS₂ catalyst after hydrogen activation, but this behavior on the basal planes will occur only if more severe conditions such as high hydrogen pressure and temperatures are applied during hydroprocessing [46-47]. It is clear that this basal plane (S-S) site will not be appropriate for the HDS reaction on the Co₉S₈/MoS₂ catalyst.

2.5.2 The C-S bond breaking of DBT on the Co₉S₈/MoS₂ sulfur-sulfur (S-S) site.

In this sequence the adsorption of DBT from the gas phase to a stable equilibrium position above the active S-H and S-H sites of the Co₉S₈/MoS₂ interface is considered (Fig. 21, state 2, first structure). The DBT ring is in the upright position slightly tilted so the second hydrogen points to the active site approximately to the C-S bond region. This process has an activation energy of \( \Delta E = +541.342 \text{ kcal/mol} (+23.4 \text{ eV}) \) (Fig 21, state 2, second structure). The \( \angle \text{Mo}_2-\text{S}_2-\text{H}_2 \) site has changed due to the presence of the organic molecule by changing the \( \text{S}_2-\text{H}_2 \) bond distance from 1.4 Å to 1.35 Å and the \( \angle \text{Mo}_1-\text{S}_1-\text{H}_1 \) and \( \angle \text{Mo}_2-\text{S}_2-\text{H}_2 \) bonding angles remain the same at 80° (Fig 21, state 2, first and second structures). The first step of the desulfurization reaction occurs in a concerted mechanism which consists of three elementary processes, (a) breaking of one C-S bond, (b) the H transfer from the S-H bond to the vacant position of the benzene ring and formation of the BPS-H-S complex on the surface of the Co₉S₈/MoS₂ (figure 21, state 3, first and second structures) [11, 24].
2.5.3 The formation of the biphenyl (BP) molecule on the $\text{Co}_9\text{S}_8/\text{MoS}_2$ sulfur-sulfur (S-S) site.

The formation of the BP molecule consists of breaking the C-S bond followed by a concerted mechanism (Figure 21, states 2 to 8). Once the BP molecule is formed, it moves away from the surface, and then a H$_2$ molecule splits into two hydrogen atoms which bind to the S atom forming S-S-H$_2$ bond (Fig. 21, state 9, second structure). The breaking of the bond for the BP molecule formation has a barrier energy of $\Delta E = +300.233$ kcal/mol (+13.01 eV) and (Fig 21, state 8, second structure). We have omitted hydrogen atoms attached to carbon on the BP molecule for visual clarity.

2.5.4 The release of the H$_2$S molecule from the $\text{Co}_9\text{S}_8/\text{MoS}_2$ catalyst sulfur-sulfur (S-S) site.

The final step consists in releasing the H$_2$S molecule from the $\text{Co}_9\text{S}_8/\text{MoS}_2$ catalyst. For this reaction to occur the BP molecule has to move away from the surface of the catalyst and a new H$_2$ molecule splits into two hydrogen atoms forming a S-H$_2$ species with $d$(S-H) = 1.41 (Fig. 21, state 9, second structure) and the release of the H$_2$S molecule (Fig. 21, state 10, second structure) has an energy barrier of $\Delta E = +1.205$ kcal/mol (+0.052 eV) (Fig. 22, state 10).

2.6 Reaction rate constant, reaction order, and temperature approximations for the (S-S), (Mo-S) and (Mo-Mo) site.

A chemical reaction is a rearrangement of the structure and a redistribution of the energy in a chemical system. The mechanism of a reaction is the microscopic sequence of events that takes place during the transformation of reactants to products. In this study we proposed a reaction surface mechanism on the catalytic sites of $\text{Co}_9\text{S}_8/\text{MoS}_2$ catalyst by comparing the reactants and products and intermediates that occur during the hydrodesulfurization reaction. If the transition state structure can be simulated then its activation energy can be obtained, using the activation
energy values (table 2) is possible to calculate the thermodynamic properties.

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Table 2. Activation energy values for the (S-S), (Mo-Mo) and (Mo-S) site

The rate constant and reaction order were calculated for the CoS$_8$/MoS$_2$ catalyst for the (S-S), (Mo-S) and (Mo-Mo) sites as shown on figure 23, 24, and 24) using equation 10, \( \frac{d\ln k}{dT} = \frac{E_a}{RT^2} \), where T=1K and R = 8.314 J/mol to calculate the rate constant. Plotting the rate constant versus time shows the pattern for a second order reaction that occurs on the three sites of catalysts.

Figure 23. A) Reaction rate constant (k) calculated from activation energy values. B) Second order reaction determined from the reaction rate constant (k) versus time (t) for the (S-S) site.
Figure 24. A) Reaction rate constant (k) calculated from the activation energy values. B) Second order reaction determined from the reaction rate constant (k) versus time (t) for the (Mo-Mo) site.

Figure 25. A) Reaction rate constant (k) calculate from the activation energy value. B) Second order reaction determined from the reaction rate constant (k) versus time (t) for the (Mo-S) site.

The temperature approximations for each transition states for the (S-S), (Mo-Mo), and (Mo-S) sites were calculated using the activation using equation 10 and solving for temperature, $T = \frac{\sqrt{E_a}}{\sqrt{R}}$.

The fix bed reactor operates between 573 K and 673 K, fig x shows that the catalyst can be activated with a minimum temperature of 490 K and 361 K for the (Mo-Mo) and (Mo-S) sites.
respectively. The (S-S) site requires a minimum temperature of 738 K in order for the hydrogen to be active on this site.

![Figure 26. Temperature approximations for hydrogen activation on the (S-S), (Mo-Mo) and (Mo-S) sites.](image)

### 2.7 Discussion

The Co₉S₈/MoS₂ catalyst model (Fig. 12) shows that the best catalytic site is (Mo-Mo) site since its overall energy for the HDS reaction is lower than the edge (Mo-S) site and the basal plane (S-S) site respectively as shown on (Fig. 16).

The Co₉S₈/MoS₂ catalyst model shows that the (Mo-Mo) site is the more active catalytic site when compared to other published results (table 1, column 3) that employ the MoS₂ slab. Although the energy barrier for the hydrogen activation is lower for the (Mo-S) sites their intermediate steps are higher than the (Mo-Mo) site, the energy barrier to release the H₂S in our calculations² for the (Mo-Mo) site (column 3, row l) is lower than the (S-S) site and (Mo-S) site (Columns 2 and 4, row l) respectively.
Table 1. Transition state (TS) number and the energy of barrier of the sulfur-sulfur (S-S) site, molybdenum-molybdenum (Mo-Mo) site, and molybdenum-sulfur (Mo-S) site for Co₉S₈/MoS₂ catalyst.

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<td>i</td>
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<td>+11.304</td>
<td>+0.281</td>
<td>+39.187</td>
</tr>
<tr>
<td>j</td>
<td>10</td>
<td>(H₂S) +1.205, +25.36</td>
<td>(H₂S) +8.806, +50.17</td>
<td>(H₂S) +8.378, +19.14</td>
</tr>
</tbody>
</table>

It is important to point out that hydrogen activation energy will occur on the three sites (Mo-Mo), (Mo-S) and (S-S) therefore the following relevant observations are made:

- The proposed reaction mechanism for hydrogen activation and the subsequent sulfur removal from the DBT on the surface of the Co₉S₈/MoS₂ gives a better insight of how the HDS reaction occurs on the surface of the catalyst.
- The reaction mechanism showed that the (Mo-Mo) site is the most efficient catalytic site on the Co₉S₈/MoS₂ catalyst and that the basal plane (S-S) site is inert.
- The information obtained from the reaction mechanism on the Co₉S₈/MoS₂ catalyst will be of high usage for designing new catalytic material.
- A Co₉S₈/MoS₂ crystal also could be grown in the specific direction that contains the most active site in this case the (Mo-Mo) site by design and crystal engineering methods.
Experiments on unsupported binary transition metal sulfides such as Co₉S₈/MoS₂ shows that this catalyst has a good HDS activity almost as good as the Ni₃S₂/MoS₂ which has the highest activity for the HDS reaction when compared to other binary transition sulfides [48]. It is well known that once a catalysis such as MoS₂ is in a reactor environment it is stabilized by carbide species on its surface enhancing the catalytic properties as shown by synchrotron studies. A study of the Co₉S₈/MoS₂ interface stabilized with carbide species is left for a future study. The catalytic activity of binary transition sulfides is based on their electronic structure and the effect of Co as promoter on such catalysis, on this study we just focused on the Co₉S₈/MoS₂ interface model surface catalytic properties [49]. We approached the catalytic activity of the Co₉S₈/MoS₂ in a theoretical way by performing computational transition state calculations following a reaction pathway for the hydrogen activation and sulfur removal from DBT molecule forming a BP molecule and finally the removal of the H₂S molecule form the surface of the Co₉S₈/MoS₂ catalysis.

2.8 Conclusion

Computational transition state calculations were performed on the Co₉S₈/MoS₂ catalysis to determine its most active site at three different catalytic sites such as basal plane (S-S) site, edge sites (Mo-Mo) and (Mo-S). By following a reaction pathway on the surface of the Co₉S₈/MoS₂ interface for HDS reaction that includes the hydrogen activation on the catalysis, the sulfur removal from the DBT, the formation of BP and H₂S removal from the surface of the Co₉S₈/MoS₂ catalyst. This study has revealed that the most catalytic active site corresponds to the edge (Mo-Mo) site, having an overall energy barriers for HDS reaction lower than edge (Mo-S) site and basal plane (S-S) site. The edge (Mo-Mo) site has a hydrogen activation with an energy barrier of +91.22 kcal/mol (3.95 eV), although this energy is higher than the commonly used MoS₂ catalyst with an activation energy of +13.86 kcal/mol (+0.60 eV) when promoted with Co [23]. This study may
lead us to explore the generation and design of more catalytic efficient binary transition metal sulfides such as Co$_9$S$_8$/MoS$_2$. The designed and engineered crystal should have a chemical structure of the established efficient site in this case the edge (Mo-Mo) site by growing a crystal of the Co$_9$S$_8$/MoS$_2$ catalyst that has the specific orientation that contains the most active (Mo-Mo) site, this design can be reached similarly to the studies of Kuo and Tatarchuk that observed an improvement on the HDS activity of RuS$_2$/Al$_2$O$_3$ with specific \{111\}/\{100\} surfaces [50].
References


Chapter 3 Stacking height effect and hydrogen activation calculations on the Co$_9$S$_8$/MoS$_2$ catalyst via computational transition states

**Problem:** To investigate if varying the stacking height number of Co$_9$S$_8$/MoS$_2$ increases or decreases the catalytic activity of the Co$_9$S$_8$/MoS$_2$ catalysis and also determine which stacking height number and catalytic site are the most effective for the hydrosulfurization (HDS) process to remove sulfur from organo-sulfur compounds found in crude oil.

**Solution:** We studied the catalytic dependence on the stacking height with different number of layers (n), 1<n<4 for the Co$_9$S$_8$/MoS$_2$ catalyst, and the most active site of the catalyst with three possible activation sites, the sulfur-sulfur (S-S), molybdenum-molybdenum (Mo-Mo), molybdenum-sulfur (Mo-S) sites and the stacking height catalytic dependence effect. The catalytic activity with respect to stacking height number and the catalysis sites were found by calculating the hydrogen activation, transition states and energy of barriers on the (S-S) site, (Mo-Mo) site, and the (Mo-S) via linear synchronous and quadratic (LST/QST) methods.

**Abstract:** We carried out computational transition states calculations for the hydrogen activation to study the catalytic dependence on the stacking height with different number of layers (n), 1<n<4 for Co$_9$S$_8$/MoS$_2$ catalyst with three possible activation sites, the basal plane sulfur-sulfur (S-S) site, edge molybdenum-sulfur (Mo-S) site, and edge molybdenum-molybdenum (Mo-Mo) site. The hydrogen activation is considered the rate determining step for the overall hydroprocessing. Understanding the hydrogen activation thermodynamically is important to determine the energy required for the hydrogen activation on the Co$_9$S$_8$/MoS$_2$ catalyst. The catalytic activity of the catalyst sites were found by calculating the hydrogen activation, transition states and energy of barriers on the basal plane (S-S) site, edge (Mo-S) site, and the edge (Mo-Mo) site respectively via linear synchronous transit and quadratic synchronous transit (LST/QST) methods integrated in a
density functional theory (DFT) program such as Dmol³. This study showed that catalytic activity was dependent on the stacking height revealing that the Co₉S₉/MoS₂ structure at the edge (Mo-Mo) site was the most efficient catalytically structure requiring less energy for the hydrogen activation.
3.0 Introduction

Layered transition metal sulfides (LTMS) such as MoS$_2$, WS$_2$ and ReS$_2$ are the most important commercial catalysts available for sulfur removal in the hydrodeulfurization (HDS) reaction. These catalytic materials all have layered structures with layers of the metal sandwiched between close-packed layers.

The activity of the MoS$_2$ catalyst has higher selectivity for direct hydrogen desulfurization when MoS$_2$ is in stacks of three or four layers when freshly prepared. The stacking height number affects the selectivity of the catalyst as proposed by Daage and Chianelli using a model that correlates the stacking height number and selectivity properties for non-supported and non-promoted MoS$_2$ catalyst [1]. We studied the catalytic properties of the Co$_9$S$_8$/MoS$_2$ catalyst based on the increase of stacking height and specifically on the surface of the catalyst that has catalytic sites such as the basal plane (S-S) site, edge (Mo-S) site and (Mo-Mo) site in order to determine if there is any catalytic dependency on the stacking height number of this binary transition metal sulfide catalyst. Formerly the Co$_9$S$_8$/MoS$_2$ interface model was used to explain the promotion effect and catalytic activity in sulfide phases, suggesting that activity is directly connected with an increase of the contact surface area between the two sulfide phases [2]. The Co$_9$S$_8$/MoS$_2$ interface was obtained from HRTEM and computational modeling (Fig 23) using this model we investigated the energy barrier required to start the hydrogen activation on the stacking height with different number of layers (n), 1<n<4 for Co$_9$S$_8$/MoS$_2$ catalyst for following catalytic sites: basal plane (S-S) yellow atoms, edge sites (Mo-Mo) turquoise atoms and (Mo-S) turquoise yellow atoms of sulfur [3].
Studies have shown that the stacking height number and dispersion of supported MoS$_2$ has been important to form CoMoS phases for achieving optimal selectivity for the (HDS) reaction [4]. The study of unsupported Co$_9$S$_8$/MoS$_2$ catalyst will be important to see if this catalyst follows the same trend and behavior of the MoS$_2$ catalyst when the stacking height is increased and also if this catalytic dependent behavior could be observed in a future study to other binary transition metal sulfides such as V$_2$S$_3$/MoS$_2$, Cr$_2$S$_3$/MoS$_2$, MnS/MoS$_2$, FeS$_x$/MoS$_2$, Ni$_2$S$_3$/MoS$_2$, CuS$_x$/MoS$_2$, and ZnS/MoS$_2$.

Alongside the stacking height number there have been identified other factors that appear to be related to the catalytic activity of the MoS$_2$ catalysis, factors such as the orbital occupation of the
highest occupied molecular orbital (HOMO), the degree of covalency of the metal sulfur bond, the metal sulfur covalent bond strength, and the promotion effect [5]. The Co₉S₈ and Ni₂S₃ phases have been described as promoters of MoS₂ and WS₂, but it has been shown that these phases themselves have activities which are of the same order as MoS₂ [6]. The addition of promoters to MoS₂ catalyst increase the stacking height number of MoS₂ catalyst, but this effect is decreased by the hydridesulfurization conditions which favor the formation of single slabs which favor the hydrogenation and C-S bond cleavage steps. Conversely edge sites which are located on the interior layer of the MoS₂ catalyst are able to cleave the C-S bond causing direct sulfur removal [7]. This study will focus from a thermodynamic view on the computational transition state calculations to determine the energy barrier of the hydrogen activation and stacking height catalytic dependence on the Co₉S₈/MoS₂ catalyst since hydrogen activation is considered the rate determining step for the overall hydroprocessing [8].

An additional factor related to the catalytically activity of Co₉S₈/MoS₂ is the contact surface area or interface which suggests that the activity is directly connected to an increase of the contact surface area between the sulfide phases, but this factor does not take in account the stacking height number and the catalytic active sites on the surface of the Co₉S₈/MoS₂ catalyst where the hydrogen activation and HDS reaction are actually occurring [9]. Certain materials such as semiconductors have interfaces with neighboring materials stacked one over the other interacting via their lattices having strain, chemical inter-diffusion and phonons for these reason materials having interfaces are very difficult to describe [10]. Recently transition metal sulfides such as MoS₂ have been found to have stacking height degree dependent properties that have attracted great attention for possible applications in nanoelectronics and optoelectronics [11]. Different materials such as graphite, vermiculite, layered metal oxides, layered double hydroxides, metal halides and layered silicates
represent a variety of layered materials that also have stacking degree dependence properties [12, 13]. For layered MoS$_2$ catalyst has been found theoretically that hydrogenation reactions occur only on the rim sites, while both rim and edge sites are responsible for the HDS activity where large molecules such as DBT have high selectivity for hydrogenation reactions when increasing the stacking height layers for MoS$_2$ catalyst [14]. We will study the stacking height catalytic effect on the binary transition metal sulfide catalyst such as Co$_9$S$_8$/MoS$_2$ by increasing the stacking height number and also comparing the catalytic sites on the catalyst (Fig. 24).

Figure 28. A) Representative “seed” of Co$_9$S$_8$/MoS$_2$ model for the first stacking height. B) “Seed” Co$_9$S$_8$/MoS$_2$ model for the second stacking height. C) “Seed” Co$_9$S$_8$/MoS$_2$ model for the third stacking height D) “Seed” Co$_9$S$_8$/MoS$_2$.

The promotion effect or synergistic effect on binary transition metal sulfides is just partially understood, however we are approaching the catalytic properties of the Co$_9$S$_8$/MoS$_2$ catalyst on thermodynamic terms of energy (kcal/mol) required for the hydrogen activation on the catalyst, since hydrogen activation is the first step on the HDS reaction which determines if the subsequent reactions will continue for sulfur removal from organo-sulfur compounds such as dibenzothiophene (DBT).
Computational modeling techniques and calculations can provide a possible approach to get a better insight into the nature of the active sites and stacking height dependence of the MoS\textsubscript{2} catalyst [15, 16]. In this study the hydrogen activation, transition states and energy barriers were calculated to determine the stacking height effect with different number of layers (n), 1≤n≤4 for the Co\textsubscript{9}S\textsubscript{8}/MoS\textsubscript{2} catalyst.

### 3.1 Computational methods

The calculations were performed via linear synchronous and quadratic (LST/QST) methods using the Dmol\textsuperscript{3} code as provided by Materials Studio 6.1. The LST/QST methods are used to calculate the transition states and the energies of barrier for the stacking height effect and the hydrogen activation of the catalyst and we were able determine the highest catalytic activity with respect to stacking height degree and the catalytic site.

The transition states (TS) were found by using the generalized LST/QST proposed by Govind from the original methods of Halgren and Lipscomb.

For the TS calculations first the LST maximization was performed, then an energy minimization in directions conjugate to the associated reaction pathway. The TS approximation found in this approach was used to find the quadratic synchronous transit (QST) maximization and another conjugate gradient minimization was performed. The cycle keeps repeating itself until a stationary point is located. The convergence criterion set for finding transition state calculations was the tolerance for all root-mean-square forces on atoms with 0.25 eV/Å. The LST/QST methods at the same level were used in searching for transition states (TS) [17-20]

The effective core potentials were used for core electrons of S (1s\textsuperscript{2},2s\textsuperscript{2}p\textsuperscript{6}) and Mo (1s\textsuperscript{2}, 2s\textsuperscript{2}p\textsuperscript{6}, 3s\textsuperscript{2}p\textsuperscript{6}d\textsuperscript{10}, 4s\textsuperscript{2}p\textsuperscript{6}) were represented by a weak pseudopotential. Double numerical basis sets with
polarization functions on all atoms such as DNP are used in the calculations. The DNP basis set has a double-ζ quality basis set with a p-type polarization function which is used for hydrogen and d-polarization functions for heavier atoms. The Dmol³ code the basis sets is localized on atoms having different configurations giving different basis sets introducing an error called the basis set superposition error (BSSE) in the calculations. The BSSE can produce a false binding of the molecules, but this can be avoid and it does not occur when DNP basis sets are used in calculations. The DNP basis set is similar to 6-31G** Gaussian basis sets with a better accuracy for similar basis set size [21-23]. For each basis function the volume was restricted with a cutoff radius of 4.4 Å allowing efficient calculations without loss of accuracy to obtain high quality numerical results.

Geometry optimization convergence threshold of 0.01 kcal/mol, 2.5 kcal/mol x Å and 0.005 Å were used between the optimization cycles for the energy change, maximum force, and maximum displacement, respectively. The charge density mixing used was 0.2 [24].

The functional used were the local density approximation (LDA) in combination with the Vosko, Wilk and Nausair (VWN) functional which specify the exchange-correlation for the correlation effect between the electrons [21,22]. The Brillouin-zone integrations were performed with a Monkhorst-Pack grid at a k-point set of (1 x 1 x 1) because of the large supercell. Spin polarization was used to all calculations for the system containing Mo and Co [27-28] Thermal smearing of 3 kcal/mol was applied in the calculations to accelerate the SCF convergence [30].

### 3.2 Results

In this work we studied the catalytic dependence on the stacking height with different number of layers (n), 1<n<4 for the unsupported Co₉S₈/MoS₂ catalyst and the most active site of the catalyst with three possible activation sites, the basal plane (S-S) site, edge (Mo-S) site and edge (Mo-Mo)
site (Fig 24). Based on the information obtained we were able to determine the most active site with respect to the stacking height layer number on the Co₉S₈/MoS₂ catalyst. The catalytic activity of the catalyst sites were found by calculating the hydrogen activation, transition states and energy barriers on the (S-S) site, (Mo-S) site, and the (Mo-Mo) respectively, via linear synchronous and quadratic (LST/QST) methods.

3.3 Hydrogen activation on the Co₉S₈/MoS₂ catalyst stacking height n=1 and (S-S) site

The calculations for the homolytic splitting where the H₂ molecule with bond length \( d(H-H) = 0.740 \) was located above Co₉S₈/MoS₂ catalyst with the a stacking height of \( n = 1 \) (Fig 25A, first structure) at \( z \)-axis = 3 Å which is the sum of the van der Waals radii of hydrogen and sulfur, \( r_H = 1.20 \) Å, \( r_S = 1.80 \) Å, after the relaxation the \( z \)-axis value decreased to 2.98 Å and the H₂ molecule with bond length decreased \( d(H-H) = 0.696 \) (Fig 22A, second structure) The geometry of the product (Fig 25B, first structure) has two S-H species with bond lengths \( d(S-H) = 1.41 \) Å, \( \angle H_1-S_1-Mo = 101.512^\circ \) Å and \( \angle H_2-S_2-Mo = 100.400^\circ \) Å. The optimized product structure (Fig 25, second structure) has two S-H species with bond lengths \( d(S-H) = 1.34 \) Å, \( \angle H_1-S_1-Mo = 99.881^\circ \) Å and \( \angle H_2-S_2-Mo = 96.0795^\circ \) Å. The transition state structure which is an intermediate structure with structural properties of the structures (Fig 25A, second structure) and (Fig 25B second structure) was found via linear and quadratic synchronous transient (LST/QST) methods, the hydrogen activation for the transition state intermediate (Fig. 25C, first and second structures) for the (S-S) site was found to have an energy barrier of 20.469 kcal/mol.
3.3.1 Hydrogen activation on the Co$_9$S$_8$/MoS$_2$ catalyst stacking height n=2 and (S-S) site.

An H$_2$ molecule with a bond length d(H-H) = 0.74 Å and the z-axis = 3.0 Å above the Co$_9$S$_8$/MoS$_2$ catalyst at the (S-S) site was selected (Fig 26A, first structure) with stacking height, n = 2, after the geometry optimization of this structure the following structural values were obtained having a bond length d(H-H) = 0.695 Å and z-axis = 2.98 Å in (Fig 26A, second structure). The product structural values of the no optimized structure (Fig 26B, first structure) has two S-H species with a bond length of d(S$_1$-H$_1$) = 1.407 Å, $\angle$H$_1$-S$_1$-Mo = 88.536° Å and bond length for d(S$_2$-H$_2$) = 1.406 Å and $\angle$H$_2$-S$_2$-Mo = 87.756° Å. The product optimized structure (Fig 26B, second structure) was calculated having the following structural values: d(S$_1$-H$_1$) = 1.334 Å, $\angle$H$_1$-S$_1$-Mo = 99.225° Å and bond length for d(S$_2$-H$_2$) = 1.343 Å, $\angle$H$_2$-S$_2$-Mo = 96.813° Å. The H$_2$ molecule was located above the (S-S) site of the Co$_9$S$_8$/MoS$_2$ interface model at z-axis= 3 Å which is the sum of the van
der Waals radii of hydrogen and sulfur, $r_H = 1.20 \, \text{Å}$, $r_S = 1.80 \, \text{Å}$, after the relaxation the $z$-value changed from 3.0 Å to 2.98 Å. The transition state energy for (Fig 26C, first and second structures) has an energy barrier of 430.36 kcal/mol.

![Diagram showing the transition state structures and energy](image)

Figure 30. Stacking height (n), n=2 for the Co$_9$S$_8$/MoS$_2$ catalyst at the (S-S) site

3.3.2 Hydrogen activation on the Co$_9$S$_8$/MoS$_2$ catalyst stacking height n=3 and (S-S) site

The calculations for the homolytic splitting where the H$_2$ molecule with bond length $d$(H-H) = 0.740 Å was located above Co$_9$S$_8$/MoS$_2$ catalyst with the a stacking height of n = 3 (Fig 27A, first structure) at $z$-axis = 3 Å which is the sum of the van der Waals radii of hydrogen and sulfur, $r_H = 1.20 \, \text{Å}$, $r_S = 1.80 \, \text{Å}$, after the relaxation the $z$-axis value decreased to 2.771 Å and the H$_2$ molecule with bond length 0.740 Å decreased $d$(H-H) = 0.699 (Fig 27A, second structure). The geometry
of the product (Fig 27B, first structure) has two S-H species with bond lengths \( d(S-H) = 1.408 \, \text{Å} \), \( \angle H_1 - S_1 - Mo = 89.310^\circ \) Å and \( d(S-H) = 1.409 \, \text{Å} \), \( \angle H_2 - S_2 - Mo = 89.463^\circ \) Å. The optimized product structure (Fig 27B, second structure) has two S-H species with bond lengths \( d(S-H) = 1.347 \, \text{Å} \), \( \angle H_1 - S_1 - Mo = 96.662^\circ \) Å and \( \angle H_2 - S_2 - Mo = 95.032^\circ \) Å. The transition state structure which is an intermediate structure with structural properties of the structures (Fig. 27A, second structure) and (Fig 27B second structure) was found via linear and quadratic synchronous transient (LST/QST) methods, the hydrogen activation for the transition state intermediate (Fig. 27C, first and second structures) for the (S-S) site was found to have an energy barrier of 465.354 kcal/mol.

Figure 31. Stacking height (n), n=3 for Co\(_9\)S\(_8\)/MoS\(_2\) catalyst at the (S-S) site.
3.3.3 Hydrogen activation on the Co₉S₈/MoS₂ catalyst stacking height n=4 and (S-S) site.

An H₂ molecule with a bond length d(H-H) = 0.74 Å and the z-axis = 3.0 Å above the Co₉S₈/MoS₂ catalyst was selected as the initial state (Fig 28A, first structure), then the geometry of optimization of reactant was calculated (Fig 28A, second structure) final state obtaining the following structural values with a bond length d(H-H) = 0.699 Å and z = 2.60 Å. The no optimized structure of the product (Fig 28B, first structure) had the following structural values for the two S-H species with bond length d(S₁-H₁) = 1.407 Å, ∠H₁-S₁-Mo = 89.249° Å and d(S₂-H₂) = 1.407 Å, ∠H₂-S₂-Mo = 90.342° Å. The structure of the final state (Fig 28B, second structure) were calculated having the following structural values: d(S₁-H₁) = 1.332 Å, ∠H₁-S₁-Mo = 95.054° Å, d(S₂-H₂) = 1.332 Å, ∠H₂-S₂-Mo = 95.849° Å. The calculations for the homolytic splitting, an H₂ molecule was located above the (S-S) site of the Co₉S₈/MoS₂ catalyst with at z-axis = 3 Å which is the sum of the van der Waals radii of hydrogen and sulfur, r_H = 1.20 Å, r_S = 1.80 Å, after the optimization of the z-axis value changed from 3.0 Å to 2.60 Å. The transition state energy (Fig 28C, first and second structures) has an energy barrier of 474.432 kcal/mol.
3.3.4 General graphical representation of the $H_2$ activation and energy barriers on the Co$_9$S$_8$/MoS$_2$ catalyst stacking height $1<n<4$ at the (S-S) site.

The general graph representation (Fig. 29) for the energy barrier calculations for the Co$_9$S$_8$/MoS$_2$ catalyst stacking height $1<n<4$ at the basal plane (S-S) site shows that the energy for the hydrogen activation on the catalysts increases for stacking height ($n$) = 1, 3, 4 with the exception of stacking height $n=2$ where the energy barrier decreases. The hydrogen activation for the stacking height ($n$) = 1 and 2 are low compared to the stacking height ($n$) = 3 and 4 which are much higher. In this
case the Co₉S₈/MoS₂ catalyst with stacking height (n) = 1 and 2 are more efficient for the hydrogen activation.

3.4 Hydrogen activation on the Co₉S₈/ MoS₂ catalyst stacking height n=1 and (Mo-S) site.

The calculations for the homolytic splitting where the H₂ molecule with bond length d(H-H) = 0.74 was located above Co₉S₈/MoS₂ catalyst for the (Mo-S) site with the a stacking height of n = 1 (Fig 30A, first structure) at z-axis = 2.60 Å which is the sum of the van der Waals radii of hydrogen and sulfur, r_H = 1.20 Å and r_Mo = 1.40 Å, after the relaxation the z-axis value changed to 2.691 Å and the H₂ molecule with bond length decreased from 0.74 Å to 0.718 Å (Fig 30A, second structure) The geometry of the product (Fig 30B, first structure) has the S-H specie with
bond length $d(S-H) = 1.410 \text{ Å}$, $\angle H_1-S_1-Mo = 89.742$ and $d(Mo-H) = 1.680 \text{ Å}$, $\angle H_2-Mo-S = 89.781^\circ \text{Å}$. The optimized product structure (Fig 30B, second structure) has the S-H specie with bond length $d(S-H) = 1.342 \text{ Å}$, $\angle H_1-S-Mo = 99.718^\circ \text{Å}$ and $d(Mo-H) = 1.914 \text{ Å}$, $\angle H_2-S-Mo = 126.664^\circ \text{Å}$. The transition state structure which is an structural properties of the structures (Fig 30A, second structure) and (Fig 30B second structure) was found via linear and quadratic synchronous transient (LST/QST) methods, the hydrogen activation for the transition state intermediate (Fig 30C, first and second structures) for the (Mo-S) site was found to have an energy barrier of 232.217 kcal/mol.

Figure 34. Stacking height $(n)$, $n=1$ for hydrogen activation on the Co$_9$S$_9$/MoS$_2$ catalyst for the (Mo-S) site
3.4.1 Hydrogen activation on the Co$_9$S$_8$/MoS$_2$ catalyst stacking height n=2 and (Mo-S) site.

The calculations for the homolytic splitting where the H$_2$ molecule with bond length d(H-H) = 0.74 was located above Co$_9$S$_8$/MoS$_2$ catalyst for the (Mo-S) site with the a stacking height of n = 2 (Fig 28A, first structure) at z-axis = 2.60 Å which is the sum of the van der Waals radii of hydrogen and sulfur, r$_H$ = 1.20 Å and r$_Mo$ = 1.40 Å, after the relaxation the z-axis value changed from 2.60 to 3.00 Å and the H$_2$ molecule with bond length decreased from 0.740 Å to 0.716 Å (Fig 28A, second structure) The geometry of the product (Fig. 31B, first structure) has the S-H specie with bond length d(S-H) = 1.410 Å, ∠H$_1$-S-Mo = 90.940° Å and d(Mo-H) = 1.680 Å, ∠H$_2$-Mo-S = 91.695° Å. The optimized product structure (Fig. 31B, second structure) has the S-H specie with bond length d(S-H) = 1.410 Å, ∠H$_1$-S-Mo = 121.590° Å and d(Mo-H) = 1.68 Å, ∠H$_2$-Mo-S = 86.289° Å. The transition state structure which is an structural properties of the structures (Fig. 28A, second structure) and (Fig. 31B second structure) was found via linear and quadratic synchronous transient (LST/QST) methods, the hydrogen activation for the transition state intermediate (Fig 31C, first and second structures) for the (Mo-S) site was found to have an energy barrier of 250.745 kcal/mol.
3.4.2 Hydrogen activation on the Co$_9$S$_8$/MoS$_2$ catalyst stacking height $n=3$ and (Mo-S) site.

The calculations for the homolytic splitting where the H$_2$ molecule with bond length $d$(H-H) = 0.74 was located above Co$_9$S$_8$/MoS$_2$ catalyst for the (Mo-S) site with the a stacking height of $n = 3$ (Fig 32A, first structure) at $z$-axis = 2.60 Å which is the sum of the van der Waals radii of hydrogen and sulfur, $r_H = 1.20$ Å and $r_{Mo} = 1.40$ Å, after the relaxation the $z$-axis with respect to the sulfur-hydrogen distance changed from 2.60 Å to 2.662 Å and from 2.60 Å to 3.192 Å with respect to the molybdenum-hydrogen distance. The H$_2$ molecule with bond length decreased from 0.740 Å to 0.719 Å (Fig 32A, second structure). The geometry of the product (Fig 32B, first
structure) has the S-H specie with bond length $d(S-H) = 1.410 \text{ Å}$, $\angle H_1-S-Mo = 90.724^\circ \text{ Å}$ and $d(Mo-H) = 1.680 \text{ Å}$, $\angle H_2-Mo-S = 89.998^\circ \text{ Å}$. The optimized product structure (Fig 32B, second structure) has the S-H specie with bond length $d(S-H) = 1.378 \text{ Å}$, $\angle H_1-S-Mo = 92.524^\circ \text{ Å}$ and $d(Mo-H) = 1.864 \text{ Å}$, $\angle H_2-Mo-S = 88.638^\circ \text{ Å}$. The transition state structure which is an structural properties of the structures (Fig 32A, second structure) and (Fig 32B second structure) was found via linear and quadratic synchronous transient (LST/QST) methods, the hydrogen activation for the transition state intermediate (Fig 32C, first and second structures) for the (Mo-S) site was found to have an energy barrier of 351.764 kcal/mol.

Figure 36. Stacking height (n), n=3 for hydrogen activation for the Co$_9$S$_8$/MoS$_2$ catalyst at the (Mo-S) site.
3.4.3 Hydrogen activation on the Co₉S₈/MoS₂ catalyst stacking height n=4 and (Mo-S) site.

The calculations for the homolytic splitting where the H₂ molecule with bond length d(H-H) = 0.740 was located above Co₉S₈/MoS₂ catalyst for the (Mo-S) site with the a stacking height of n = 4 (Fig 33A, first structure) at z-axis = 2.60 Å which is the sum of the van der Waals radii of hydrogen and sulfur, r_H = 1.20 Å and r_Mo = 1.40 Å, after the relaxation the z-axis value changed from 2.60 to 2.615 Å and the H₂ molecule with bond length decreased from 0.740 Å to 0.720 Å (Fig 33A, second structure). The geometry of the product (Fig. 33B, first structure) has the S-H specie with bond length d(S-H) = 1.410 Å, ∠H₁-S-Mo = 92.475° Å and d(Mo-H) = 1.680 Å, ∠H₂-Mo-S = 87.003° Å. The optimized product structure (Fig 33B, second structure) has the S-H specie with bond length d(S-H) = 1.375 Å, ∠H₁-S-Mo = 94.306° Å and d(Mo-H) = 1.852 Å, ∠H₂-Mo-S = 85.082° Å. The transition state structure which is an structural properties of the structures (Fig 30A, second structure) and (Fig 33B second structure) was found via linear and quadratic synchronous transient (LST/QST) methods, the hydrogen activation for the transition state intermediate (Fig 33C, first and second structures) for the (Mo-S) site was found to have an energy barrier of 337.877 kcal/mol.
3.4.4 Graphical representation of the $H_2$ activation and energy barriers on the Co$_9$S$_8$/MoS$_2$ catalyst stacking height $1<n<4$ for the (Mo-S) site

The general graph representation (Fig. 34) for the energy barrier calculations for the Co$_9$S$_8$/MoS$_2$ catalyst stacking height $1<n<4$ at the edge (Mo-S) site shows that the energy for the hydrogen activation on the catalyst increases for stacking height $(n) = 1, 2, 3$, with the exception of the stacking height 4 for which the hydrogen activation energy decreases slightly. In this case the Co$_9$S$_8$/MoS$_2$ catalyst with stacking height $(n) = 1$ at the edge (Mo-S) site is more efficient for the hydrogen activation.
3.5 Hydrogen activation on the Co$_9$S$_8$/MoS$_2$ catalyst stacking height n=1 and (Mo-Mo) site

The calculations for the homolytic splitting where the H$_2$ molecule with bond length d(H-H) = 0.74 Å was located above Co$_9$S$_8$/MoS$_2$ catalyst for the (Mo-Mo) site with a stacking height of n = 1 (Fig. 35A, first structure) at z-axis = 3.00 Å, after the relaxation the z-axis value changed from 3.00 Å to 4.00 Å and the H$_2$ molecule with bond length decreased from 0.740 Å to 0.698 Å (Fig. 35A, second structure). The geometry of the product (Fig 35B, first structure) has two Mo-H species with bond lengths d(M-H) = 1.68 Å, $\angle$H$_1$-Mo-S = 69.612° Å and $\angle$H$_2$-Mo-S = 69.567° Å.
The optimized product structure (Fig. 35B, second structure) has two M-H species with bond lengths $d(\text{Mo-H}_1) = 1.87 \text{ Å}$, $\angle \text{H}_1-\text{Mo}-\text{S} = 55.7^\circ \text{ Å}$ and $d(\text{Mo-H}_2) = 1.835 \text{ Å}$, $\angle \text{H}_2-\text{Mo}-\text{S} = 57.2^\circ \text{ Å}$. The transition state structure which is an structural properties of the structures (Fig 35A, second structure) and (Fig. 35B, second structure) was found via linear and quadratic synchronous transient (LST/QST) methods, the hydrogen activation for the transition state intermediate (Fig 35C, first and second structures) for the (Mo-Mo) site was found to have an energy barrier of 200.315 kcal/mol.

Figure 39. Stacking height (n), n=1 for hydrogen activation on the Co₉S₈/MoS₂ catalyst, (Mo-Mo) site.

3.6 Hydrogen activation on the Co₉S₈/ MoS₂ catalyst stacking height n=2 and (Mo-Mo) site
The calculations for the homolytic splitting where the H₂ molecule with bond length d(H-H) = 0.775 Å was located above Co₉S₉/MoS₂ catalyst for the (Mo-Mo) site with the a stacking height of n = 2 (Fig 36A, first structure) at z-axis = 2.60 Å which is the sum of the van der Waals radii of hydrogen and sulfur, rₜₜ = 1.20 Å and rₘₐₜ = 1.40 Å, after the relaxation the z-axis value changed from 2.60 to 4.00 Å and the H₂ molecule with bond length decreased from 0.775 Å to 0.701 Å (Fig 36A, second structure). The geometry of the product (Fig. 33B, first structure) has the M-H species with bond length d(Mo-H) = 1.684 Å, ∠H₁-Mo-S = 102.527° Å and d(Mo-H) = 1.684 Å, ∠H₂-Mo-S = 112.794°Å. The optimized product structure (Fig 36B, second structure) has the M-H species with bond lengths d(Mo-H₁) = 1.684 Å, ∠H₁-Mo-S = 108.348° Å and d(Mo-H₂) = 1.684 Å, ∠H₂-Mo-S = 108.960° Å. The transition state structure which is an structural properties of the structures (Fig 36A, second structure) and (Fig 36B second structure) was found via linear and quadratic synchronous transient (LST/QST) methods, the hydrogen activation for the transition state intermediate (Fig 36C, first and second structures) for the (Mo-Mo) site was found to have an energy barrier of 233.871 kcal/mol.
Figure 40. Graphical representation of the $\text{H}_2$ activation and energy barriers on the $\text{Co}_9\text{S}_8/\text{MoS}_2$ catalyst stacking height $n=2$ for the (Mo-Mo) site.

### 3.6.1 Hydrogen activation on the $\text{Co}_9\text{S}_8/\text{MoS}_2$ catalyst stacking height $n=3$ and (Mo-Mo) site

The calculations for the homolytic splitting where the $\text{H}_2$ molecule with bond length $d(\text{H-H}) = 0.740$ was located above $\text{Co}_9\text{S}_8/\text{MoS}_2$ catalyst for the (Mo-Mo) site with the a stacking height of $n = 3$ (Fig 37A, first structure) at $z$-axis = 2.60 Å which is the sum of the van der Waals radii of hydrogen and sulfur, $r_\text{H} = 1.20$ Å and $r_\text{Mo} = 1.40$ Å, after the relaxation the $z$-axis value changed from 2.60 to 3.0 Å and the $\text{H}_2$ molecule with bond length decreased from 0.740 Å to 0.703 Å (Fig. 37A, second structure) The geometry of the product (Fig 37B, first structure) has two Mo-H species with bond length $d(\text{Mo-H}) = 1.680$ Å, $\angle \text{H}_1\text{-Mo-S} = 120.753^\circ$ Å and $\angle \text{H}_2\text{-Mo-S} = 123.007^\circ$
Å. The optimized product structure (Fig 37B, second structure) has two Mo-H species with bond length $d$(Mo-H) = 1.680 Å, $\angle$H$_1$-Mo-S = 109.897° Å and $\angle$H$_2$-Mo-S = 106.686° Å. The transition state structure which has structural properties of the structures (Fig 37A, second structure) and (Fig 37B second structure) was found via linear and quadratic synchronous transient (LST/QST) methods, the hydrogen activation for the transition state intermediate (Fig 37C, first and second structures) for the (Mo-Mo) site was found to have an energy barrier of 335.755 kcal/mol.

Figure 41. Graphical representation of the H$_2$ activation energy barrier on the Co$_9$S$_8$/MoS$_2$ catalyst stacking height n= 3 for the (Mo-Mo) site.
3.6.2 Hydrogen activation on the Co₉S₈/MoS₂ catalyst stacking height n=4 and (Mo-Mo) site.

The calculations for the homolytic splitting where the H₂ molecule with bond length $d(H-H) = 0.740$ Å was located above Co₉S₈/MoS₂ catalyst for the (Mo-Mo) site with the stacking height of $n = 4$ (Fig 38A, first structure) at $z$-axis = 2.60 Å which is the sum of the van der Waals radii of hydrogen and sulfur, $r_H = 1.20$ Å and $r_{Mo} = 1.40$ Å, after the relaxation the $z$-axis value changed from 2.60 to 3.740 Å and the H₂ molecule with bond length decreased from 0.740 Å to 0.703 Å (Fig 38A, second structure). The geometry of the product (Fig 38B, first structure) has the Mo-H species with bond length $d(Mo-H) = 1.880$ Å, $\angle H_1-Mo-S = 120.753^\circ$ Å and $\angle H_2-Mo-S = 123.007^\circ$ Å. The optimized product structure (Fig 38B, second structure) has the M-H species with bond length $d(Mo-H_1) = 1.874$ Å, $\angle H_1-S-Mo = 119.804^\circ$ Å and $d(Mo-H_2) = 2.074$ Å, $\angle H_2-Mo-S = 76.273^\circ$ Å. The transition state structure which is an structural properties of the structures (Fig. 38A, second structure) and (Fig. 38B second structure) was found via linear and quadratic synchronous transient (LST/QST) methods, the hydrogen activation for the transition state intermediate (Fig 38C, first and second structures) for the (Mo-Mo) site was found to have an energy barrier of 327.634 kcal/mol.
3.6.3 Graphical representation of the \( \text{H}_2 \) activation and energy barriers on the \( \text{CoS}_9/\text{MoS}_2 \) catalyst stacking height \( n=4 \) for the (Mo-Mo) site.

The general graph representation (Fig 39) for the energy barrier calculations for the \( \text{CoS}_9/\text{MoS}_2 \) catalyst stacking height \( 1<n<4 \) at the edge (Mo-Mo) site shows that the energy for the hydrogen activation on the catalyst increases for stacking height \( n=1, 2, 3 \), with the exception of the stacking height 4 for which the hydrogen activation energy decreases slightly. In this case the \( \text{CoS}_9/\text{MoS}_2 \) catalyst with stacking height \( n=1 \) at the edge (Mo-Mo) site is more efficient for the hydrogen activation.
3.6.4 A general graphical representation of the H₂ activation and energy barriers on the Co₉S₂/MoS₂ catalyst stacking height 1<n<4 at the basal (S-S) site, edge (Mo-S) and (Mo-Mo) site.

A general graphical representation of the H₂ activation and energy barriers on the Co₉S₂/MoS₂ catalyst stacking height 1<n<4 at the basal plane (S-S) site, edge (Mo-S) site and (Mo-Mo) site (Fig 40). This graph shows that the hydrogen activation on the Co₉S₂/MoS₂ catalyst has better overall catalytic properties for the edge (Mo-Mo) site for the stacking height 1<n<4 than the other two catalytic sites such as the basal plane (S-S) site and edge (Mo-S) site that also have the same stacking height number.
Figure 44. A general graphical representation of the H$_2$ activation and energy barriers on the Co$_9$S$_8$/MoS$_2$ catalyst stacking height 1<n<4 for the basal plane (S-S) site and edge (Mo-S) and edge (Mo-Mo) sites.

### 3.7 Discussion

The purpose of this study was to determine the relationship between the stacking height and the catalytic activity of hydrogen activation on the surface of the Co$_9$S$_8$/MoS$_2$ catalyst by computational transition state calculations where models of Co$_9$S$_8$/ MoS$_2$ catalyst were used by increasing a layer of sulfur and molybdenum atoms. The transition state calculations also were carried out on each stacking height on different sites such as the basal plane (S-S) site, edge (Mo-S) site and edge (Mo-Mo) site. The Co$_9$S$_8$/MoS$_2$ stacking height 1<n<4 and edge (Mo-Mo) site revealed that these structures are the most catalytic active also it showed that as the layers on the
Co$_9$S$_8$/MoS$_2$ were increased the catalytic properties were decreased since the energy for the hydrogen activation in kcal/mol increased (Fig 40).

This observation lead us to believe that Co$_9$S$_8$/MoS$_2$ catalysis has to be tuned up structurally by changing the atomic layers to reach the point of maximum catalytic performance, a goal that could be achieved by computational modeling and design and crystal engineering to reduce the time consuming experiments in the laboratory. In an upcoming study we will investigate stacking height effect on the catalytic performance via density of states and electronic band gap structures for binary transition metal sulfides such as V$_2$S$_3$/MoS$_2$, Cr$_2$S$_3$/MoS$_2$, MnS/MoS$_2$, Ni$_3$S$_2$/MoS$_2$, CuS$_x$/MoS$_2$, ZnS/MoS$_2$ and FeS$_x$/MoS$_2$, the goal of this study will be to improve the catalytic activity of these low cost materials by tuning up computationally their layered structure by decreasing or increasing their stacking height, a goal that was done experimentally on FeS$_x$/MoS$_2$ having selectivity for hydrodenitrification (HDN) [31]. Combining computational methods the binary transition metal sulfide catalysts could be optimized aiming for the following objectives:

- Determining the most catalytic structure of the binary transition metal sulfides based on their stacking height number and most active site via computational transition states calculations.
- Modifying “tuning up” computationally the structure of the binary transition metal sulfides to enhance their maximum catalytic performance of these materials.
- Designing and engineering binary transition metal sulfide catalyst with the best catalytic properties from the computational “tuned up” structures to synthesize binary transition metal sulfides.

Experimentally and by changing its stacking height number a binary transition metal sulfide such as FeS$_x$/MoS$_2$ was structurally modified “tuned up” by Chianelli et al showing good
catalytic properties for the HDN reaction. Tuning up the structures of the binary transition metal sulfides via computational methods open the possibilities of enhancing the catalytic properties of binary transition metal sulfide for HDS and HDN reactions. In this study we just focused on hydrogen activation which is the crucial step for the HDS and HDN reactions on the Co₉S₈/MoS₂ models to determine the most effective structure with respect to its stacking height number where it was observed that as the stacking height is increased the energy barrier for the hydrogen activation was higher using the Co₉S₈/MoS₂ models with stacking heights 1<n<4.

3.8 Conclusion

In this study we determined a dependency on the catalytic activity of the Co₉S₈/MoS₂ catalyst by calculating the transition states and energy barriers by varying the stacking height number (n) = 1<n<4, where the Co₉S₈/MoS₂ structures at the edge (Mo-Mo) site resulted as the most efficient catalytic structure when compared with Co₉S₈/MoS₂ structures at the basal plane (S-S) site and edge (Mo-S) site. The structural changes such as increasing the stacking height showed a change on the catalytic efficiency increasing the energy barriers and as consequence decreasing the catalytic properties for the hydrogen activation. In this way modifying “tuning up” via computational modeling the structures of the binary transition metal sulfides will be a useful method to design and engineer materials with enhanced catalytic properties.
References


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Chapter 4 Synthesis and characterization of nano-spherical metallic organic framework

Problem: Modification of size and morphology of the Metal Organic Framework (MOF) of the type HKUST-1 from its octahedral morphology and size range of 2-4 micrometers into a nano-spherical morphology with a size range of 50-100 nanometers.

Solution: Using decanoic acid as modulator to adjust morphology and size obtaining a nano-spherical shape by modification of the HKUST-1 synthesis at room temperature.

Abstract

Typically a KUST-1 metal organic framework (MOF) has an octahedral structure and average size of 1 µm. We synthesized a nano-spherical metal organic framework type KUST-1 with a range size from 50 to 100 nm. The compositional parameters that can be modified to control the size and shape of MOF crystals include solvent pH, metal source, molar ratio of the reactants, reactant concentration, and modulators. We used decanoic acid as modulator to adjust structural size and shape obtaining a nano-spherical shape at room temperature. The synthesis of defined MOF’s materials via hydrothermal or diffusion methods normally requires hours to days, on this paper a simple precipitation route at room temperature was used yielding nano-spherical MOF of the HKUST-1 type.
**4.0 Introduction**

Pioneered by Yaghi, Kitagawa, and Ferey [1-3], Metal–organic frameworks (MOFs) are an interesting class of crystalline materials that can be readily assembled by combining metal ions (components of nodes) and different organic ligands (structural linkers) via coordination chemistry, typically under solvothermal reaction conditions [4-9]. The assemble of multifunctional organic ligands with metal ions, numerous functional MOFs can be synthesized with particular pore shape, size, volume, and chemistry [10, 11]. MOFs are frameworks with all or most atoms on internal surfaces, which leads to remarkably high surface areas (up to 6500 m² g⁻¹) and pore volumes (up to 3.6 cm³ g⁻¹) [12,13]. MOF’s porosity is much higher than that of their corresponding inorganic zeolites analogues (up to 90% higher) [14-16]. MOFs can be designed and systematically tuned by predesign in synthesis and post synthetic modifications. These modifications allow a simple optimization of the pore structure, surface functions, and other properties for specific applications [17], such as novel desulfurization technology [18,19], catalytic [20,21], magnetic, optoelectronic [22], gas adsorption [23-26], gas separation [27-29], gas storage [30-33], environmental [34,35], drug delivery [36,37], heme biomimetic catalysis [38], sensor technology [39]; bio-imaging, functional peptidomics, enzymatic, gene therapy [40] and numerous medical applications [41].

Controlling the size and shape of the crystals is an evolving area in MOF research, since controlling and manipulation are means for optimizing the physical properties of the solids for specific applications [42]. Compositional parameters that can be modified to control and manipulate the size and shape of MOF crystals include solvent pH, metal source, molar ratio of the reactants, reactant concentration, and modulators [43].
The successful functionalization of HKUST-1 with many organic ligands has encouraged us to explore the effects of HKUST-1 at different concentrations with decanoic Acid and 1,3,5 benzenetricarboxyl acid as modulators. Modulators have been employed to adjust the size and shape of MOF crystals.

Ligands with different functionalities such as decanoic acid and 1,3,5-benzenetricarboxylate at different concentrations were used as modulators in HKUST-1 as part of our study on the effect of the decanoic acid and 1,3,5-benzenetricarboxylate on the crystal structure and morphology of functionalized HKUST-1[44].

4.1 Metal Organic Frameworks as catalysis for removal of organo-sulfur compounds

The oil refinery process for the removal of sulfur from organo-sulfur compounds found in crude oil is called hydrodesulfurization (HDS). This process depends on alumina supported heterogeneous catalyst with about 100,000 tons used per year having molybdenum-cobalt or molybdenum-nickel sulfides as the active component. MOFs have been found to have catalytic applications for HDS catalysis [45] therefore there has been an increasing interest in this kind of materials the removal of organo-sulfur compounds.

Metal organic frameworks (MOF’s) contain different components that can be classified as metallic component, organic ligand and a pore system. Therefore there is three types of catalytic MOFs based on these three different components. Our component of interest in this study is the pore system of the MOF which has a physical space where the catalysis takes place or serves as cages where the organo-sulfur molecules are encapsulated [46].
4.1.2 Metal Organic Frameworks in liquid phase for removal of organo-sulfur compounds

Adsorption of organo-sulfur compounds by MOFs have been an alternative for the removal of these compounds since MOFs exceed gas absorption better than the well studied porous materials such as activated carbon and zeolites.

The absorption capacity MOFs for organo-sulfur compounds was tested by Matzager et al. for five different MOFs (Fig. 41) with three organo-sulfur compounds (Fig. 42) using different concentrations of organo-sulfur compounds in isooctane. Adsorption isotherms results showed that these MOFs are good materials for removing organo-sulfur compounds from crude oil [47].

![Figure 45. Crystal structures of (a) MOF-177 (b) MOF-5 (c) UMCM-150 (d) HKUST-1 (e) MOF-505 with one molecule of dibenzothiophene added in the pore of each MOF from [ref 47].](image)

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4.2 Synthesis and characterization of HKUST-1 nano-spherical metallic organic frameworks.

A spray-drying technique has been used by Maspoch et al. since 2013 to synthesize nano-MOFs, but this method requires an especial spray-drying equipment that has to be purchased and adopted to the required MOF synthesis. We were not aware of this method since we started working on the synthesis of nano-MOFs back in 2011 when we were searching for a method to form nano-MOFs of the HKUST-1 type. The only ways known to synthesized nano-MOFs was by means of solvothermal, microwave, fast precipitation methods and using capping agents [48]. The synthesis of defined MOF’s materials via hydrothermal or diffusion methods normally requires hours to days, on this study a simple precipitation route at room temperature was used yielding nano-spherical MOF of the HKUST-1 type.

4.2.1 Materials and Methods

Experimental Section

Figure 43a shows the synthesis route for the synthesis of bipyramidal HKUST-1 MOF as reported and published [49] and (Fig. 43b) displays our synthesis route of spherical HKUST-1 MOF prepared with a slightly modification via fast synthesis at room temperature.
For the synthesis of the spherical HKUST-1 nano-MOF the synthesis was as follows. *Solution A* was prepared by dissolving Cu(II) acetate (5.24 mmol) and 1,3,5-benzenetricarboxyl acid (82.8 mmol) in 5 ml of DMSO mixed under vigorous stirring in a round flask at room temperature for 1 h obtaining a blue colored solution. *Solution B* was prepared by dissolving 82.8 mmol of decanoic acid in 5 ml of DMSO at room temperature for 1 h obtaining an oil like solution. *Solution A* was added to *Solution B* drop wise and the mixed solution was left stirring overnight. The following day the turquoise colored mixture was washed with methanol and centrifuged three times. The centrifuged compound was filtered and dried are room temperature. Figure 40a shows the route synthesis used in (ref 49) and (Fig. 43b) shows the synthesis modified by using decanoic acid in DMSO to form a spherical nano-MOF. XRD powder diffraction patterns are shown in (Fig. 44) where HKUST-1 MOF and its XRD pattern is shown in black color pattern as synthesized from [ref 49] and the spherical nano-MOF as shown in red color.
Figure 48. XRD powder diffraction patterns: HKUST-1 MOF as synthesized (black color pattern [ref 49]). HKUST-1 spherical-nano MOF from modified synthesis (red color pattern).

Scanning Electron Microscope (SEM) pictures inserts in (Fig. 44) shows the HKUST-1 with an octahedral shape and size range of 10-20 µm and the HKUST-1 with a nano-spherical shape and a size range of 50-100 nm. Transmission electron microscope (TEM) confirms the nano-spherical structure of the HKUST-1 MOF (Fig. 45). By using surfactants or selected capping ligands, the shape and size can often be precisely controlled [50].
Figure 49. Transition Electron Microscope (TEM) image of the nano-spherical MOF of the type HKUST-1.

4.3 Conclusion

The XRD, SEM and TEM results demonstrated that HKUST-1 MOF with octahedral structure was modified into a nano-spherical structure by using a simple precipitation route at room temperature. Pure cubic microporous HKUST-1 MOF usually crystallizes in an octahedral shape. In the presence of 1,3,5-benzenetricarboxyl acid and decanoic acid we observed the effects on the size
and morphology of the HKUST-1. Manipulation of the size and shape of the crystals is an important area in MOF research for specific applications. We are interested in the adsorption of the organo-sulfur compounds on the nano-spherical MOF. Future studies of the nano-MOF catalytic activity will be carried out to compare it with catalytic activity of the MOF with the octahedral structure and determine if the size and morphology increase or decreases its catalytic properties. In previous studies HKUST-1 MOF with the octahedral structure has been found to have the highest adsorption capacity for both DBT and DMDBT [51].
References


Curriculum Vitae

Gabriel A. Gonzalez, was born in January 5, 1979 in Mexico. He attended Lydia Patterson Institute for his freshman and sophomore years and transferred for his junior and senior years to Stephen F. Austin High School at El Paso TX, graduating in 1999. He obtained an Associates of Arts degree in 2002 from El Paso Community College (EPCC). Gabriel received his Bachelors of Science degree and Masters of Science degree in chemistry in 2007 and 2010 respectively from the University of Texas at El Paso (UTEP). Gabriel has worked at the UTEP’s chemistry department as undergraduate and graduate research assistant as well as a teacher assistant. In 2010 he was accepted as doctoral student in the Materials Science and Engineering multidisciplinary program where he has been working under the supervision of Dr. Russell R. Chianelli since 2011. Gabriel worked under the supervision of Dr. Luis A. Echegoyen in the synthesis of ScN₃@C₈₀ from 2010 to 2011. Gabriel started working at El Paso Community College (EPCC) as laboratory technician from 2011-2013 and he has been an adjunct professor of chemistry since 2013. Gabriel has worked at distance with military personnel whom were deployed oversees during taking chemistry courses at EPCC receiving a recognition certificate in 2014 from the Camp Bastion Role 3 Hospital personnel at Helmand Providence, Afghanistan. Gabriel was nominated for El Paso Community College Adjunct Achievement Faculty Award in 2015. In 2014 Gabriel worked with Dr. Carlos Diaz from Universidad Autonoma de Ciudad Juarez (UACJ) on the synthesis of LiNbO₃ nanoparticles via wet chemistry methods. Gabriel received the Graduate Research Award in 2014 from the department of Metallurgical and Materials Engineering under the supervision of Dr. Namsoo Kim. As graduate student in chemistry Gabriel received the Outstanding Graduate Student in Chemistry Award in 2010 and he was also the Graduate College of Science Student Marshall. Gabriel attended the Graduate Research Expo at UTEP in 2014 and the International Materials
Research Congress (IMRC) at Cancun Mexico in 2013 and 2014 where he presented posters about catalysis research. During the summers of 2013 and 2014 Gabriel worked and supervised undergraduate students for undergraduate research program at UTEP. Gabriel also worked on thermoelectric materials for the MRTI-UTEP and TXL group from 2011 to 2013, and he also worked at the Texas A & M El Paso station as laboratory technician from 2007 to 2008. Gabriel joined the chemistry department at the Universidad Autonoma de Ciudad Juarez (UACJ) in 2015 working under the supervision of Dr. Bonifacio Alvarado and his former mentor Dr. Juan C. Noveron (UTEP) on anticancer platinum compounds. Gabriel has contributed to two publications in 2013 and 2014 as co-author and he also contributed in writing the general chemistry study guide custom edition 2013 for El Paso Community College under the supervision of Dr. Enrique A. Olivas. Gabriel is currently working on three articles as the main author.