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Review

Theoretical investigations of the structures and properties of molybdenum-based sulfide catalysts

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Abstract

The development of new hydrotreating catalysts to meet the need for producing cleaner transportation fuels requires a better understanding of the structures and properties of active sites of industrially relevant catalysts. Molecular modeling and simulation has made important contributions towards achieving this goal. This review summarizes theoretical results and conclusions regarding the structures and properties of molybdenum-based hydrotreating catalysts through a logical discussion of surface structures, hydrogen activation, and adsorption and reaction of organosulfur molecules. Ab initio calculations of molybdenum-based sulfide catalysts have been used to predict the equilibrium sulfur coverage on the edge planes of promoted and unpromoted MoS_2 catalysts, identify the energetically favorable locations of promoter (Ni, Co) atoms, consider the mechanism of hydrogen dissociation and adsorption, and characterize the bonding of organosulfur molecules by evaluating the adsorption energies as a function of catalyst composition. We summarize published computational results from the previous decade, and in the process highlight the need to consider the appropriate model when performing calculations. In this review, we conclude the single slab MoS_2 model containing two rows of molybdenum atoms is adequate for discussing general energetic trends when sulfur coverage changes on the edge surface, however more substantive models are required to obtain accurate energetic and structural data. The stable structures at reaction conditions also have to be considered when discussing the locations of promoter atoms, the dissociation of hydrogen, and the adsorption of molecules on the edge surface. Additional challenges and future applications to increase the fundamental understanding of molybdenum-based sulfide catalysts are discussed.

Keywords: Molybdenum sulfide; Molecular modeling; Density-functional theory; Quantum chemistry; Hydrotreating; Hydrodesulfurization; Adsorption

1. Introduction

Combinational efforts in characterizations by various techniques and activity investigations have provided many insights into the nature of the active phase on various catalyst systems. One specific group of industrially relevant materials that has received considerable attention are hydrotreating catalysts [1,2]. The increasing interest in upgrading heavy oils and the demand for cleaner fuels continue to drive the research and development of new hydrotreating catalysts with higher activity and selectivity. Consequently, a better understanding of the relationship between the activity and structure of catalysts is of great interest for both industry and academia.

Transition metal sulfides, specifically molybdenum-based sulfides, are widely used in the oil refining industry as hydrotreating catalysts. These industrial catalysts are typically composed of nickel (or cobalt) and molybdenum supported on γ-Al_2O_3, which are prepared in an oxidic state and converted to sulfidic state before use. The mixed CoMo and NiMo sulfide catalysts have higher activities than corresponding monometallic molybdenum, cobalt, or nickel sulfide catalysts. The maximum activities of CoMo or NiMo catalysts are obtained at a M/[M + Mo] ratio of approximately 0.3. When supported alone on alumina, molybdenum sulfide has much higher activity than cobalt or nickel sulfides; thus, molybdenum sulfide has traditionally been considered to be the catalytically active phase and cobalt and nickel to be catalyst promoters [1,2]. Although

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many proposals have been made according to different experimental observations, a complete understanding of the promoting effects of cobalt and nickel on Mo-based catalysts has not yet been achieved.

It is well known that molybdenum exists as MoS_2 clusters in Mo-based sulfide catalysts. MoS_2 has a layered structure with molybdenum atoms in a plane situated between two sulfur planes for each S–Mo–S layer, and the active sites are located at edge surfaces of MoS_2 crystallites. In order to explain the synergetic effect between cobalt and molybdenum, Delmon et al. [3] proposed the presence of two distinct phases. The cobalt sulfide phase would activate hydrogen that would then spill-over toward the molybdenum sulfide phase. The activated hydrogen would maintain a fraction of surface molybdenum coordinatively unsaturated (*cus*) and form S–H groups. In such a way, a "remote control" of the active phase on molybdenum sulfide is exerted by the promoter phase (cobalt sulfide). On the other hand, Topsoe et al. proposed the CoMoS theory to explain the promotional effect of cobalt on MoS_2 [4]. The success of the CoMoS theory stands on the discovery of a special signal in Mössbauer emission spectroscopy, which could not be ascribed to any known cobalt phase at that time. Topsoe et al. attributed it to a mixed CoMoS phase, in which cobalt is located on the edges of MoS_2 crystallites. However, the detailed structure of the CoMoS phase is still unclear after many years of efforts.

Duchet et al. [5] questioned the assumption of cobalt being the promoter in CoMo catalysts based on the higher intrinsic activity of carbon-supported cobalt catalysts when compared to a carbon-supported molybdenum catalyst. Thus, cobalt itself could be considered the catalytically active phase. This observation was supported by the fact that carbon-supported cobalt catalysts had similar activities to carbon-supported CoMo catalysts [6]. Therefore, MoS_2 could act as a secondary support for cobalt sulfide particles that would be more active than molybdenum sulfides.

Despite considerable experimental efforts, the exact structure of the active phase at the atomic level and the precise origin of the synergetic effect between cobalt and molybdenum are still not fully understood. Additionally, the adsorption geometry and bonding mode of organic molecules on the MoS_2 catalyst edge surfaces remains uncertain. Although experimental techniques, including numerous surface-specific spectroscopies, have been used to elucidate the fundamental relationship between catalyst composition and reactivity, many of the fundamental questions cannot be adequately addressed using current experimental techniques.

During the past decade, considerable attention has been given to the theoretical investigation of Mo-based sulfide catalysts in order to further understand the structure of active sites and reaction mechanisms at the atomic level [7–26]. Early theoretical studies of hydrodesulfurization (HDS) on molybdenum sulfide using extended Hückel tight binding method [27,28] and molecular orbital techniques [29,30] demonstrated the potential of computational chemistry in the area of transition metal sulfide catalysts. The rapid development in computational theories and the significant advances in computational tools have accelerated the theoretical studies in areas of heterogeneous catalysis [31]. Most of the calculations [7–16,19–26] have been based on density-functional theory (DFT), while few employed semi-empirical methods [18], which could also be useful for calculating electronic properties of transition metal catalysts. In this regard, the correlation of theoretical calculations and experimental results has offered new insights into numerous fundamental aspects, such as the stable structure of MoS_2 edge surfaces [7,12,14–16,19], the promotional effects of cobalt and nickel [7,12,16,22,23], the formation of vacancies on different edge surfaces [26], hydrogen activation [10,20,23], and interactions between organic compounds and active sites [8,10,13,18,24,25].

The objective of this article is to review the computational results about molybdenum-based sulfide catalysts published in the past decade. A detailed description of the calculation methods and techniques can be found in individual referenced papers and additional articles (for example, see [32]). The information reviewed in this manuscript is organized according to the following aspects of molybdenum-based sulfide catalysts: Section 2 describes the structure and properties of MoS_2 edge surfaces; Section 3 discuses the activation of hydrogen on MoS_2 edge surfaces; Section 4 presents the possible locations and the effects of the promoter atoms on MoS_2 catalysts; and Section 5 discusses the adsorption and reaction of sulfur-containing compounds on various MoS_2 edge surfaces.

2. MoS_2 edge structures

Different atomic models have been used to describe the edge structure of MoS_2 catalysts based on previous experimental characterization. Byskov et al. [7,12,14] used a chain model containing a single S–Mo–S slab constructed from two MoS_6 prisms, while Raybaud et al. [8,9,11,15,16] and Payen and coworkers [13,19,23,26] used a larger model containing two S–Mo–S sheets exposing Mo- and S-edges alternatively. Both the "chain model" and the "two-sheet model" are repeated periodically along directions perpendicular to the edge surfaces. Cluster models including a finite number of atoms have also been used as model MoS_2 catalysts [14,22,28,29].

Fig. 1 shows a hexagonal MoS_2 crystallite consisting of a single layer of S–Mo–S, which was proposed by Kasztelan et al. [33]. Theoretical studies predict that the hexagonal shape is stable under working conditions [21], while a triangular shape that was previously observed by scanning tunnelling microscopy (STM) [34] is stable at high hydrogen sulfide partial pressures. The basal plane (0 0 0 1) is fully covered by sulfur atoms and is inactive for catalytic reactions, while the catalytically active sites are located at the

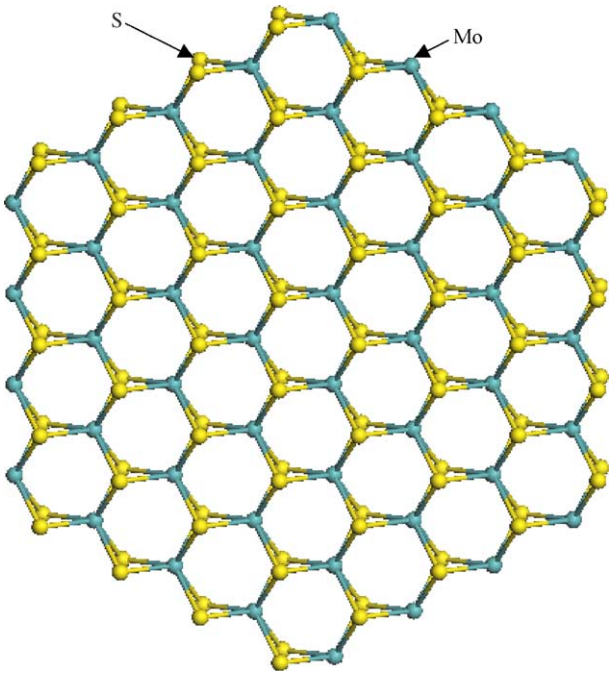

Fig. 1. Hexagonal MoS_2 crystallite exposing Mo- and S-edges.

edge surfaces and contain coordinatively unsaturated molybdenum and sulfur atoms. In the MoS_2 bulk structure, each molybdenum atom is coordinated to six sulfur atoms and each sulfur atom is coordinated to three molybdenum atoms in a prismatic unit. Cleavage of the MoS_2 bulk structure parallel to (1 0 0) or (0 1 0) planes produces an edge surface exposing coordinatively unsaturated molybdenum or sulfur atoms. On the as-cleaved molybdenum terminated edge (named Mo-edge, or $1\,0\,\bar{1}\,0$ edge plane) each of the exposed molybdenum atoms is coordinated to four sulfur atoms, while on the as-cleaved sulfur terminated edge (named S-edge, or $\bar{1}\,0\,1\,0$ edge plane) each of the terminal sulfur atoms is coordinated to two molybdenum atoms (Fig. 1).

Under reaction conditions the perfect as-cleaved edge surfaces of MoS_2 on a hydrotreating catalyst are not stable [15,16,19,23]. In the presence of hydrogen and hydrogen sulfide in the hydrotreating reactor, hydrogen may react with the surface sulfur atoms to form gas phase hydrogen sulfide; thus, creating sulfur vacancies on the S-edge. The hydrogen sulfide may dissociatively adsorb on unsaturated molybdenum atom sites on the Mo-edge as a mechanism to replace the sulfur. Before one could further study the interaction between organic molecules and the catalyst surface on a more meaningful basis, one should first understand the edge structures that are stable in presence of hydrogen and hydrogen sulfide under reaction conditions.

Byskov et al. [7,12] and Raybaud et al. [15] approached this question by investigating the equilibrium sulfur coverages on MoS_2 edge surfaces using different models. Byskov et al. used a model consisting of a periodic single layer of a S–Mo–S slab with two molybdenum atoms in cross-section (2-Mo model) [7,12]. This model exposes the Mo-edge

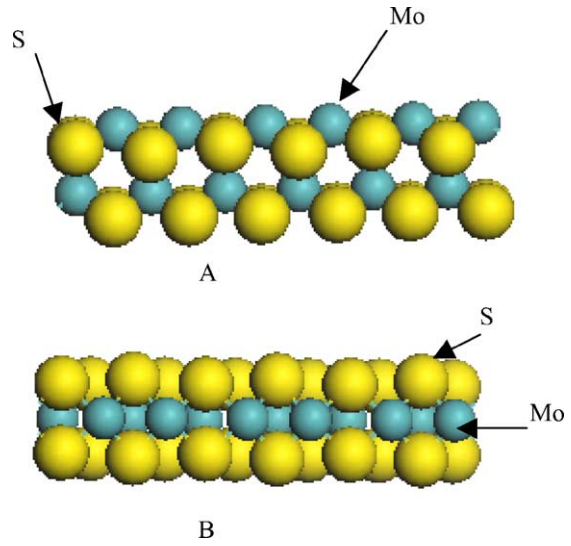

Fig. 2. Stoichiometric MoS_2 model including two rows of MoS_2 units: (A) side view; (B) top view.

at one side and the S-edge at the opposite side (Fig. 2). They added two sulfur atoms per molybdenum atom on the Mo-edge of the stoichiometric model, and thus, the two edges are fully covered by sulfur atoms. They then allowed the structure to relax (geometric optimization) in order to identify the minimum energy geometric configuration. After relaxation, the sulfur atoms at both edges moved from the normal lattice positions and dimerized [12]. While Raybaud et al. agreed that on fully sulfided Mo-edge planes sulfur atoms had a tendency to dimerize [15], their results did not predict the formation of S–S dimers on the S-edge. Raybaud et al. used a model consisting of two layers of S–Mo–S sheets as shown in Fig. 3 [15]. The $Mo_{24}S_{48}$ unit is periodically repeated along the directions parallel to the edge surfaces, while perpendicular to the edge surface a vacuum layer of 12.8 Å separates the neighboring units. The 2-Mo model also produced too short Mo–Mo distances [12]. This discrepancy might be due to the smaller size of the model used by Byskov et al. Adding an additional Mo-row on the small 2-Mo model to represent the bulk-like molybdenum atoms produced better structural data [12].

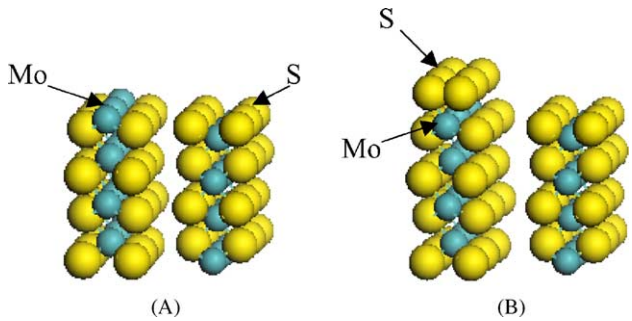

Fig. 3. Perspective view of optimized MoS_2 edge surfaces: (A) with bare Mo-edge and fully saturated S-edge; (B) with fully sulfided Mo- and S-edge.

In addition, the equilibrium sulfur coverage on the Mo- and S-edge planes was studied by considering the energy requirements for both sulfur removal and addition. Byskov et al. reported the removal of one-half of the sulfur atoms from the fully covered Mo-edge by reacting with gas phase hydrogen requires 0.15 eV per sulfur atom (1 eV = 23.061 kcal/mol) [12]. Further removal of sulfur atoms from the half-covered molybdenum edge is not energetically favorable, requiring an additional 0.59 eV per sulfur atom to remove half of the remaining sulfur atoms. The inverse process of removing sulfur atoms from the fully covered Mo-edge is adding sulfur to bare Mo-edge. These two processes should have the same absolute value of the reaction enthalpy with opposite sign. Raybaud et al. first added sulfur atoms to the bare Mo-edge to model the dissociation of hydrogen sulfide on the Mo-edge [15]. Their results show that adding sulfur atoms to the Mo-edge is an exothermic process up to a sulfur coverage of 50%. The reaction enthalpy for further addition of sulfur atoms is small.

On the fully sulfided S-edge, Raybaud et al. reported the energy requirement for the removal of sulfur is 0.91 eV per vacancy, while the removal of a sulfur atom from a 50% coverage S-edge required 1.87 eV per vacancy [15]. In comparison, Byskov et al. determined the energy requirement for the removal of one sulfur atom from the fully sulfided S-edge is 0.13 eV, and further removal of sulfur atoms from the 75% covered S-edge required 1.45 eV per sulfur atom [12]. The removal of sulfur from the S-edge is always an endothermic process [7,12,15], and the energy requirement increases as the sulfur coverage decreases.

The two studies discussed above used different structural models, and consequently produced different structure data. However, their results regarding the relative energy at equilibrium sulfur coverage on the Mo-edge are qualitatively consistent. Byskov's results indicate that removing one-half of the sulfur atoms from a fully covered Mo-edge requires only small amount of energy (0.15 eV per sulfur atom), but further removal of the remaining 50% sulfur would require an average of 1.6 eV per sulfur atom. Correspondingly, Raybaud et al. found that adding one sulfur atom to each surface molybdenum atom (up to 50% sulfur coverage) releases on average 2.0 eV per sulfur atom, and the reaction enthalpy for adding one more sulfur atom to each molybdenum atom (to 100% sulfur coverage) is very small (less than 0.15 eV on average per sulfur atom). They also agreed that the most stable configuration with 50% sulfur coverage was obtained when the sulfur atoms were bridged to two neighboring molybdenum atoms. Fig. 4 shows the comparison of the results from the two research groups who used different structural models [12,15]. The data have been adjusted to the same number (three) of edge molybdenum atoms in a unit cell.

Fig. 5 re-plots the reaction enthalpy for removing the sulfur atoms from the S-edge by reacting with hydrogen at different sulfur coverages using the data of [12,15] in a similar way as in Fig. 4, with the fully sulfided S-edge as the reference. Again, these two groups produced similar results

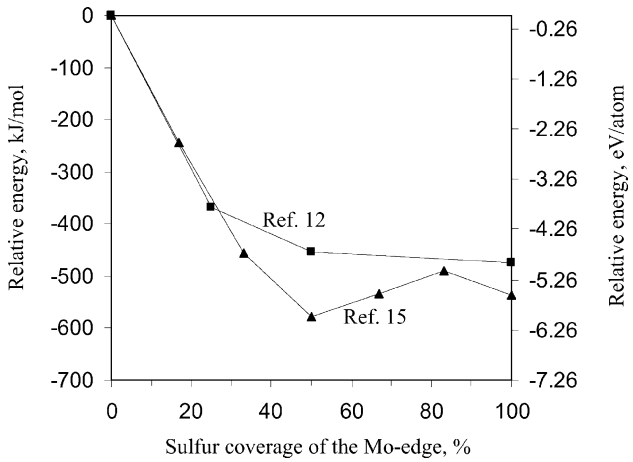

Fig. 4. Changes in relative energy (kJ/mol at left axis and eV per atom at right axis) with sulfur coverage on the Mo-edge plane. The uncovered bare surface is the energy reference.

regarding the stable sulfur coverage on the S-edge. From Figs. 4 and 5 one can observe that removing all the sulfur atoms (three sulfur atoms in one unit cell) from the 50% coverage surface requires about 5.5 eV for the Mo-edge and about 9.5 eV for the S-edge. This implies that the sulfur atoms are more strongly bound to molybdenum atoms at the S-edge than at the Mo-edge. These results indicate that it is energetically unfavorable to obtain a sulfur coverage lower than 50% on the MoS_2 edge surfaces. As a result, this suggests that on both the S- and Mo-edge planes, the presence of a large number of sulfur vacancies is unlikely.

Chemical equilibrium between the catalyst surface and the reactive environment containing hydrogen and hydrogen sulfide influences the energetics of adsorption and desorption of sulfur on MoS_2 edge surfaces. High temperature and hydrogen partial pressure favors the desorption of sulfur from catalyst surfaces, while high partial pressure of

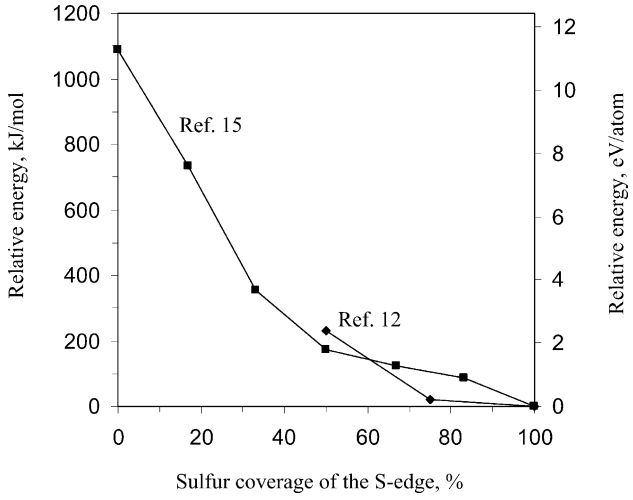

Fig. 5. Changes in relative energy (kJ/mol at left axis and eV per atom at right axis) with sulfur coverage on the S-edge plane. The fully sulfided surface is the energy reference.

hydrogen sulfide leads to saturation of sulfur vacancies on the edge surfaces. Depending on the reaction temperature and the ratio of hydrogen sulfide to hydrogen, the sulfur coverage on MoS_2 edges can vary between 50 and 100%. Taking into account the presence of hydrogen and hydrogen sulfide in the gas phase will allow the determination of the stable structures of MoS_2 edge surfaces under reaction conditions [15,19]. At typical reaction conditions (350 °C, $H_2S/H_2 < 0.01$), the most stable sulfur coverage on both S-edge and Mo-edge surfaces is 50%, with each surface molybdenum atom adsorbing one sulfur atom at a bridge position. At a higher H_2S/H_2 ratio, the S-edge could be fully covered by sulfur atoms, making the creation of sulfur vacancies on the edge surfaces more difficult [15,19]. Even at very high hydrogen pressures and reaction temperatures (for example, 100 bar and 350 °C) the 50% covered edge surfaces are still the most stable [35]. These models predict the number of unsaturated molybdenum sites is very small on MoS_2 edge surfaces at normal hydrotreating conditions.

However, it is generally accepted that the active sites on MoS_2 catalysts include coordinatively unsaturated molybdenum sites located at the edge of MoS_2 crystallites. Many proposed reaction mechanisms on MoS_2 catalysts consider the involvement of the coordinatively unsaturated molybdenum sites. In order to explain the discrepancies between the theoretical calculations that predicted no vacancies present on the stable MoS_2 edge surfaces and experimental studies supporting the presence of vacancies, Paul and Payen studied the mechanism and kinetics of the creation of vacancies on the stable MoS_2 edge surface [26].

In order to form a vacancy in a unit cell containing three edge molybdenum atoms on the stable Mo-edge (50% sulfur coverage with one surface sulfur atom per edge molybdenum atom), a series of surface reactions may occur, including: (1) dissociation of diatomic hydrogen, (2) migration of the hydrogen atom to form adsorbed H_2S, and (3) desorption of H_2S and the formation of a vacancy. The rate-determining step in the formation of a vacancy on the stable Mo-edge is the dissociation of diatomic hydrogen to form Mo–H and S–H [26]. This is due to the fact that hydrogen dissociation activation energy is approximately 0.97 eV. Although the entire process is endothermic, the mild activation energy indicates that it may occur at reaction conditions. Once the vacancy formed, H_2S may dissociate and a sulfur atom may be re-adsorbed on this vacancy. This reverse process is exothermic and requires a very low activation energy. Therefore, the presence of H_2S in the gas phase has a strong inhibition effect on the formation of vacancies on Mo-edge planes. The removal of a second sulfur atom from the Mo-edge is more difficult, as the rate-determining step requires a much higher activation energy (1.8 eV) [26]. On the edge surface containing a single vacancy, dissociation of H_2S on this vacancy is much faster than the formation of the second vacancy. Thus, the formation of a two-fold vacancy is very unlikely on the Mo-edge plane. The creation of a vacancy on the S-edge is more difficult, requiring much higher activation energy. The direct departure of one sulfur atom from the S-edge required an activation energy of 1.8 eV, and the process still required 1.25 eV to create a vacancy on the S-edge plane through an isomerization mechanism [26].

Combining the information from thermodynamic and kinetic calculations, one can develop a better understanding of the dynamic character of the MoS_2 edge surfaces under reaction conditions. Thermodynamically, the formation of vacancies on stable MoS_2 edges is unfavorable. However, on the basis of kinetics it is possible to separate this endothermic process into several elementary steps with mild activation energies [26]. On the MoS_2 surfaces at reaction conditions, a dynamic equilibrium exists between the formation and saturation of vacancies, which displace towards the fully saturated stable edge surface in the presence of hydrogen sulfide. The dynamic equilibrium allows the presence of a small amount of vacancies with a short lifetime. Low hydrogen sulfide partial pressure and high temperature favors the formation of vacancies, while high hydrogen sulfide partial pressure and low temperature decreases the number of vacancies on MoS_2 edge surfaces.

3. Hydrogen activation on MoS_2 edge surfaces

Hydrogen can activate MoS_2 edge surfaces by reacting with surface sulfur to create vacancies on MoS_2 edge planes. It is also possible for hydrogen to exist on the surface as adsorbed surface species. The presence of hydrogen on catalyst surfaces has been proposed in discussions of reaction mechanisms on transition metal sulfide catalysts [36–38]. The existence of S–H groups on catalyst surfaces has been evidenced by physical characterizations [39–42], and limited experimental evidence for the possible presence of Mo–H has also been reported [43]. The dissociation of hydrogen on the catalyst surface is an important factor in hydrotreating reactions. A recent review by Breysse et al. summarized experimental work and theoretical studies on hydrogen activation on transition metal sulfide catalysts [44]. Additionally, Rodriguez-Arias et al. [45] and Raybaud et al. [46] discussed the possible roles of Mo–H on the hydrodenitrogenation (HDN) of pyridine and the HDS of thiophene, respectively.

Diatomic hydrogen can dissociate on the catalyst surface heterolytically on an unsaturated metal site and a sulfur atom, or homolytically on sulfur couples, as shown in Eqs. (1) and (2), respectively [47]:

$$H_2 + Mo^{\square}\text{–}S \rightarrow Mo\text{–}H + SH \quad (1)$$

$$H_2 + 2S \rightarrow 2SH \quad (2)$$

where $Mo^{\square}$ is a molybdenum atom with a sulfur vacancy. How and where hydrogen molecules dissociate on MoS_2 catalyst surfaces is still not fully understood. Alexiev et al. reported that hydrogen preferentially bonds to the sulfur atoms of S–S couples on the S-edge of MoS_2, and the formation of

Mo–H on the Mo-edge was very unlikely [20]. The dissociative adsorption of hydrogen on a single S–S couple was homolytic since the two S–H groups formed were practically equivalent. According to Cristol et al., the heterolytic dissociation of hydrogen into one S–H and one Mo–H was more favorable than the homolytic dissociation forming two S–H groups on a S-edge surface that was half covered by sulfur atoms [19].

The bonding locations of dissociated hydrogen atoms on the catalyst surface depend on the structure of the edge surfaces. In a DFT study [12], Byskov et al. assumed the dissociation of diatomic hydrogen had already occurred, and studied the possible configurations of hydrogen atoms on the surface. Hydrogen adsorption on the catalyst surface was described using the following reaction:

$$\mathrm{A} + \tfrac{1}{2}z\mathrm{H_2} \rightarrow \mathrm{B} \tag{3}$$

where A and B were the structures before and after hydrogen adsorption. The hydrogen binding energy per hydrogen atom was defined as

$$\Delta E_{\mathrm{H}} = \frac{1}{z}\left[E(\mathrm{B}) - E(\mathrm{A}) - \frac{z}{2}E(\mathrm{H_2})\right] \tag{4}$$

where E(A), E(B), and E(H_2) are the total energies of structures A, B, and hydrogen, respectively. Negative values of ΔE_{H} indicate bonding of hydrogen atoms on the surface relative to hydrogen molecules, while positive values do not.

According to this model, basal planes could not bond hydrogen since the ΔE_{H} value was a high positive number (0.97 eV) [12]. On a fully sulfided S-edge, there are no unsaturated metal sites on the surface [12,15]. The bonding of a hydrogen atom to a terminal sulfur atom resulted in a negative ΔE_{H} quantity [35,48], meaning the sulfur atoms on the fully sulfided edge surface are capable of adsorbing hydrogen atoms. Bonding two hydrogen atoms on both sulfur atoms of a S–S dimer (Eq. (5)) and on two sulfur atoms of different S–S dimers (Eq. (6)) were both exothermic, but reaction (6) had higher negative ΔE_{H} value (−1.38 eV) than reaction (5) ($\Delta E_{\mathrm{H}} = -0.78$ eV) [35]:

$$\mathrm{H_2} + \begin{Bmatrix}\mathrm{S}\\ \mathrm{S}\end{Bmatrix}\begin{Bmatrix}\mathrm{S}\\ \mathrm{S}\end{Bmatrix}^{*} \rightarrow \begin{Bmatrix}\mathrm{HS}\\ \mathrm{HS}\end{Bmatrix}\begin{Bmatrix}\mathrm{S}\\ \mathrm{S}\end{Bmatrix}^{*} \tag{5}$$

$$\mathrm{H_2} + \begin{Bmatrix}\mathrm{S}\\ \mathrm{S}\end{Bmatrix}\begin{Bmatrix}\mathrm{S}\\ \mathrm{S}\end{Bmatrix}^{*} \rightarrow \begin{Bmatrix}\mathrm{HS}\\ \mathrm{S}\end{Bmatrix}\begin{Bmatrix}\mathrm{HS}\\ \mathrm{S}\end{Bmatrix}^{*} \tag{6}$$

In these reactions, $\{\mathrm{S}\}^{*}$ and $\begin{Bmatrix}\mathrm{HS}\\ \mathrm{HS}\end{Bmatrix}^{*}$ denote an adsorbed sulfur atom and a pair of adsorbed S–H groups on the surface, respectively. The formation of Mo–H and S–H by heterolytic dissociation and the formation of two Mo–H groups were highly endothermic reactions, with calculated ΔE_{H} values of 0.32 and 0.46 eV, respectively [35]. Further addition of hydrogen on the S-edge was less exothermic, and complete hydrogenation of the S-edge was an endothermic process [35]. This is in agreement with Alexiev et al. [20], where they predicted that bonding of one hydrogen atom to a S–S dimer was energetically more favorable than the adsorption of two hydrogen atoms on both sulfur atoms of an S–S dimer.

The removal of one sulfur atom from each S–S couple on the fully sulfided S-edge of MoS_2 yields 50% surface sulfur coverage, which has been reported to be the most energetically stable structure at reaction conditions [15,19,23]. Dissociative adsorption of hydrogen on the 50% sulfur-covered S-edge is an endothermic process [19,23,35,48]. However, heterolytic dissociation of a hydrogen molecule into Mo–H and S–H, as described in Eq. (1), was less endothermic than the formation of two S–H groups [19,35]. The dissociation of hydrogen into two Mo–H groups appeared impossible as one of the hydrogen atoms shifted from the molybdenum to the sulfur atom during the geometry optimization. The removal of one bridging sulfur atom from every third sulfur atom produces highly unsaturated molybdenum sites on the S-edge surface. The formation of two bridging Mo–H groups are exothermic (−0.62 eV) [35], however, the adsorption energy on this defective surface could not compensate for the energy requirement for the creation of such a vacancy. The overall reaction of vacancy formation accompanied with hydrogen addition is still endothermic [19,35].

On a fully sulfided Mo-edge (100% sulfur coverage), which is stable at high hydrogen sulfide partial pressures, dissociative hydrogen adsorption on S–S dimers produces S–H groups. According to Cristol et al. [35], this process is exothermic ($\Delta E_{\mathrm{H}} = -0.27$ eV), but less exothermic when compared to the fully sulfided S-edge ($\Delta E_{\mathrm{H}} = -1.38$ eV). Both the formation of Mo–H and S–H groups, and that of two Mo–H groups, are endothermic processes. For the addition of a second hydrogen molecule, the formation of two adsorbed H_2S species on two sulfur atoms of a S–S dimer was the most stable configuration. However, Bollinger et al. [48] reported that the adsorption of hydrogen atoms on the fully sulfided Mo-edge was endothermic. They reported this process requires 0.03 eV for one hydrogen atom, and 0.17 eV for two hydrogen atoms for a unit cell [48].

Sulfur atoms bond to two molybdenum atoms at bridge positions on the 50% sulfur coverage Mo-edge surface. Dissociative adsorption of hydrogen on this edge is an endothermic process, and the heterolytic dissociation of hydrogen to Mo–H and S–H requires less energy than other configurations. This is similar to the energetics of the 50% sulfur coverage S-edge [19,35]; however, adsorption on the S-edge is energetically preferred than on the Mo-edge. On the 50% sulfur coverage Mo-edge, molybdenum atoms still maintain six-fold coordination. Therefore, the absence of unsaturated molybdenum sites on the Mo-edge can explain why the adsorption on this surface is highly unfavorable. The removal of one bridging sulfur atom from every third sulfur atom produces five-coordinated molybdenum atoms as well as six-coordinated atoms. The heterolytic dissociation of hydrogen with one hydrogen atom on the remaining sul-

fur atom and the other on the bridge position between two five-coordinated molybdenum atoms is slightly exothermic (−0.10 eV) [23]. However, the energy released is much less than that required for the removal of sulfur from the 50% sulfur coverage Mo-edge.

Bollinger et al. also reported the adsorption of the first hydrogen atom was exothermic ($\Delta E_H = -0.30$ eV) on a 50% sulfur-covered Mo-edge [48]. Comparing the exothermic adsorption on the 50% sulfur-covered Mo-edge and the endothermic adsorption on a fully sulfided Mo-edge, they concluded that the sulfur monomer configuration on 50% sulfur-covered Mo-edge was more active than the sulfur dimer configuration on the fully sulfided Mo-edge for the adsorption of hydrogen atoms [48]. This is in contrast to the results obtained by other researchers. Cristol et al. reported dissociative hydrogen adsorption was always endothermic on the 50% sulfur-covered Mo-edge [19,35]. The formation of two S–H groups on the 50% sulfur-covered Mo-edge requires 0.37 eV ($\Delta E_H = +0.37$ eV), while the ΔE_H was −0.27 eV for the formation of two S–H groups by dissociation of hydrogen on the fully sulfided Mo-edge [19,35].

A possible explanation for the discrepancy in the relative activities of the fully covered and 50% sulfur-covered Mo-edge is the modeling of dissociative hydrogen adsorption. Cristol et al. simultaneously bonded two hydrogen atoms on the catalyst surface to simulate the dissociation of hydrogen on the surface, while Bollinger et al. bonded hydrogen atoms on the surface one by one. When two hydrogen atoms were put on the 50% sulfur-covered Mo-edge, the hydrogen binding energy also became endothermic in calculations by Bollinger et al. ($\Delta E_H = +0.16$ eV). Consequently, the adsorption of the first hydrogen atom influences the adsorption of the second hydrogen atom. An additional source of the discrepancies between these studies may be attributed to the different structural models used [35,48]. The unit cell in the model used by Cristol et al. consists of two layers of S–Mo–S sheets, with three molybdenum atoms located along the edge and four molybdenum atoms in the direction perpendicular to the edges [35]. The hydrogen atoms in S–H groups interact with the neighboring slabs by hydrogen bonding, which further stabilizes the hydrogen atoms. The unit cell in the model used by Bollinger et al. contains a single layer of MoS_2, with two molybdenum atoms along the edges and six molybdenum atoms in the direction perpendicular to the edges [48]. Therefore, using a single slab model or a two-layer model will produce different adsorption energies because the single layer model cannot simulate slab-slab interactions through hydrogen bonding.

In summary, the mechanism of hydrogen dissociation depends of the structure of the surface of MoS_2 on which the dissociation occurs. The homolytic dissociation of hydrogen to two S–H groups is preferred on a fully sulfided S-edge, as well as on a fully sulfided Mo-edge; and the heterolytic dissociation of hydrogen to Mo–H and S–H is possible only on a partially sulfided edge surface. However, the adsorption of hydrogen on the basal plane is highly unflavored because each sulfur atom on the basal surface is already coordinated to three molybdenum atoms.

4. The effect of promoters (Ni, Co) on MoS_2 edge structures

The incorporation of cobalt or nickel to the MoS_2 structure can significantly increase catalyst activity for hydrotreating reactions [1,2]. Despite extensive research efforts in elucidating the effects of cobalt and nickel on molybdenum-based catalysts, the origin of the promotional effect is still not fully understood. Among many proposals that were made in explaining the promoter effect, the CoMoS theory [4] and the "remote-control" theory [3,49] are dominant [50].

It is well accepted that promoter atoms are located at MoS_2 edges, but the exact location of the promoter atoms relative to molybdenum and sulfur, and the mechanism of their promotional effect is still under debate. Using the 2-Mo model, Byskov et al. [12] found that the configuration with molybdenum atoms substituted by cobalt atoms at the S-edge (Fig. 6A) is more stable than the structure with molybdenum atoms substituted by cobalt atoms at the Mo-edge (Fig. 6B). However, after investigation of different possible configurations, Raybaud et al. [16] concluded the substitution of molybdenum atoms on the Mo-edge (Fig. 6C) is energetically preferred over the fully sulfided S-edge (Fig. 6D). The discrepancy in the most stable cobalt location between these

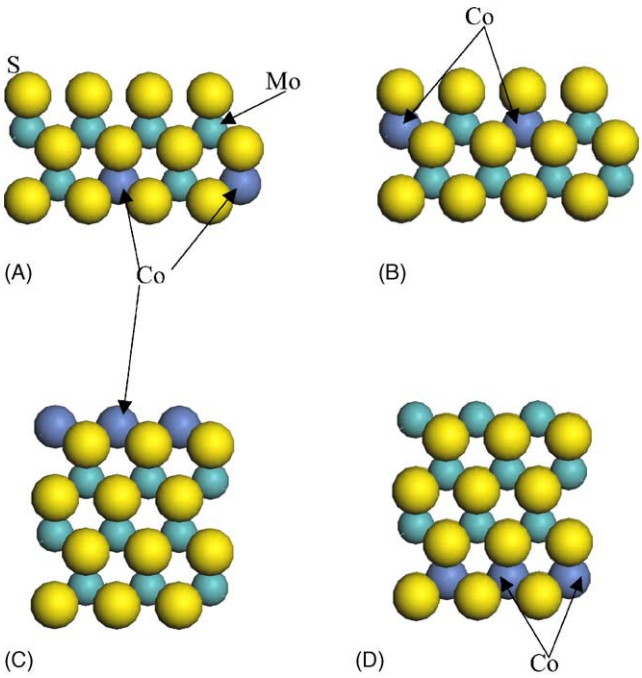

Fig. 6. Co–Mo–S models with cobalt atoms at different locations: (A) two Mo atoms are substituted by Co atoms at the fully sulfided S-edge; (B) two Mo atoms are substituted by Co atoms at the fully sulfided Mo-edge; (C) three Mo atoms are substituted by Co atoms at the bare Mo-edge; (D) three Mo atoms are substituted by Co atoms at the fully sulfided S-edge.

two studies should not be the result of their using different models, since these two models produced a similar conclusion regarding the equilibrium sulfur coverage on MoS_2 edges (Figs. 4 and 5).

It should be noted in the calculations performed by Byskov et al. [12], both edges are fully covered with sulfur atoms as shown in Fig. 6A and B. However, in the calculations performed by Raybaud et al. [16], the metal edge is uncovered and the S-edge is fully covered. In order to evaluate these results on a constant basis, one should either remove all the sulfur atoms on the metal edges from the 2-Mo model used by Byskov et al., or add sulfur to the model studied by Raybaud et al. The energy requirement for removing the sulfur atoms from the Mo-edge in Fig. 6A would be 0.86 eV per sulfur atom [12]. However, removing sulfur atoms from the fully sulfided Co-substituted metal edge, as in Fig. 6B, would be an exothermic process until the sulfur coverage reached 25%. Although further removal of the remaining sulfur atoms might require additional energy, the total energy consumed for removing all the sulfur atoms from the Co-substituted edge should be very small (if positive). The energy difference between models in Fig. 6A and B is only 0.70 eV. If the sulfur atoms on the Mo-edge are removed from both models of Fig. 6A and B, the Mo-edge substitution model would be more stable than the S-edge substitution model.

A further comparison of Mo- and S-edge substitution models can be considered following the addition of sulfur on the metal-edges of Figs. 6C and D to make these structures fully sulfided, as Byskov et al. used in their studies [12]. Adding two sulfur atoms to each molybdenum atom on the bare Mo-edge is a highly exothermic process; the energy of the structure with a fully sulfided Mo-edge is 5.61 eV lower than that with bare Mo-edge [15]. Adding one sulfur atom to a Co-substituted metal edge (Fig. 6C) is slightly exothermic (−0.04 eV), and adding more sulfur to this surface is endothermic [16]. The relative energy for the structure with a fully sulfided Co-substituted metal edge is not provided in the same study [16], however it is estimated to be 0.9 eV higher than the structure with the bare surface [51]. Table 1 lists the relative energies of the structures of Fig. 6C and D, and the corresponding fully sulfided edge surfaces.

After this recalculation, the results from these two studies are actually in agreement. If the Mo-edge as well as S-edge remained fully covered by sulfur atoms, cobalt substitution of molybdenum at the S-edge was preferred; however, if the Mo-edge was uncovered while the S-edge was fully covered by sulfur, cobalt substitution of molybdenum at the metal edge was preferred. The sulfur coverage on the edge

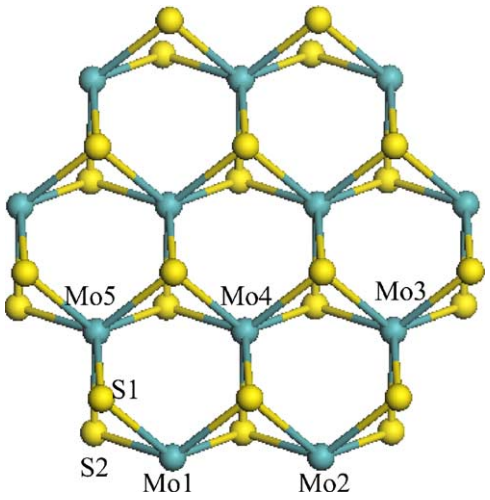

Fig. 7. $Mo_{12}S_{24}$ cluster used in studying substitution of molybdenum by cobalt in [52].

planes before and after promoter substitution influences the final conclusion as to what is the most favorable configuration for the promoted catalyst. Under typical operating conditions, the unpromoted Mo-edge could not be completely bare (0% sulfur coverage), and similarly the promoted metal edge could not remain fully sulfided. As a consequence, the equilibrium sulfur coverage before and after promoter substitution should be considered in discussing this question to make a more meaningful conclusion.

While the previous two studies [12,16] yielded similar results regarding the preferred location of cobalt on MoS_2 edge surfaces, Faye et al. [52] obtained an opposite conclusion about most stable location of cobalt in MoS_2. They found that the substitution of molybdenum atoms in the bulk of MoS_2 structure by cobalt atoms was more stable than substitutions on both fully sulfided S-edge and bare Mo-edge surfaces. However, they used a cluster ($Mo_{12}S_{24}$) model exposing bare Mo-edge and saturated S-edge surfaces containing 24 molybdenum atoms (Fig. 7). The stability of the substituted structures decreased in the following order when the corresponding molybdenum atom was substituted by cobalt: Mo4 > Mo5 > Mo1. If Mo4 is considered representative of molybdenum in the bulk structure, Mo5 molybdenum at the S-edge, and Mo1 molybdenum at the Mo-edge, this order is completely opposite of that reported by Raybaud et al. [16]. This apparent discrepancy may result from their using different structural models to represent MoS_2 catalysts. Faye et al. [52] used a cluster model containing a finite number of atoms, while Raybaud et al. [16] used a periodic model representing an infinitely extended surface. While the edge sub-

Table 1
Relative energies of Co-substituted MoS_2 structures

Model	Fig. 6C	Fig. 6D	Co-edge of Fig. 6C (fully sulfided)	Mo-edge of Fig. 6D (fully sulfided)
Relative energy (eV)	0.0	5.1	0.9	−0.5

stitution model can accurately explain the optimum atomic ratio of Co/(Co + Mo) for maximum HDS activity, the bulk substitution model is inadequate.

Substitution of molybdenum by cobalt also changes the binding of sulfur atoms on the catalyst edge surfaces. The removal of sulfur atoms from the Co-substituted edges is an exothermic process, in contrast to that for unpromoted MoS_2 catalysts [12,16]. This implies the substitution of molybdenum atoms by cobalt decreases the binding energy of sulfur on the edge planes. The lower binding energy of sulfur leads to a lower equilibrium sulfur coverage on the edges of cobalt-promoted catalysts with more unsaturated metal sites, which are believed to be the active sites for hydrotreating reactions. Substitution of molybdenum atoms on the S-edge [12] and on the Mo-edge [16] with nickel atoms has a similar effect as with cobalt atoms, but the sulfur binding energy on nickel-promoted edges is weaker than the cobalt edges. At the same condition, the sulfur coverage on the edges decreases (unsaturated sulfur vacancies increase) in the order MoS_2 > CoMoS > NiMoS. Additionally, decoration of the edge surfaces with cobalt or nickel decreases the binding energy of sulfur on the catalyst surface, allowing the stable edge surface to contain sulfur vacancies [12,16,23]. Under reaction conditions, 50% sulfur coverage (one sulfur per metal atom at bridging position) was the most stable structure for unpromoted Mo-edge surfaces (Fig. 8A). However, substitution of one molybdenum atom in three (33% substitution) by cobalt decreased the equilibrium sulfur coverage from 50 to 17% (one sulfur atom remained between the two molybdenum atoms) (Fig. 8B), and a bare metal surface was the most stable for a fully substituted surface (Fig. 8C) [23]. The change in the sulfur coverage can be partially responsible for the promotional effects of nickel and cobalt on MoS_2 catalysts.

Additionally, the changes in electronic structure caused by the promoters also play important roles in increasing catalytic activities. The electronic properties of unpromoted MoS_2 surfaces were studied by Raybaud et al. using DFT calculations [9,15]. On bare Mo-edge surfaces, the unsaturated molybdenum atoms had high density of states near the Fermi level. Adsorption of sulfur atoms on the Mo-edge occupied the free valences of molybdenum and reduced the density of states near and below the Fermi level. Hence, sulfur adsorption significantly reduces the electron reactivities of surface molybdenum atoms. The molybdenum atoms on the fully sulfided S-edge showed low density of states localized below and above the Fermi level, indicating very low reactivities.

Substitution of the molybdenum atoms on the edge surfaces by cobalt atoms bring about cobalt atoms on the surface, which have high density of states below the Fermi level and relatively low density of states above the Fermi level [16]. For unsaturated molybdenum atoms on unpromoted Mo-edge planes, the d_{yz} states are unoccupied, which are 1.26 eV above the Fermi level. For cobalt atoms on a Co-substituted surface, the d_{yz} states are lowered to or slightly higher than the Fermi level. The d_{yz} states on nickel atoms on Ni-substituted surface are 0.41 eV lower than the Fermi level [16]. Therefore, the main effect of the promoter on the electronic structure is the shift of the d_{yz} states to or below the Fermi level. This shift is larger for nickel than for cobalt, and the shift in the d_{yz} states can be used to explain the change in the binding energy of sulfur on these metal sites [16].

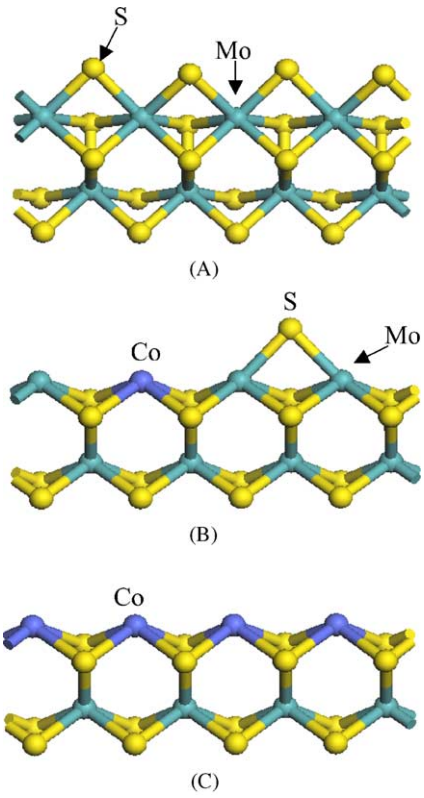

Fig. 8. Stable structure with different cobalt ratios on the edge planes: (A) stable unpromoted Mo-edge; (B) stable Mo-edge with one-third of molybdenum substituted by cobalt; (C) stable surface with complete substitution of Mo by Co.

Substitution of molybdenum by cobalt on MoS_2 edge surfaces also affects the activation of hydrogen on the modified edge surface. The most stable configuration for the fully substituted metal edge is the bare surface (0% sulfur coverage). In this case, the heterolytic dissociation of hydrogen only occurred on a site formed by a cobalt atom and a sulfur atom of the basal plane, which is athermic (0.04 eV) due to the low energy of S–H bonding [23]. Hydrogen bonding of the hydrogen atom with the neighboring S–Mo–S slab might stabilize this surface species. On a partially substituted surface, 17% sulfur coverage is stable. Heterolytic dissociation of hydrogen on a five-coordinated molybdenum atom and a sulfur atom bridging a molybdenum atom and a cobalt atom was exothermic [23]. Cobalt increases the electron density around the bridging sulfur, and the higher electron density increases the ability of the sulfur to bind the hydrogen atom. The heterolytic dissociation on a Co–S pair is more exother-

mic than on a Mo–S pair, in which sulfur is bridging molybdenum and cobalt atoms.

These results indicate that cobalt strongly enhances hydrogen activation as an adsorption center, and that cobalt also increases the ability of sulfur atoms to bind protons. This is in agreement with numerous surface acidity investigations using ammonia as a probe molecule. The acidity of cobalt sites is weaker than that of molybdenum sites with the same sulfur coordination, and the basicity of sulfur atoms binding to cobalt atoms are stronger than sulfur atoms binding to molybdenum atoms [23]. On a Ni-promoted edge surface, the sulfur binding on a nickel atom is unstable; thus, no S–Ni pair is available for hydrogen activation. This may explain why cobalt substitution could accelerate H_2–D_2 exchange [53] and Ni substitution did not [54].

5. Adsorption and reaction of sulfur compounds on MoS_2 edge surfaces

In order to understand the reaction mechanism of HDS on molybdenum sulfide catalysts at the atomic level, many theoretical studies were performed to model the adsorption and reaction of thiophene-type molecules on MoS_2 model catalysts [8,10,13,18,24,25,46]. Thiophene is most often used as a model compound, and coordinatively unsaturated molybdenum atoms on MoS_2 edge surfaces are considered as active sites.

Raybaud et al. compared different possible configurations of thiophene adsorption on Mo-edge planes of a periodic MoS_2 model including two layers of S–Mo–S sheets with alternating exposed uncovered Mo-edges and fully sulfided S-edges [8]. They reported positive adsorption energies were obtained on the Mo-edge, and adsorption on the S-edge was an endothermic process. On the Mo-edge, side-on adsorption (η^5) with the thiophene ring parallel to the surface was always energetically more favorable than end-on adsorption (η^1) through the sulfur atom with the thiophene ring perpendicular to the edge surface. The side-on adsorption was further studied by considering the initial location of the thiophenic sulfur atom relative to the surface molybdenum atoms, either directly above a molybdenum atom or in a bridge position between two molybdenum atoms on Mo-edge. They found that the latter configuration (sulfur atom bridges two molybdenum atoms) produced a higher adsorption energy (−2.00 eV) in comparison to the other configuration (sulfur atom directly on top of one molybdenum atom, 1.44 eV) [8].

Following the adsorption calculations, the initial adsorption geometry was studied to determine the effect of adsorption on the aromatic structure of thiophene. Thiophene remained planar in the η^1(S) configuration whereas it was tilted about the C_2–C_5 axis in $\eta^5(\pi)$ configuration. Furthermore, $\eta^5(\pi)$ adsorption destroyed the aromatic character of the thiophene ring, and thus activated the molecule for further reactions including hydrogenation and C–S bond cleavage. The analysis of the change in density of states and charge distribution before and after adsorption of thiophene indicates electrons are donated from thiophene highest occupied bonding orbitals into non-bonding Mo d surface states, and from occupied surface d states to antibonding C–S π states (back donation). The depletion of the π-bonding states and the filling of the antibonding states weaken the C–C and C–S bonds of thiophene, and in turn activate the saturation of the aromatic ring and cleavage of the C–S bond.

Analysis of the electrostatic potential field indicates that the electron-rich regions around thiophene are located at two sides of the thiophene ring, and that the unsaturated molybdenum atoms on Mo-edge of a $Mo_{10}S_{18}$ cluster are surrounded by positive electrostatic potential. This structure supports the side-on adsorption configuration [18]. Although they did not perform a geometric optimization before and after bonding thiophene on the Mo-edge surface, Ma et al. [18] also concluded that side-on adsorption was energetically more favorable than the end-on adsorption. However, their most stable configuration is different from the one proposed by Raybaud et al. [8]. In the most stable configuration reported by Ma et al., the sulfur atom of thiophene was fixed at the sulfur atom position in the sulfur plane as in the bulk MoS_2 structure. In contrast, the most stable configuration reported by Raybaud et al. indicated that the sulfur was located between two molybdenum atoms on the molybdenum plane. Orita et al. used the same model as Ma et al., but they performed a geometric optimization before and after adsorption [24]. Among their side-on adsorption configurations, they included a similar configuration as the most stable one proposed by Raybaud et al. [8]. The adsorption energy for this configuration was −1.81 eV [24], which is comparable to −2.00 eV reported by Raybaud et al. [8]. However, Orita et al. determined they could produce a more stable configuration by rotating the thiophene molecule and locate the sulfur atom slightly away from top of the molybdenum plane [24]. The more stable configuration resulted in an adsorption energy of −2.72 eV. Despite the fact that these two groups used different models and computational packages, the comparable adsorption energies they determined for a similar configuration indicates that the most stable configuration reported by Orita et al. should be more stable than the one suggested by Raybaud et al.

The adsorption of thiophene on unsaturated corner molybdenum sites has also been studied using a $Mo_{12}S_{22}$ cluster in which two sulfur atoms on the S-edge previously coordinated to the corner molybdenum atom were removed. This corner molybdenum atom is only coordinated to two sulfur atoms [10]. The adsorption of thiophene on this corner site through the sulfur atom of thiophene is not energetically favored. As a result, the side-on adsorption through π system is more stable. The same general conclusion is also valid for the adsorption dibenzothiophene on a bare Mo-edge, where the side-on adsorption configurations are energetically more favorable than the end-on adsorption through the thiophenic atom [25]. The presence of methyl groups on the phenyl

rings does not affect the flat on adsorption on the uncovered Mo-edge, while the methyl groups at 4- and 6-positions severely hinder the end-on adsorption through the sulfur atom. The charge distribution analysis shows that while the middle molybdenum atom on the Mo-edge (to which the sulfur ring is bonded) has a net gain in negative charges from the sulfur atom and the π system, there is a net loss of negative charge for the entire catalyst cluster. This indicates that electron back donation into antibonding orbitals of dibenzothiophene dominates over electron donation into the unoccupied states on edge molybdenum atoms of the catalyst cluster [25].

The adsorption of sulfur on the coordinatively unsaturated molybdenum atoms on both Mo- and S-edge planes is energetically preferred [7,12,15]; therefore, it is unlikely to have a bare Mo-edge on a MoS_2 catalyst under reaction conditions in the presence of H_2S. On bare Mo-edge surfaces, each molybdenum atom is coordinated to four sulfur atoms. Theoretically, two sulfur atoms can be added to each molybdenum atom (100% sulfur coverage) to obtain six-fold coordination. Depending on the reaction conditions, the sulfur coverage on MoS_2 edge surface varies between 50 and 100%. Calculations have shown that when one sulfur atom is added to each molybdenum atom, the sulfur atoms prefer bridge positions between two molybdenum atoms on the edge. Consequently, the edge molybdenum atoms are six-fold coordinated at 50% sulfur coverage and thus, inactive to the adsorption of sulfur compounds. Therefore, it is necessary to investigate the effect of the surface sulfur atoms on the adsorption of sulfur-containing molecules on the partially covered edge surfaces.

The removal of one sulfur atom from the stable Mo-edge containing three adsorbed sulfur atoms in a unit cell requires about 1.3 eV [13,15], producing an edge structure containing five-fold coordinated molybdenum sites between six-fold coordinated sites (site 1, Fig. 9A). On such an edge structure, only the end-on adsorption through the sulfur atom is possible for benzothiophene [13]. If an additional sulfur atom is removed from each unit cell, an edge structure containing one four-fold molybdenum atom between two five-fold molybdenum atoms will be created (site 2, Fig. 9B), which requires 3.4 eV [13,15]. On such an edge, side-on adsorption of benzothiophene through the thiophene ring is energetically more favorable than the end-on adsorption through the sulfur atom or the side-on adsorption through the benzene ring [13]. Removal of three sulfur atoms from the fully sulfided S-edge in a unit cell requires 2.9 eV, creating site 3 (Fig. 9C) [13]. The adsorption of benzothiophene on site 3 is only possible with an end-on configuration [13]. 4-Methylbenzothiophene produced a similar adsorption energy for side-on adsorption and a lower adsorption energy for end-on adsorption than benzothiophene. The effect of the methyl group on the adsorption of benzothiophene was confirmed by Yang et al. [25] in their calculations for the adsorption of dibenzothiophene on a Mo-edge plane.

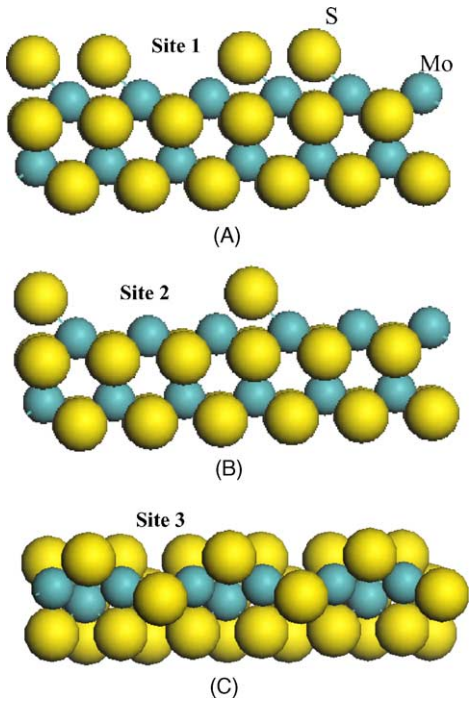

Fig. 9. Representation of different active sites on MoS_2 edge surfaces: (A) site 1 (side view); (B) site 2 (side view); (C) site 3 (top view).

According to Cristol et al. [13], HDS reactions could occur on both Mo- and S-edge planes on a 50% sulfur-covered surface. The HDS of benzothiophene follows two parallel pathways; the hydrogenation of the thiophene ring followed by C–S bond cleavage and C–S bond cleavage prior to complete hydrogenation of the thiophene ring. The side-on adsorption on site 2 (Fig. 9B) through the thiophene ring favors the hydrogenation pathway and the end-on adsorption on site 3 (Fig. 9C) through the sulfur atom allows a direct C–S bond hydrogenolysis mechanism [13]. The sulfur coverage influences the configuration of adsorption, and consequently the overall reaction mechanism. The adsorption of benzothiophene on site 1 (Fig. 9A) assisted in the creation of site 2 (Fig. 9B) [13]. The removal of a sulfur atom near a site 1 to form site 2 required 3.4 eV without the presence of the benzothiophene, whereas removal of a sulfur atom near a site 1 with adsorbed benzothiophene present only required 1.61 eV. The sulfur coverage and the structure of vacancies on the edge surfaces of MoS_2 are influenced not only by the hydrogen and hydrogen sulfide partial pressures, but also by the adsorption of reacting molecules.

The presence of Mo–H and S–H on the Mo-edge surface was included in a calculation of energy profiles for thiophene HDS performed by Raybaud et al. [46]. The presence of Mo–H and S–H groups significantly decreased the adsorption energies of thiophene and hydrogenated derivatives in comparison with the bare surface. On such a surface, the flat-on mode was still more favorable than end-on adsorption. Hydrogenation of thiophene has an activation energy barrier of 0.64 eV in the gas phase without a catalyst.

Starting from the heterolytic dissociation of hydrogen on the Mo-edge including a pre-adsorbed sulfur atom, no energy barriers were observed with the hydrogen source being Mo–H or S–H groups [46]. This is consistent with the previous discussion that the high stability of the free thiophene was perturbed upon flat-on adsorption on catalyst surface [8]. For the end-on adsorption configuration, the stability of the molecule was less disturbed. The hydrogenation of the adsorbed thiophene still had 0.48 and 0.62 eV energy barriers for the first and the third mono-hydrogenation steps, respectively, if the hydrogen source was from Mo–H. However, the energy barriers disappeared if the hydrogen source was from S–H group. This indicates the presence of S–H groups on the surface favors the HDS of end-on adsorbed thiophene.

6. Conclusions

Theoretical calculations have brought about many insights into the structures and properties of Mo-based sulfide catalysts that are not achievable by experiments. For unpromoted MoS_2 catalysts, the most stable surface structure at reaction conditions has one sulfur atom adsorbed per edge molybdenum atom at a bridging position between two metal atoms. At higher hydrogen sulfide partial pressures, a higher sulfur coverage is possible on the surface, but it is very difficult to produce a surface with a sulfur coverage lower than 50%. The substitution of edge molybdenum by cobalt or nickel significantly reduces the binding energy of sulfur on catalyst edge. Depending on the degree of substitution, the edge sulfur coverage can be reduced below 50%, or possibly to zero on fully cobalt or nickel-substituted surface. One of the important effects of the promoter atoms is the creation of more coordinatively unsaturated vacancies on the catalyst edge surfaces, which are the catalytically active sites for hydrotreating reactions. By controlling the ratio of promoter to molybdenum at edge surfaces one can determine the sulfur coverage on catalyst surface, thereby adjusting the catalytic properties. The promoter atoms can also enhance hydrogen dissociation on the catalyst surface by increasing the electron density around the bridging sulfur. The dissociation of hydrogen and the presence of S–H groups on the catalyst surface are very important in hydrodesulfurization reactions.

Compared with the rich information about catalyst structure, the studies of the adsorption and interaction of organic molecules on different catalyst surfaces are less complete. Several studies discussed the adsorption and reaction of thiophene or benzothiophenes on MoS_2 edge surfaces. However, few studies considered the most stable surface and the presence of hydrogen on the surface, and none of them investigated the role of promoters in activating the organic molecules. The results from published literature indicate flat-on adsorption through π-electrons is energetically more favorable than the end-on adsorption on Mo-edge planes that have more than one vacancy. However, the geometrical requirement for flat-on adsorption makes it impossible on surfaces with high sulfur coverages. In the process of completing the study about HDS reactions, it is also necessary to extend the theoretical calculation work into HDN reactions.

Acknowledgements

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