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Adsorption and dissociation of H_2 and H_2S on MoS_2 and NiMoS catalysts

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Abstract

The formation and stable structures of surface hydrogen species on unpromoted and nickel-promoted MoS_2 catalyst surfaces is studied by investigating the adsorption and dissociation of molecular hydrogen and hydrogen sulfide using periodic DFT calculations under generalized gradient approximation (GGA). On the stable $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge, the dissociation of hydrogen with the formation of –SH groups is an exothermic process and energetically most favoured. On a partially nickel-promoted $(1\,0\,\bar{1}\,0)$ surface, the dissociation of molecular hydrogen to form a surface –SH group and a Mo–H or Ni–H species is an endothermic process, and requires higher energy than on an unpromoted $(1\,0\,\bar{1}\,0)$ Mo-edge surface. On a fully promoted $(1\,0\,\bar{1}\,0)$ Ni-edge, associative adsorption of H_2 is exothermic, and dissociation to a pair of Ni–H and –SH groups or two Ni–H species is endothermic. Hydrogen sulfide can be strongly adsorbed on the vacant nickel sites on the partially and fully nickel-promoted $(1\,0\,\bar{1}\,0)$ Mo-edge surface, and surface –SH groups can be formed by dissociation of adsorbed H_2S.

Keywords: Hydrotreating; MoS_2; NiMoS; Molecular modeling; Density-functional theory; Hydrogen sulfide; Hydrogen; Adsorption

1. Introduction

The removal of sulfur and nitrogen from petroleum fractions occurs simultaneously over molybdenum sulfide based catalysts in hydrotreating processes [1,2]. Because of increasingly stringent environmental regulations and interest in upgrading heavy oil and vacuum residue, additional insight into hydrotreating catalysts and reactions is required to develop new active and selective catalysts. Molecular modeling and computational investigations have made important contributions towards understanding the structures and properties of molybdenum-based hydrotreating catalysts [3–18], such as the equilibrium sulfur coverage on the edge planes of promoted and unpromoted MoS_2 catalysts [4–6], the energetically favourable locations of promoter (Ni, Co) atoms [7,8], the adsorption and activation of hydrogen on various edge surfaces [9–14], and the adsorption of sulfur compounds on unpromoted edge surfaces of MoS_2 catalysts [15–18].

Nickel-promoted molybdenum sulfide catalysts (NiMoS) have been widely used in industry, especially for hydrodenitrogenation (HDN) and hydrotreating of heavy oil fractions. Previous studies have shown that nickel prefers the $(1\,0\,\bar{1}\,0)$ metal-edge in the nickel-promoted molybdenum sulfide catalyst [7,8]. The sulfur coverage on the fully nickel-promoted metal-edge tends to be zero at reaction conditions [6–8]; however, on partially nickel-promoted metal-edge planes, sulfur atoms prefer to be adsorbed on the top of molybdenum atoms with nickel atoms uncovered by sulfur atoms [8].

While many published results on the stable surface structures of molybdenum sulfide catalysts have gradually converged, more attention is required to understand the mechanism of HDN and HDS (hydrodesulfurization) on well-defined catalyst surfaces. In studying HDS and HDN reaction mechanisms, the significance of H_2S and H_2 must

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be considered. For example, the hydrogenation of aromatic rings is required for the denitrogenation of heterocyclic nitrogen-containing compounds [19,20], and consequently, the source of surface hydrogen must be considered when studying HDN reaction mechanisms.

The possible sources of hydrogen species are surface metal hydrides and –SH groups generated by the dissociation of hydrogen and hydrogen sulfide on the catalyst surface. The adsorption and dissociation of hydrogen on molybdenum-based catalysts has been the subject of several studies [9–14], and most of these have focused on unpromoted MoS_2 surfaces [9,11–13]. Published studies of hydrogen activation on promoted surfaces, specifically on nickel-promoted MoS_2 surfaces, are very limited [14,21]. Therefore, the objective of this work is to fill this information gap by studying the adsorption and dissociation of H_2 and H_2S on nickel-promoted MoS_2 catalyst surfaces to elucidate the possible sources of surface hydrogen for hydrotreating reactions. Additionally, the adsorption and dissociation of H_2 and H_2S on the unpromoted Mo-edge of MoS_2 are also discussed in detail for further comparison.

2. Methods

2.1. Catalyst model

The details of MoS_2-edge surfaces unpromoted and promoted with different loadings of nickel and cobalt have been previously reported [8]. The supercell MoS_2 model used in the present study is shown in Fig. 1. It is repeated in x-direction with a periodicity of six MoS_2 units, and separated by vacuum layers of 15 Å in the y- and z-directions. The volume of the unit supercell is 19.0 Å × 24.6 Å × 18.4 Å. The large supercell allows more variations of surface coverages of H_2S and H_2 on the surfaces. In this representation

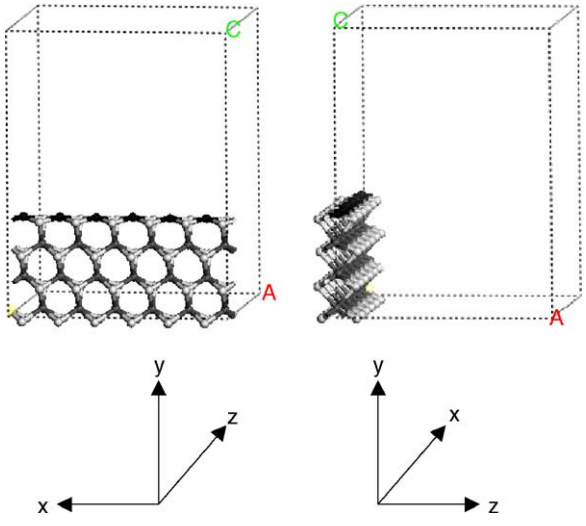


Fig. 1. Periodic model of MoS_2. Black: nickel, dark grey: molybdenum, light grey: sulfur.

(Fig. 1), molybdenum atoms on the $(1\,0\,\bar{1}\,0)$ edge surface have been substituted by nickel atoms to obtain the fully nickel-promoted catalyst surface, termed the Ni-edge. Substitution of one-half of the surface molybdenum atoms on the $(1\,0\,\bar{1}\,0)$ edge yields a 50% nickel-promoted edge surface, termed the Ni(50)Mo-edge. Prior to and after the adsorption of H_2 or H_2S, the supercell is geometrically optimized with the two bottom rows of MoS_2 constrained and other atoms free for optimization.

2.2. DFT calculations

The energy calculations are based on density-functional theory (DFT), and have been performed using Materials Studio DMol^3 from Accelrys® (version 2.2) [22]. The same software package has been previously used in calculating surface structures of MoS_2-based hydrotreating catalysts [8]. The electronic wavefunctions are expanded in numerical atomic basis sets defined on an atomic-centered spherical-polar mesh. The double-numerical plus polarization functions (DNP) and Becke exchange [23] plus Perdew–Wang approximation [24] non-local functionals (GGA-PW91) are used in all calculations. The real space cutoff radius is 4.5 Å. The Kohn–Sham equations [25] are solved by a self-consistent field (SCF) procedure. The convergence criterion for the SCF cycle is set at 0.0001. The geometry optimization (atom relaxation) convergence thresholds for energy change, maximum force, and maximum displacement between optimization cycles are 0.0001 Ha, 0.02 Ha/Å, and 0.05 Å, respectively. All electron basis sets are used for light elements, such as hydrogen, oxygen, and sulfur. Effective core potentials [26,27] are used to treat core electrons of molybdenum and nickel, and a k-point of $(1 \times 1 \times 1)$ was used because of the large supercell. Spin polarization was applied to all calculations for the systems containing nickel.

2.3. Thermodynamic calculations

The adsorption energy of H_2 ($\Delta E_{a,H_2}$) on an edge surface is calculated according to the following equation:

$$\Delta E_{a,H_2} = E_{Surface(nH_2)} - E_{Surface(ref)} - nE_{H_2} \quad (1)$$

where $E_{Surface(nH_2)}$, $E_{Surface(ref)}$, and E_{H_2} represents total electronic energies of an edge surface with n adsorbed H_2 molecules, the clean surface, and free H_2 molecule at 0 K, respectively. Similarly, the adsorption energy of H_2S ($\Delta E_{a,H_2S}$) on an edge surface is calculated according to the following equation:

$$\Delta E_{a,H_2S} = E_{Surface(nH_2S)} - E_{Surface(ref)} - nE_{H_2S} \quad (2)$$

In addition to molecular adsorption on the surface, one H_2S molecule can also dissociate to adsorbed sulfur and gas-phase molecular hydrogen, in which case the dissociation energy ($\Delta E_{d,H_2S}$) is calculated by the following equation that

has been used in studies of sulfur coverage on catalyst surfaces [4–6]:

$$\Delta E_{d,H_2S} = E_{Surface(S)} - E_{Surface(ref)} + E_{H_2} - E_{H_2S} \quad (3)$$

Another possible mechanism for H_2S dissociation on the catalyst surface involves two H_2S molecules that dissociate to two surface –SH groups and one gas phase H_2 molecule. The dissociation energy ($\Delta E_{d,2H_2S}$) is then calculated by the following equation:

$$\Delta E_{d,2H_2S} = E_{Surface(2HS)} - E_{Surface(ref)} + E_{H_2} - 2E_{H_2S} \quad (4)$$

These energy changes defined in Eqs. (1)–(4) were used to evaluate the relative stabilities of different surface species taking the clean catalyst surface and gas-phase molecules as energy references. Corresponding free energy changes for the adsorption and dissociation of H_2 and H_2S can be calculated by adding temperature correction and partial pressure terms [8,12–14]. Based on the free energy changes, the relative probabilities of different structures at reaction conditions are calculated using Boltzmann population analysis, as has been done by Travert et al. [14].

3. Results and discussion

3.1. On the $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge surface

Fig. 2 shows the relative probabilities of the $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge structures with zero (structure **a**), one (structure $\mathbf{a_1}$), and two (structure $\mathbf{a_2}$) sulfur vacancies (coordinated unsaturated sites, cus) per supercell. Structure $\mathbf{a_3}$ has three sulfur vacancies in the supercell, which is unlikely at significant levels at reaction conditions (relative probability $< 10^{-4}$). When the P_{H_2S}/P_{H_2} ratio is lower than 0.1, the surface structure with one vacancy per supercell is significantly populated on the edge planes, although the structure without sulfur vacancies (structure **a**) is dominant. The population of the structure with a single vacancy (structure $\mathbf{a_1}$) increases with a decreasing P_{H_2S}/P_{H_2} ratio. At very low P_{H_2S}/P_{H_2} ratios (<0.001), the surface structure with two sulfur vacancies (structure $\mathbf{a_2}$) is present in significant quantities, and structure $\mathbf{a_1}$ becomes dominant.

Previous studies, however, have concluded that the most stable surface structure on the $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge has no vacancies (structure **a**) at reaction conditions, and that removing a sulfur atom to create a cus site is very difficult [4,5,8,12,28]. These studies used models containing two [4,8] or three [5,12,14,28] molybdenum atoms on the edge surface of a cell, and creating one cus site per cell using these models would produce a surface with 50 or 33% sulfur vacancies, respectively. Using cluster models, Schweiger et al. found that removing a bridge sulfur atom from the stable Mo-edge containing nine molybdenum atoms required less energy than from the Mo-edge of a three-Mo periodic cell [29]. In the present study, a periodic supercell containing six surface molybdenum atoms was used, which allows the possibility to generate a surface structure with a lower concentration of sulfur vacancies on the Mo-edge than 33%. Fig. 2 shows that it is indeed very difficult to have a surface structure with vacancy concentrations higher than 33%, but it is very likely that sulfur vacancies are present on $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge planes at low concentrations (structure $\mathbf{a_1}$). The investigations on the adsorption and dissociation of H_2 and H_2S on the Mo-edge will focus on structures **a** and $\mathbf{a_1}$, which are more relevant at reaction conditions (P_{H_2S}/P_{H_2} ratios between 0.001 and 0.1, 650 K).

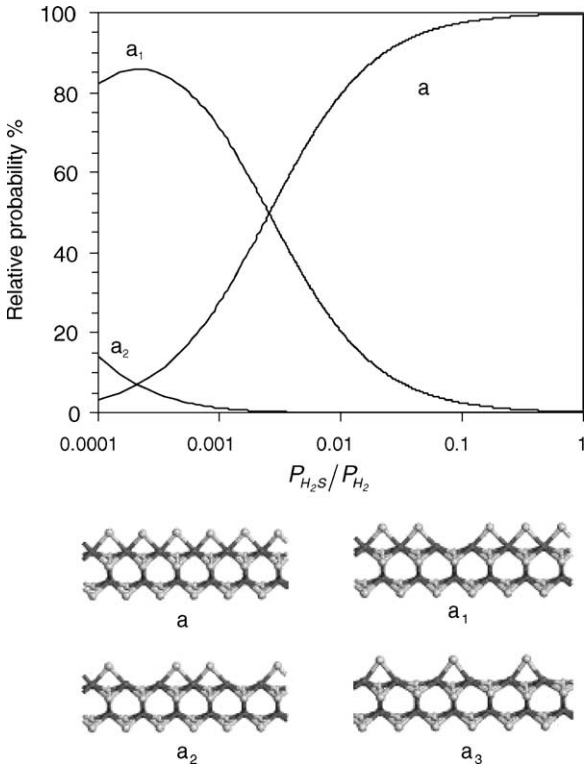
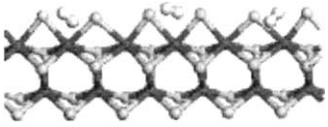
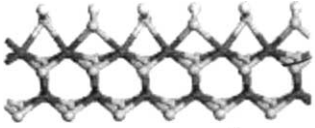
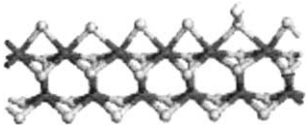
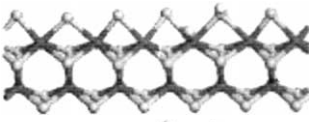
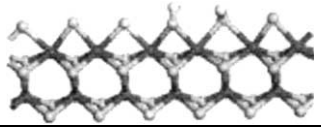


Fig. 2. Relative probabilities of $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge structures with different numbers of edge sulfur vacancies as a function of P_{H_2S}/P_{H_2} at 650 K. The relative probabilities of structure $\mathbf{a_3}$ is $<10^{-4}$ over the entire range of P_{H_2S}/P_{H_2} studied. Dark grey: molybdenum, light grey: sulfur.

Table 1 shows different surface configurations with three hydrogen molecules on the $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge of the supercell that has no sulfur vacancies. Structure **1a** is the optimized geometry for weak adsorption of molecular hydrogen. The total adsorption energy is +0.01 eV for three hydrogen molecules. The H–H bond distance remains 0.75 Å, and there is almost no interaction between the surface and hydrogen. Another configuration for molecular hydrogen adsorption is shown in structure **1b**, in which hydrogen molecules are adsorbed on top of bridge sulfur atoms to form adsorbed H_2S molecules. This is an endothermic process, with an energy requirement of ΔE = +0.60 eV/H_2. Dissociation of hydrogen to –SH and Mo–H pairs (structure **1c**) is also an endothermic process, requiring +0.15 eV/H_2. When the three hydrides migrate to the bridge sulfur atoms to form a structure with six bridge –

Table 1
Relative energies and optimized surface structures of hydrogen species on the $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge without sulfur vacancies

	Structure	ΔE (eV/H_2)
1a		+0.00
1b		+0.60
1c		+0.15
1d		−0.20
1e		+0.60
1f		−0.05
1g		−0.37

The clean surface and gas phase hydrogen molecule(s) are taken as references. Dark grey: molybdenum, light grey: sulfur, white: hydrogen.

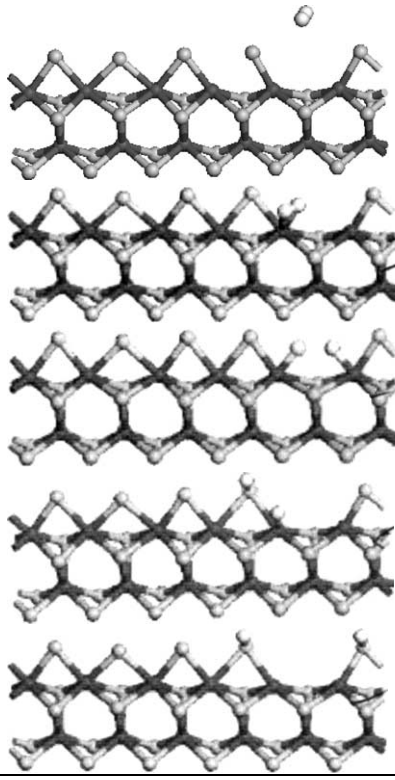
SH groups on the Mo-edge surface, the edge structure is stabilized. Thus, the dissociation energy for hydrogen molecules to form surface bridge –SH groups is an exothermic process with $\Delta E = -0.20$ eV/H_2 (structure **1d**). The dissociation of molecular hydrogen to form bridge –SH groups on the Mo-edge is energetically most favoured; the total reaction energy to generate this configuration is $\Delta E = -0.60$ eV per unit cell from three gas phase hydrogen molecules.

Previous studies have shown that the dissociation of molecular hydrogen on the stable $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge is an endothermic process, regardless of the adsorption mode. Cristol et al. [12,13] reported the dissociation of molecular hydrogen to form a –SH and Mo–H pair required +0.27 eV/H_2, two –SH groups required +0.37 eV/H_2, and adsorbed H_2S required +0.89 eV/H_2, all of which are higher than those reported in the present study. Our results agree well with published studies that the dissociation of molecular hydrogen to a –SH and Mo–H pair is an endothermic process; 0.15 eV (structure **1c**, Table 1) compared to 0.27 eV (Table 4) [12]. However, our results do not agree that the dissociation of molecular hydrogen to two –SH groups is an endothermic process; −0.20 eV (structure **1d**, Table 1) compared to 0.37 eV (Table 1) [12]. The present results were verified using a smaller model cell and two-slab model cell, similar to the approach used in Ref. [12], with both numerical basis sets and planewave functionals (Accelrys®, CASTEP). Using this methodology, only minor differences were found in the adsorption energies, and our previous conclusion that two –SH groups are more stable than a pair of Mo–H and –SH groups was confirmed. Thus, this discrepancy cannot be due to a different catalyst model or to using different basis sets. Spectroscopic experimental data [21] show that a vibration frequency between 2500 and 2600 cm^{-1} is observed on MoS_2 catalyst surfaces with adsorbed hydrogen, which is due to the stretching vibration of –SH groups. The stretching frequencies of –SH and Mo–H groups were calculated in the present study as 2574 and 1647 cm^{-1}, respectively. No frequency near to 1647 cm^{-1} was reported in the spectroscopic studies of hydrogen adsorption on MoS_2 [21], and therefore this confirms –SH groups are more stable than Mo–H groups on MoS_2.

In order to further study the relative stabilities of different surface hydrogen species on the $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge, one H_2 molecule was positioned on the Mo-edge and three surface structures were investigated (Table 1). The reaction energy is +0.60 eV for the formation of adsorbed H_2S (structure **1e**), −0.05 eV for a –SH and Mo–H pair (structure **1f**), and −0.37 eV for two –SH groups (structure **1g**). The surface –SH groups are the most stable structures on the Mo-edge surface. The reaction energy per H_2 for the formation of adsorbed H_2S is the same when there is one or three H_2 molecules per supercell. It should be noted that the three adsorbed H_2S molecules in structure **1b** are not in the same plane, as they shift to minimize an observed repulsion effect. The reaction energy for the formation of a pair of –SH and Mo–H on the Mo-edge (structure **1f**) is slightly exothermic ($\Delta E = -0.05$ eV/H_2), which is compared to a positive value (+0.15 eV/H_2) for three H_2 molecules in a supercell. The reaction energy per H_2 for the formation of two –SH groups is more exothermic when only one H_2 molecule is in the supercell ($\Delta E = -0.37$ eV/H_2, structure **1g**) than when three H_2 molecules are in the supercell (−0.20 eV/H_2, structure **1d**). This trend has been verified with two molecules of hydrogen in a supercell, where the reaction energy is −0.24 eV/H_2 for the dissociation of two H_2 molecules to yield four –SH groups on the Mo-edge. The absolute value of the reaction energy decreases from 0.37 through 0.24 to 0.20 eV/H_2 with the increase of hydrogen coverage from one through two to three hydrogen molecules per supercell.

These results indicate that –SH and Mo–H groups have a repulsion effect at high concentrations on the $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge surface, and become more stable at lower concentrations. Bollinger et al. also reported that the adsorption of hydrogen on bridge sulfur atoms was an exothermic process when one hydrogen atom was adsorbed on every two sulfur atoms, and the process became slightly

Table 2
Relative energies and optimized surface structures with hydrogen species on the $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge with one sulfur vacancy

	Structure	ΔE (eV/H_2)
2a		+0.04
2b		+0.13
2c		+0.58
2d		−0.05
2e		+0.53

The clean surface and gas phase hydrogen molecule are taken as references. Dark grey: molybdenum, light grey: sulfur, white: hydrogen.

endothermic when one hydrogen atom was placed on every sulfur atom [30]. Therefore, the dissociation H_2 on the Mo-edge is not always an endothermic process [12,13]; the dissociation of molecular hydrogen to form two –SH groups is exothermic at low coverages. By comparing structures **1c** and **1d**, or structures **1f** and **1g**, it can be noted that the –SH group is more stable than the Mo–H group on the Mo-edge surface (by about 0.3 eV). This further explains why more experimental evidence has been reported for the presence of –SH groups than that of Mo–H groups [21], as discussed previously.

Table 2 presents the optimized configurations of hydrogen on the $MoS_2(1\,0\,\bar{1}\,0)$ Mo-edge with one sulfur vacancy (structure $\mathbf{a_1}$ in Fig. 2). Molecular adsorption of hydrogen on the bridge sulfur atom that bonds a five-coordinated molybdenum atom (Mo_V) and a six-coordinated molybdenum atom (Mo_{VI}) cannot generate a stable configuration, and the hydrogen molecule moves away from surface during geometry optimization (structure **2a**). Molecular adsorption on the Mo_V site is a slightly endothermic process (ΔE = +0.13 eV/H_2, structure **2b**). For dissociative hydrogen adsorption, a hydrogen molecule may dissociate into two Mo_V–H groups (structure **2c**, Table 2), or a pair of –SH and Mo_V–H at the sulfur vacancy (structure **2d**, Table 2). The reaction energy is +0.58 eV/H_2 for the formation of two Mo_V–H groups. The formation of two Mo_{VI}–H on the saturated molybdenum sites is not possible; Mo_{VI}–H is possibly present only when it pairs with an –SH group. The dissociation energy is −0.05 eV/H_2 for the formation of an –SH and Mo_V–H pair at the vacancy. Structure **2e** shows the formation of two –SH groups at both sides of the vacancy, which requires +0.53 eV/H_2 relative to gas phase molecular hydrogen. This is compared to formation of two –SH groups on the saturated surface, where it is an exothermic process (structure **1g**, Table 1). The hydrogen atoms on the sulfur atoms bound to unsaturated molybdenum atoms are less stable than those on the sulfur atoms that bond to saturated molybdenum atoms.

Similar dissociation energy values on sulfur vacancies have been reported using a three-Mo cell [13,14], but the optimized configuration was slightly different. The most stable position for the hydride was to bridge the two Mo_V sites. In the present calculations, the bridge hydride is less stable than the one shown in structure **2d**.

There is another way to examine the formation of hydrogen species on the Mo-edge surface. On the surface with one sulfur vacancy, H_2S can be adsorbed on the vacancy to form structure **1e**, as shown in Table 1, with an adsorption energy of −0.11 eV/H_2S. Dissociation of the adsorbed H_2S to gas phase H_2 and adsorbed sulfur yields a structure that has no sulfur vacancies on the Mo-edge (structure **a**), with a dissociation energy of −0.6 eV/H_2S. The adsorbed H_2S may also dissociate to –SH and Mo–H (structure **1f**, Table 1), which yields a dissociation energy of −0.65 eV/H_2; a more stable structure can be generated through converting the hydride to a –SH group (structure **1g**, Table 1).

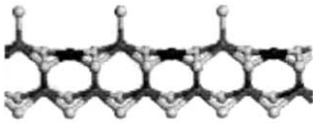
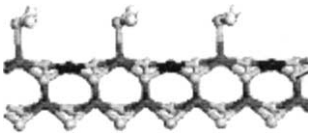
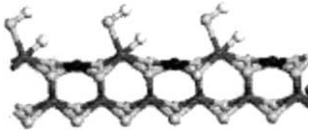
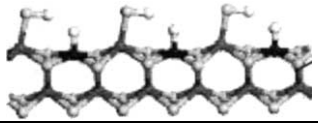
3.2. On the Ni(50)Mo-edge $(1\,0\,\bar{1}\,0)$ surface

Substituting one of every two molybdenum atoms on the $(1\,0\,\bar{1}\,0)$ metal-edge of MoS_2 by nickel atoms generates a partially promoted edge surface, denoted as Ni(50)Mo-edge. The most stable structure on the Ni(50)Mo-edge is with one sulfur atom directly atop of each molybdenum atom and nickel atoms being uncovered, as shown in structure **3a** in Table 3 [8].

The adsorption of hydrogen on the Ni(50)Mo-edge surface may occur on the sulfur sites or on the nickel sites. The adsorption of hydrogen molecules on sulfur atoms is an endothermic process; the adsorption energy is +0.90 eV/H_2 (structure **3b**, Table 3). When hydrogen molecules are initially located on nickel sites, they move away from the surface during geometry optimization (structure **3c**, Table 3) yielding an adsorption energy of +0.04 eV/H_2. The associative adsorption of hydrogen on both sulfur and nickel sites is thermodynamically unfavourable.

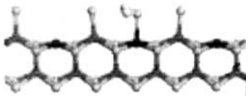
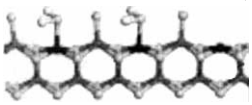
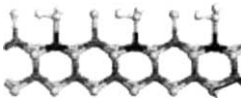
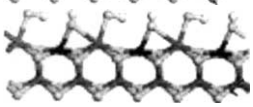
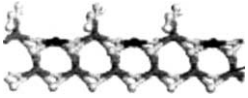
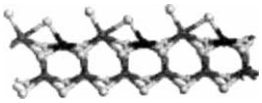
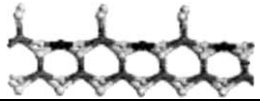
Heterolytic dissociation of hydrogen on the Ni(50)Mo-edge may occur on S–Mo sites to –SH and Mo–H, or on Mo–Ni sites to Mo–H and Ni–H. The dissociation energy from gas phase molecular hydrogen to –SH and Mo–H (structure **3d**, Table 3) is +0.74 eV/H_2. When molecular hydrogen is

Table 3
Relative energies and optimized surface structures with hydrogen species on the Ni(50)Mo-edge of NiMoS

	Structure	ΔE (eV/H_2)
3a		0
3b		+0.90
3c		+0.04
3d		+0.74
3e		+0.77

The clean surface and gas phase hydrogen molecule(s) are taken as references. Black: nickel, dark grey: molybdenum, light grey: sulfur, white: hydrogen.

Table 4
Relative energies and optimized surface structures with H_2S on the Ni(50)Mo-edge of NiMoS

	Structure	ΔE (eV/H_2)
4a		−0.64
4b		−0.48
4c		−0.46
4d		−0.34
4e		−0.21
4f		+0.78
4g		+0.34

The clean surface and gas phase hydrogen sulfide molecule(s) are taken as references. Black: nickel, dark grey: molybdenum, light grey: sulfur, white: hydrogen.

placed between a nickel site and a molybdenum site with one hydrogen atom bonding to nickel and the other to molybdenum, the hydrogen atom bonding to molybdenum is unstable and moves to the sulfur atom during optimization (structure **3e**) with a dissociation energy of +0.77 eV/H_2. This is also a strong indication that –SH species are much more stable than Mo–H. In both scenarios, the dissociation of hydrogen on the Ni(50)Mo-edge is an endothermic process, and it requires higher energy than on the Mo-edge. These results indicate that while partial substitution of molybdenum by nickel on the Mo-edge provides more open sites, nickel substitution does not promote hydrogen dissociation.

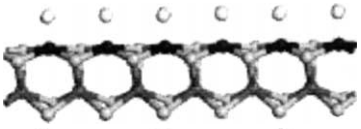
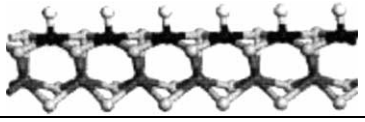
H_2S molecules can also be adsorbed on the vacant nickel sites. When one, two, and three H_2S molecules are adsorbed on the Ni(50)Mo-edge surface, structures **4a**–**4c** (Table 4) are obtained, respectively. The ΔE values per H_2S relative to the clean surface and gas phase H_2S are given in Table 4. The negative ΔE values indicate that the adsorption of H_2S on the Ni(50)–Mo-edge is an exothermic process. The absolute value of the adsorption energy per H_2S molecule decreases from structures **4a**–**4c** with the increase of H_2S coverage. This decrease is due to the increasing repulsion effect between the sulfur atoms on molybdenum sites and adsorbed H_2S molecules on nickel sites.

The adsorbed H_2S can dissociate to surface –SH groups or to adsorbed sulfur and gas phase hydrogen, as shown by structures **4d**–**4g** (Table 4). One of the hydrogen atoms in an adsorbed H_2S molecule combines with a sulfur atom on the neighbouring molybdenum atom to generate surface –SH groups on nickel and molybdenum sites (structure **4d**). It was observed the –SH groups on the nickel sites tilt to bond the molybdenum sites. Thus, the probability for the –SH groups on nickel sites to move completely to the molybdenum sites was also investigated. It requires an additional 0.13 eV per –SH group to transform structures **4d** and **4e**, where structure **4e** includes open nickel sites and –SH groups on the molybdenum sites. For hydrotreating reactions, the open sites can serve as adsorbing sites and –SH groups as sources of hydrogen. The sulfur atoms on the nickel sites after releasing hydrogen as free molecules are not stable and tend to migrate to the molybdenum sites, as shown by structure **4f**. In structure **4g**, the two sulfur atoms form a S–S dimer, which generates a more stable structure. The dissociation to hydrogen and adsorbed sulfur is always an endothermic process, and the reaction energy is +0.80 eV per H_2S from structures **4c** to **4g**.

3.3. On the Ni-edge $(1\,0\,\bar{1}\,0)$ surface

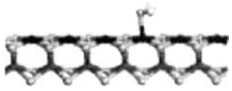
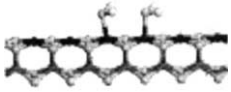
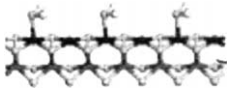
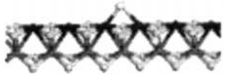
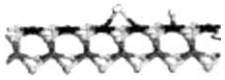
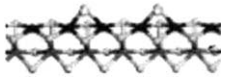
Substitution of all molybdenum atoms on the $MoS_2(1\,0\,\bar{1}\,0)$ edge surface by nickel atoms produces a fully promoted metal-edge, denoted the Ni-edge. The bare Ni-edge is the most stable structure at reaction conditions [6,8], as shown in structure **5a** (Table 5).

Table 5
Relative energies and optimized surface structures with hydrogen on the Ni-edge of fully promoted NiMoS

	Structure	ΔE (eV/H_2)
5a		0
5b		−0.21
5c		−0.19
5d		−0.14
5e		+0.36
5f		+0.32

The clean surface and gas phase hydrogen molecules are taken as references. Black: nickel, dark grey: molybdenum, light grey: sulfur, white: hydrogen.

Table 6
Relative energies and optimized surface structures with H_2S on the Ni-edge of fully promoted NiMoS

	Structure	ΔE (eV/H_2)
6a		−0.82
6b		−0.82
6c		−0.74
6d		−0.76
6e		+0.46
6f		−0.09
6g		−0.31
6h		−0.38
6i		−0.08

The clean surface and gas phase hydrogen sulfide molecules are taken as references. Black: nickel, dark grey: molybdenum, light grey: sulfur, white: hydrogen.

On a bare Ni-edge, hydrogen molecules can be weakly adsorbed on the nickel sites at low coverage. The adsorption energy is −0.21 eV/H_2 when the hydrogen coverage is very low (structure **5b**, Table 5). At higher coverages, the repulsion effect between hydrogen molecules decreases the value of the average adsorption energy per hydrogen molecule. When one hydrogen molecule is adsorbed on each nickel site, the adsorption energy is reduced to −0.14 eV/H_2.

Adsorbed molecular hydrogen on the Ni-edge surface may dissociate to form a pair of Ni–H and –SH or two Ni–H groups, as shown in structures **5e** and **5f**. When there are three molecules of hydrogen on the surface, the dissociation energies for these two structures are +0.36 eV/H_2 (structure **5e**) and +0.32 eV/H_2 (structure **5f**), respectively. The dissociation energies reduce to +0.29 and +0.32 eV/H_2, respectively, when only one hydrogen molecule is on the surface of the supercell. In either case, the dissociation of H_2 on the Ni-edge is an endothermic process, while molecular adsorption is exothermic.

The adsorption of H_2S on the fully substituted Ni-edge is more energetically favoured than on the Ni(50)–Mo-edge. Table 6 summarizes the total adsorption energies and corresponding optimized structural geometries with one, two, and three H_2S molecules adsorbed on the Ni-edge surface per supercell. The adsorption energy for one H_2S molecule on the Ni-edge of the supercell is −0.82 eV (structure **6a**, Table 6), compared to −0.64 eV on the Ni(50)–Mo-edge (structure **4a**, Table 4). The adsorption energy is −0.82 eV/H_2S for two H_2S molecules and −0.76 eV/H_2S for three H_2S molecules when they are evenly distributed on the six nickel sites of the supercell. The decrease in the absolute value of the adsorption energy per H_2S molecule with the increase in H_2S coverage is due to the repulsion effect between two neighbouring H_2S molecules. The adsorption energy is −0.43 eV/H_2S when all nickel sites were covered by H_2S molecules (not shown).

The repulsion effect can also be illustrated by comparing the adsorption energies between structures **6b** (−0.82 eV/H_2S) and **6c** (−0.74 eV/H_2S). Thus, when two H_2S molecules are adsorbed on the surface of a supercell containing six nickel sites, they prefer to be adsorbed on separated sites far away from each other to minimize the repulsion effect. The magnitude of the repulsion effect can be estimated by the repulsion energy, defined by the decrease in the average adsorption energy per H_2S molecule. There is no repulsion effect when two adsorbed H_2S molecules are separated by two or more nickel sites, and very little when they are separated by one nickel site. However, the repulsion energy is 0.39 eV/H_2S when all nickel sites are occupied.

When one adsorbed H_2S molecule on the Ni-edge dissociates to adsorbed sulfur and gas phase hydrogen, the sulfur atom on the edge surface prefers a bridging position between two nickel sites. This sulfur atom also forms a S–S bond with a sulfur atom in the basal plane (structure **6e**). The reaction energy for one H_2S to dissociate to adsorbed sulfur and gas phase hydrogen is +0.46 eV, which is an endothermic process. The dissociation of H_2S to a bridge –SH group on the edge surface and a –SH group with a basal-plane sulfur atom (structure **6f**) is slightly exothermic, and dissociation to a bridge –SH group and a Ni–H (structure **6g**) is more exothermic relative to the clean surface and gas phase H_2S. The adsorbed H_2S is the most stable configuration on the surface.

When two adsorbed H_2S molecules are adsorbed on neighbouring nickel sites, it is possible to form two surface –SH groups and one gas phase hydrogen molecule, as shown in structure **6h**. The reaction energy for this process is -0.38 eV/H_2S. The –SH groups on the surface prefer the bridge positions between nickel sites, while the adsorbed H_2S prefers adsorption on top of nickel sites (structure **6c**). The configuration with an –SH group directly atop of a nickel site is about 0.20 eV higher in energy than a bridge –SH group (structure not shown). The formation of a S–S dimer from two H_2S molecules is slightly exothermic (structure **6i**).

In summary, the most stable hydrogen species on the Ni-edge is adsorbed H_2S (structures **6a**–**6c**), followed by surface –SH groups (structure **6h**). The Ni–H (structure **5f**) is less stable than associatively adsorbed H_2 (structures **5b** and **5c**). In studying hydrotreating reaction mechanisms on the Ni-edge surface, the presence of adsorbed H_2S and –SH groups must be considered, as well as the presence of Ni–H.

4. Conclusions

On the Mo-edge where all molybdenum atoms are covered by bridge sulfur atoms, and thus six-fold coordinated, the dissociation of hydrogen to –SH groups is an exothermic process and the exothermicity increases with the decrease of hydrogen coverage on the surface. The formation of –SH and Mo–H pairs is endothermic at high hydrogen coverages, but slightly exothermic (or athermic) at low coverages. At very low partial pressures of H_2S, the generation of a sulfur vacancy on the Mo-edge is possible. The dissociation of hydrogen to –SH and Mo–H at the vacancy is slightly exothermic. The dissociation of hydrogen is more endothermic on the nickel-promoted Ni(50)Mo-edge and Ni-edge than on the Mo-edge. The adsorption of H_2S on the open nickel sites of the nickel-promoted surfaces is always highly exothermic. The formation of surface –SH groups on the nickel-promoted edge surfaces by the dissociation of adsorbed H_2S is endothermic, and the surface –SH groups on the promoted edge surfaces are more stable relative to the clean surface and gas phase species.

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