

Transition states energies for catalytic hydrodesulfurization reaction in $\text{Co}_9\text{S}_8/\text{MoS}_2$ theoretical interface using computer-assisted simulations



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ABSTRACT

Transition state computational studies of the sulfur removal from dibenzothiophene (DBT) molecule have herein been performed considering the $\text{Co}_9\text{S}_8/\text{MoS}_2$ interface existing on unsupported Co/MoS_2 catalysts. The linear synchronous transit (LST) and quadratic synchronous transit (QST) methods integrated in a density functional theory (DFT) program such as Dmol³ were used for the calculations of energy barriers of the transition states. Three different configurations present on the $\text{Co}_9\text{S}_8/\text{MoS}_2$ interface have been envisaged as possible catalytic sites: sulfur–sulfur (S, S) sites, and molybdenum–sulfur (Mo, S) and molybdenum–molybdenum (Mo, Mo) edge sites. This study revealed that the (Mo, Mo) edge site is the most catalytically active site for the hydrodesulfurization (HDS) reaction followed by the (Mo, S) edge site while the (S, S) site shows almost inertness for the HDS reaction. This information allows us to propose clues to design new catalysts based on bulk $\text{Co}_9\text{S}_8/\text{MoS}_2$ phases with higher efficiency by increasing the proportion of (Mo, Mo) edge sites.

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1. Introduction

MoS_2 is a transition metal sulfide catalyst used in the hydrodesulfurization process used to remove sulfur, an impurity present in petroleum feedstock and source of emission of pollutants during the combustion of vehicle transportation fuels [1]. MoS_2 catalytic activity is known to be markedly improved when Co or Ni is added as promoter atoms [2,3]. Different models: intercalation, monolayer, decoration, synergy by contact, have been used to explain the origin of the synergetic effect related to the addition of Co or Ni to MoS_2 [4–9]. Intensive efforts have been done to determine the catalytic properties of Co-promoted and unpromoted MoS_2 , both experimentally and theoretically [10–16].

No studies have been done using LST/QST computational methods to determine the catalytic properties of the $\text{Co}_9\text{S}_8/\text{MoS}_2$ interface, but theoretical studies on the origin of the catalytic properties of the MoS_2 catalyst have been done extensively applying the LST/QST methods and first principles density functional methods. Todorova et al. using LST/QST computational methods found the hydrogen activation energies of 2H– MoS_2 surfaces with a MoS_2 slab model. The MoS_2 slab model was first proposed by Raybaud

et al. cleaving a 2H– MoS_2 single crystal to generate MoS_6 prisms stacked along $(10\bar{1}0)$ direction. This model consist of both sandwiches present in the unit cell and, thus, the interlayer interactions are accounted for in the calculations, also this model has been used to investigate the active sites on the $(10\bar{1}0)$ MoS_2 surface. Using Raybaud's model Todorova used LST/QST methods to calculate hydrogen dissociation, 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) and two S–H surface groups (homolytic), favoring heterolytic adsorption of hydrogen. Furthermore, the Ni and Co promoted MoS_2 effect on the H_2 dissociation observing a negative promotional effect on the H_2 dissociation in the case of Ni-promoter MoS_2 , while Co was observed to have a positive effect [21,22].

Another, density functional theory study presented by Weber et al. a reaction mechanism for the direct desulfurization (DDS) on a single-layer of a NiMoS cluster that consist of several individual steps where the dibenzothiophene (DBT) reacts with H_2 on the surface of the NiMoS removing the sulfur from DBT and producing biphenyl (BP) and H_2S believing that the surface of the catalyst is completely covered with hydrogen at the time when DBT molecule approaches to the surface of the MoS_2 catalyst [23]. Cristol et al. calculated the activation energy on a cobalt promoted catalyst for the direct desulfurization mechanism for sulfur removal of

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the 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 [24].

Topsoe et al. found MoS₂ nanoclusters 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 [25–27].

A combined experimental and computational study, has proposed the formation of Co₉S₈/MoS₂ interface, indicating a synergy effect from a direct contact between two bulk phases, Co₉S₈ and MoS₂ resulting in a Co₉S₈/MoS₂ interface for which electronic promotion of Mo by Co can be evidenced [10]. Even though a full description of the localized structure of this interface was done in our previous work [10,37], from a thermodynamically point of view no studies have been done using LST/QST numerical computational methods to determine the catalytic properties the Co₉S₈/MoS₂ interface model. Therefore, a theoretical approach to understand catalytic properties, by proposing a complete mechanism for hydrodesulfurization (HDS) reaction using dibenzothiophene (DBT) molecule in this particular bulk interface have been herein determined through 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 (H₂S) molecule at selected sites (S, S) site, (Mo, Mo) site and (Mo, S) site in Co₉S₈/MoS₂ interface model.

In this respect, the initial step corresponding to the hydrogen activation is central for the following steps in the HDS process [17,18]. Moreover, performing computational transition state calculations for the Co₉S₈/MoS₂ interface can help to understand its catalytic properties for the HDS process. However, it is generally very difficult to locate transition states as is stated by Govind et al. [19] who proposed a generalized transition state location scheme where the molecular, amorphous and crystal models such as the amorphous Co₉S₈/MoS₂ can be treated within the same framework and with general applicability. This approach was based on the Halgren and Lipscomb algorithms for the linear (LST) and quadratic synchronous methods (QST) to locate transition

state structures, transition state energies and reaction pathways [19,20]. Theoretical studies have applied the LST/QST methods and also first principles density functional methods using pseudo-potentials that model the ionic cores of atoms to determine the chemical properties and catalytic reactions of MoS₂-based catalysts [21,22]. We are using these concepts here to study the catalytic properties of the Co₉S₈/MoS₂ interface model.

2. Computational methods

All the transition states calculations were performed using DFT methods, implementing Dmol³ code as provided by Material Studio 6.1 (Accelrys® Inc.). The transition states (TS) were calculated using Halgren–Lipscomb algorithm with generalized LST/QST approximation. The reaction path was divided into several steps between the respective reactant and products by interpolating along the path segments of the potential energy surface. First, the LST performs a single interpolation to a maximum energy, the QST method alternates searches for energy maximum with constrained minimizations in order to refine the transition state and also a conjugate gradient minimization was performed. The convergence criterion set for finding transition state calculations was determined considering tolerance for all root-mean-square forces on atoms of 0.25 eV/Å. The vibrational frequency of possible TS was calculated, and each TS was identified to have one imaginary frequency [18,19]. In here, we had used only one portion of the Co₉S₈/MoS₂ interface model primarily the thiocubane cluster, considering inner core electrons of Co, Mo, and S were kept frozen and replaced with an effective core potential (ECP). Double numerical basis sets comprising polarization functions on all atoms such as double numerical basis set with polarization (DNP) are used in the calculations to describe the valence orbital of Co, Mo and S atoms. The DNP basis set belongs to a double- ζ quality basis set with a p-type polarization function, which is added to hydrogen and d-polarization functions added to heavier atoms. For each basis function, the volume was restricted with a real space global cutoff radius of 4.4 Å allowing efficient calculations without loss of accuracy to obtain high quality numerical results [21]. Local density approximation (LDA) functional combined with Vosko,

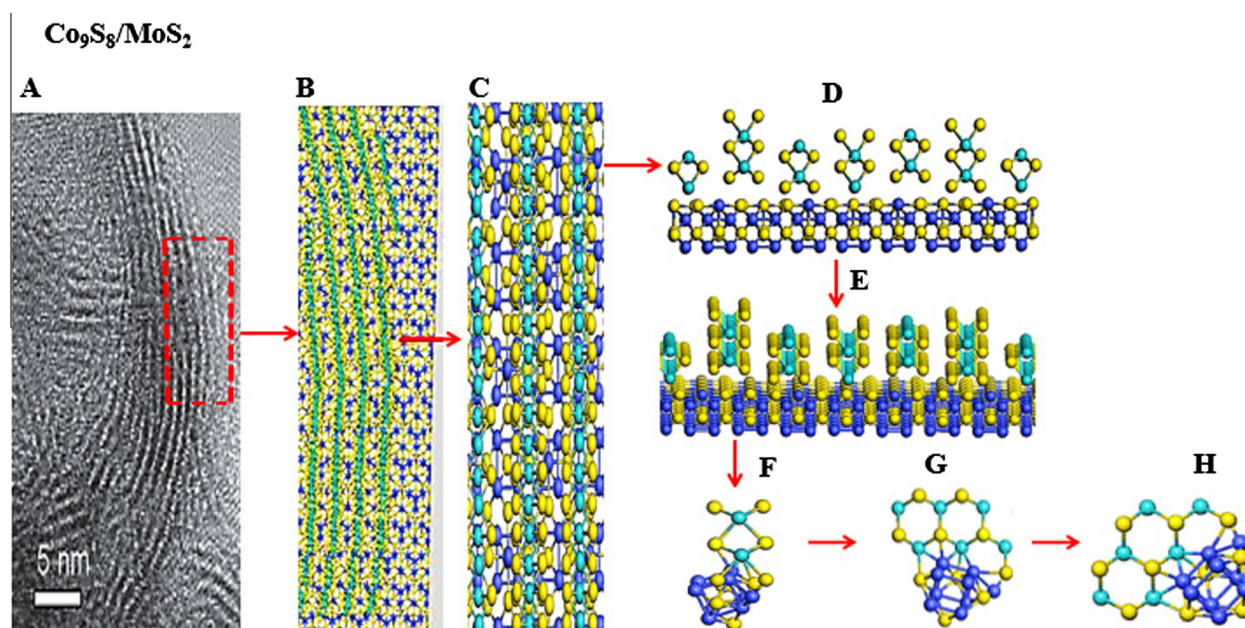


Fig. 1. A) HRTEM image of the MoS₂/Co₉S₈ bulk interface [10]. B) Stick model image of the MoS₂/Co₉S₈ bulk structure. C) Ball stick model image of the MoS₂/Co₉S₈ bulk structure. D) Front view of the MoS₂/Co₉S₈ bulk structure. E) Tilted down view of the MoS₂/Co₉S₈ bulk structure. F) Front view of MoS₂/Co₉S₈ “seed model”. G) Side view of MoS₂/Co₉S₈ “seed model”. H) Tilted down view of the MoS₂/Co₉S₈ “seed model”. Sulfur atoms (yellow color), molybdenum atoms (turquoise color) and cobalt atoms (purple color).

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