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A DFT study of WS_2, NiWS, and CoWS hydrotreating catalysts: energetics and surface structures

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Abstract

Tungsten-based hydrotreating catalysts differ from molybdenum-based catalysts in many aspects. Although theoretical studies have offered many insights into the structures and properties of MoS_2-based catalysts, no similar study has been reported for WS_2-based catalysts. Theoretical studies on tungsten sulfide will provide an increased understanding of the difference between theses two groups of catalysts, and contribute to the development of highly active and selective hydrotreating catalysts. The present study investigates the details of the edge surfaces of unpromoted and Ni(Co)-promoted WS_2 catalysts using density-functional theory (DFT) under generalized gradient approximation (GGA) considering the effect of reaction conditions. For unpromoted WS_2 catalysts, the edge surfaces favor sulfur coverage of 50% under reaction conditions for both the metal edge and the sulfur edge. Nickel tends to substitute the tungsten on the W edge in the Ni-promoted catalysts, while cobalt prefers to take the position of tungsten at the S edge in Co-promoted catalysts. The incorporated edge structures are stable for both nickel and cobalt relative to individual promoter sulfides.

Keywords: WS_2; NiWS; CoWS; Hydrotreating catalysts; Density-functional theory

1. Introduction

Industrial hydrotreating catalysts consist of molybdenum or tungsten promoted by nickel or cobalt supported on alumina. Tungsten disulfide has a similar structure as molybdenum disulfide, and thus it is usually assumed that tungsten catalysts are similar to molybdenum catalysts. However, tungsten-based catalysts differ from molybdenum-based catalysts in many aspects. First, tungsten catalysts in oxidic form are much more difficult to convert to sulfidic form than molybdenum catalysts [1–3]. Secondly, tungsten-based catalysts have higher activities for the hydrogenation of aromatics [4–6]. Adding cobalt to MoS_2 catalysts significantly increases their activities in hydrodesulfurization (HDS) reactions [7,8], but no similar effect has been observed for tungsten catalysts by adding cobalt to WS_2 [9]. Additionally, NiW catalysts have been reported to be more susceptible to the inhibition effect of H_2S in the HDS of dibenzothiophenes than NiMo catalysts [10]. However, the distinct chemical and morphological properties of tungsten-based catalysts are poorly understood when compared to the current level of information available for molybdenum-based catalysts.

The superior hydrogenation activity of tungsten-based catalysts makes them a promising option in upgrading heavy oils and producing diesel fuels with low-sulfur and low-aromatics content. Most information about hydrotreating catalysts was obtained through extensive studies of molybdenum-based catalysts, and much less attention has been given to tungsten-based catalysts [7,8,11]. In addition to tremendous experimental studies, theoretical investigations have contributed many insights into the structures and properties of molybdenum-based catalysts at the atomic scale [12–17]. However, no theoretical study on tungsten catalysts has been reported in the literature, with the noted exception of WS_2 bulk properties that were reported by Raybaud et al. in their series of theoretical studies of transition metal sulfides [18,19]. The objective of the present study is to fill this information gap by investigating the edge structures of unpromoted and promoted WS_2 catalysts us-

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ing a similar approach as we have previously reported for molybdenum-based catalysts [20].

2. Methods

2.1. DFT calculations

The energy calculations are based on density-functional theory (DFT) and have been performed using Material Studio DMol^3 from Accelrys (version 2.2) [21,22]. The details of the calculation method have been described elsewhere [20]. The double-numerical plus d-functions (DND) all-electron basis set and Becke exchange [23] plus Perdew correlation [24] nonlocal functionals (GGA-BP) are used in all calculations. The real space cutoff radius is 4.5 Å. The Kohn–Sham equations [25] are solved by a SCF (self-consistent field) 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. Based on the convergence test for k-point sampling, the k-point set of $(2 \times 1 \times 1)$ was used for calculations of the Ni- and Co-promoted and unpromoted WS_2 slab models, and $(5 \times 5 \times 5)$ and $(3 \times 3 \times 3)$ were used for Ni_3S_2 and Co_9S_8, respectively, to ensure the quality of the results. Spin polarization was applied to all calculations for the systems containing magnetic elements (nickel or cobalt). Techniques of Direct Inversion in an Iterative Subspace (DIIS) [26] with a size value of 6, thermal smearing [27], and a range of 0.005 Ha are applied to accelerate convergence.

2.2. Tungsten-based catalyst models

The catalyst model consists of one layer WS_2 sheet with four rows of S–W–S units as shown in Fig. 1. The four-row WS_2 slab is cut from a bulk crystal structure that is based on crystallographic data [28], and geometrically optimized using DMol^3. The calculation results for the edge structures of MoS_2 catalysts obtained using different sizes of catalyst models have been previously evaluated, and it has been concluded that the four-row single layer model is appropriate for calculating relative energies of specific surface structures [20]. Using a larger model, including two layers in z direction or more than four rows in y direction, would not improve the quality of the results [20]. In the model shown in Fig. 1, the WS_2 slabs are repeated in the x direction with a periodicity of two S–W–S units, and are separated by vacuum layers of 9.3 Å in the z direction and 10 Å in the y direction. The volume of the supercell is $(6.36 \times 21.02 \times 12.5$ Å).

In this representation (Fig. 1), the top edge surface exposes uncovered tungsten atoms, analogous to the MoS_2 model, and is termed the W edge or metal edge, while the bottom edge surface is the fully sulfided S edge. The W edge and S edge can have different sulfur coverages by adding sulfur on the W edge and removing sulfur from the S edge, as has been done for MoS_2 catalysts [12–14,20]. The structures with different sulfur coverages on edge surfaces are optimized before calculating total energies. During the geometry optimization, the atoms in the two inner S–W–S rows are fixed as in the bulk structure and other atoms at both edge surfaces are relaxed. Full geometry optimizations were also performed for WS_2 models with 0 and 100% sulfur coverages on the W edge, in which all atoms are relaxed. However, no difference was observed in the relative energies of the different structures. Therefore, the two inner S–W–S rows were fixed for all other calculations to decrease computational resources and time.

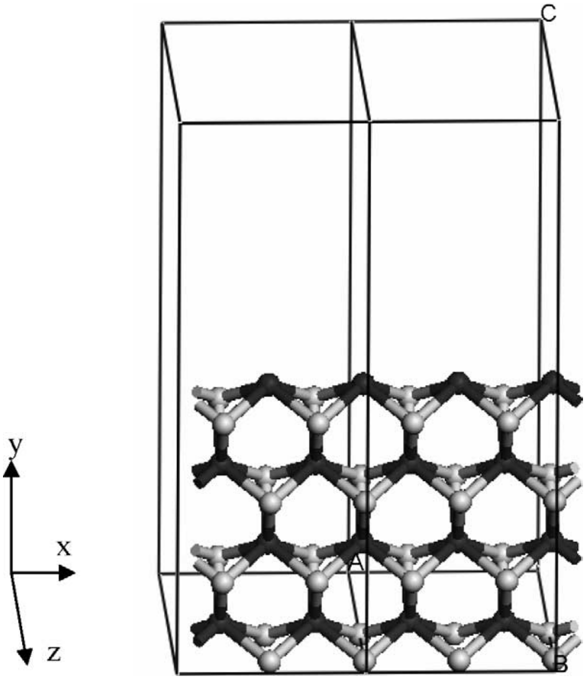


Fig. 1. Single-layer WS_2 model representation consisting of four S–W–S rows in the y direction and two units of supercells in x direction (black indicates tungsten atoms, gray indicates sulfur atoms).

3. Results and discussion

3.1. Energetics of unpromoted and promoted WS_2 for different sulfur coverages on the W edge and S edge

The same methodology we previously used for molybdenum catalysts was used to determine the stable sulfur coverage on the W edge and the S edge of WS_2 catalysts [20]. Relative energies of the surfaces with different sulfur coverages are calculated according to

$$\mathrm{Structure}(0) + n\mathrm{H_2S} = \mathrm{Structure}(n) + n\mathrm{H_2}, \qquad (1)$$

where Structure(0) represents the structure with a bare edge surface, and Structure(n) represents the structure with n sulfur atoms adsorbed on the edge surface of each supercell.

When the sulfur coverage on the W edge is calculated, the S edge is maintained fully sulfided. Similarly, when the sulfur coverage on the S edge is being considered, the W edge remains fully sulfided. The maximum possible number of sulfur atoms that can be added to each edge tungsten atom is two. Thus, 25% sulfur coverage corresponds to one sulfur atom added to two edge tungsten atoms on average, and 50% sulfur coverage corresponds to one sulfur atom added to one edge tungsten atom on average. The relative energies for one supercell are calculated according to

$$\Delta E_0^0 = E^0_{0,\mathrm{Strucure}(n)} - E^0_{0,\mathrm{Strucure}(0)} + n\left(E^0_{0,\mathrm{H_2}} - E^0_{0,\mathrm{H_2S}}\right), \tag{2}$$

where $E^0_{0,\mathrm{Structure}(n)}$, $E^0_{0,\mathrm{Structure}(0)}$, $E^0_{0,\mathrm{H_2}}$, and $E^0_{0,\mathrm{H_2S}}$ are total energies of Structure(n), Structure(0), hydrogen, and hydrogen sulfide at 0 K, respectively.

Fig. 2 shows the relative energies of optimized WS_2 structures with different sulfur coverages on the W edge and the S edge. The optimized geometries of the edge surfaces of WS_2 are the same as those of MoS_2 [13,15,20]. The relative energy for the structure with a fully sulfided W edge and S edge is used as the reference. These results indicate that removing the same amount of sulfur atoms from the S edge always requires more energy than from the W edge. For example, it requires 6.53 eV to remove the four sulfur atoms from the S edge (1.63 eV/atom), and only 3.38 eV (0.85 eV/atom) to remove the four sulfur atoms from the W edge. The same trend has been observed for MoS_2 [12–14,20]. This indicates that sulfur bonds to the tungsten atoms on the S edge much more strongly than on the W edge. The difference in the binding energies of sulfur atoms on the W edge and the S edge results in different equilibrium sulfur coverages on these two edge planes. For the W edge, the structure with 50% sulfur coverage has the lowest energy, and for the S edge the fully sulfided structure has the lowest energy.

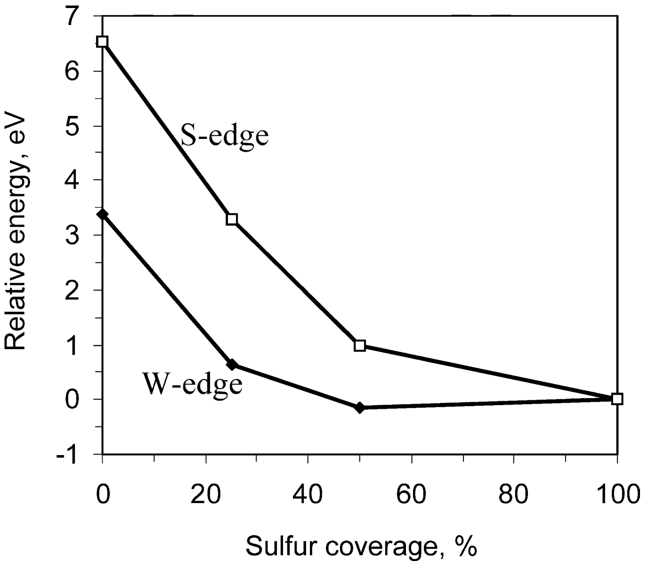


Fig. 2. Relative energies of WS_2 as function of sulfur coverage on the S edge and W edge, with the fully sulfided surface being used as the reference.

As it has been shown for molybdenum catalysts, incorporation of nickel and cobalt into the edge structure decreases the sulfur bonding strength, and thus reduces the sulfur coverage on the edge surface [12,14,20]. A similar effect is expected for promoted tungsten catalysts. Substitution of one tungsten atom on either the W edge or the S edge of a WS_2 supercell (Fig. 1) by a promoter atom (nickel or cobalt) produces the 50% promoter-substituted W- or S-edge surfaces. A 100% promoter-substituted edge surface can be generated by the substitution of all the tungsten atoms on the W-edge or the S-edge surface by promoter atoms (nickel or cobalt). Relative energies of structures with different degrees of promoter substitution on the W edge and S edge are calculated according to Eq. (1) and Eq. (2). The results for the promoter-substituted W-edge structures are presented in Fig. 3 and for the promoter-substituted S-edge structures are shown in Fig. 4. For comparison, the data for the unpromoted W edge and S edge are also included in Figs. 3 and 4. For each model catalyst series, the structure with a bare edge surface is taken as the energetic reference. The relative energies shown in Fig. 3 indicate the bonding strength of sulfur atoms on the W edges; negative values indicate that dissociation of hydrogen sulfide on the edge surface to adsorbed sulfur and free hydrogen is an exothermic process, and positive values indicate that the dissociation of hydrogen sulfide is an endothermic process.

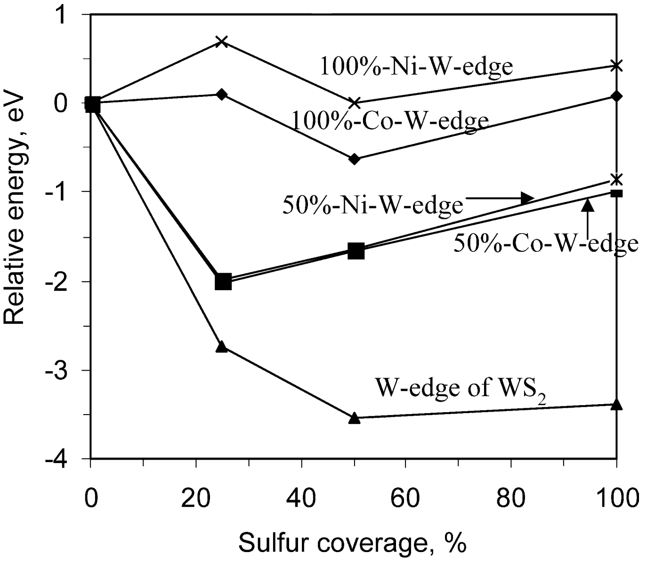


Fig. 3. Relative energies of WS_2 promoted by cobalt or nickel as function of sulfur coverage on the W edge, with the bare surfaces being used as references (50%-Co-W edge refers to Co-promoted catalyst with 50% of tungsten atoms on the W edge substituted by cobalt atoms, 100%-Co-W edge to Co-promoted catalyst with 100% of tungsten atoms on the W edge substituted by cobalt atoms, 50%-Ni-W edge to Ni-promoted catalyst with 50% of tungsten atoms on the W edge substituted by nickel atoms, and 100%-Ni-W edge to Ni-promoted catalyst with 100% of tungsten atoms on the W edge substituted by nickel atoms).

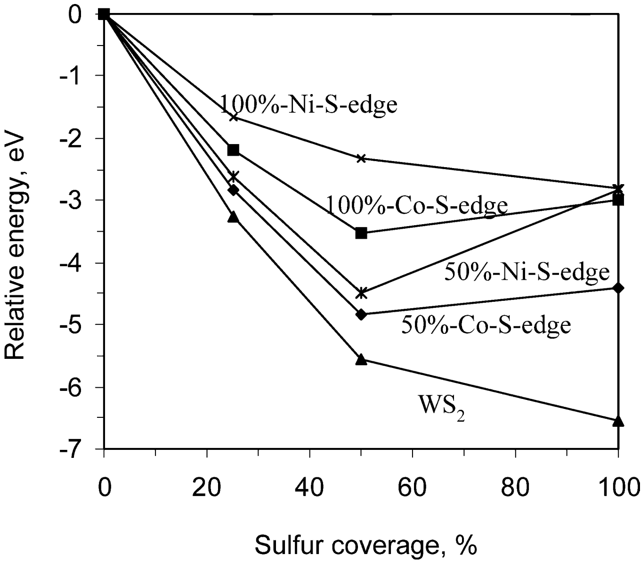


Fig. 4. Relative energies of WS_2 promoted by cobalt or nickel as function of sulfur coverage on the S edge, with the bare surfaces being used as references (50%-Co-S edge refers to Co-promoted catalyst with 50% of tungsten atoms on the S edge substituted by cobalt atoms, 100%-Co-S edge to Co-promoted catalyst with 100% of tungsten atoms on the S edge substituted by cobalt atoms, 50%-Ni-S edge to Ni-promoted catalyst with 50% of tungsten atoms on the S edge substituted by nickel atoms, and 100%-Ni-S edge to Ni-promoted catalyst with 100% of tungsten atoms on the S edge substituted by nickel atoms).

For the unpromoted W edge, adding one sulfur atom to the surface of the supercell by the dissociation of hydrogen sulfide, generating a W-edge surface with 25% sulfur coverage, is a highly exothermic process releasing 2.7 eV/sulfur atom. Adding an additional sulfur atom on the 25% sulfur coverage unpromoted W-edge surface is still an exothermic process, producing an additional 0.80 eV/sulfur atom. The further addition of sulfur on a 50% sulfur coverage surface is a slightly endothermic process. Adsorption of one sulfur atom on the 50% Ni(Co)-substituted W edge is an exothermic process, releasing 2.0 eV/sulfur atom, and the further addition of sulfur atoms on the 50% Ni(Co)-promoted W edge is an endothermic process. For the fully substituted metal edge, adsorption of one sulfur atom is a slightly endothermic process ($\Delta E_0^0 = 0.11$ eV) on the 100% Co-promoted metal edge, and strongly endothermic ($\Delta E_0^0 = 0.70$ eV) on the 100% Ni-promoted metal edge. Adding another sulfur atom to form a surface S–S dimer stabilizes the surface sulfur atoms. Thus, the reaction enthalpies for the dissociation of two hydrogen sulfide molecules on the 100% substituted metal edges of the supercell to form a S–S dimer are −0.32 eV/sulfur atom for Co-promoted metal edge, and −0.003 eV/sulfur atom for Ni-promoted metal edge.

These results indicate that the bonding of sulfur on the unpromoted W edge is stronger than that on the promoter-substituted metal edge. Furthermore, the bonding of sulfur on the Co-promoted metal edge is stronger than that on Ni-promoted metal edge. The weaker sulfur bonding on the promoted edge surfaces makes it easier to create sulfur vacancies, which are active sites for HDS and HDN reactions. Incorporation of nickel or cobalt into the edge surfaces of WS_2 decreases the bonding of sulfur atoms, thus making it easier to generate coordinately unsaturated sites (*cus*) on the edge surfaces of promoted catalysts. In this respect, nickel is a better promoter than cobalt.

3.2. *Effect of reaction conditions on the relative stability of edge structures*

The relative stabilities of different structures vary with reaction conditions. The dependence of free energy changes of Eq. (1) on p_{H_2S}/p_{H_2} ratios has been previously established at reaction temperature in studies for molybdenum catalysts [13–16,20]. The free energy change for adding n sulfur atoms on the reference surface can be calculated by

$$\Delta G = \Delta G_T^0 - nRT \ln \frac{p_{H_2S}}{p_{H_2}}, \tag{3}$$

where ΔG_T^0 is the standard free energy change at temperature T, and p_{H_2S} and p_{H_2} are partial pressures of hydrogen sulfide and hydrogen in the gas phase above the surface, respectively. ΔG_T^0 can be calculated from the standard energy change at 0 K, ΔE_0^0, and the temperature corrections for free energies ($\Delta G_{T_{\mathrm{corr}}}^0$),

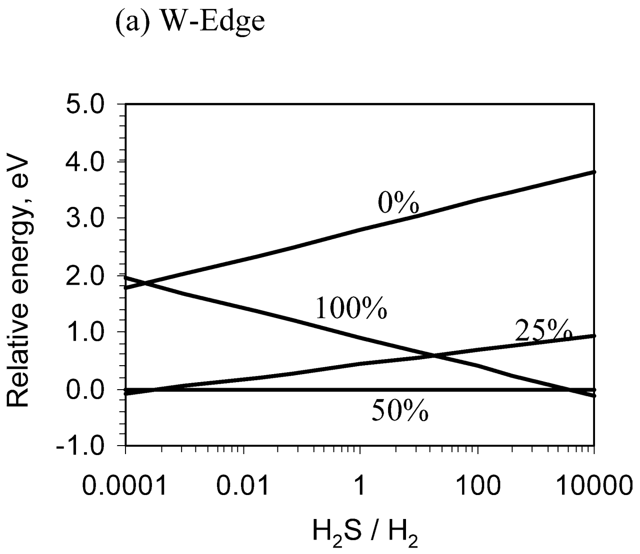
$$\Delta G_T^0 = \Delta E_0^0 + n\Delta G_{T_{\mathrm{corr}}}^0, \tag{4}$$

where ΔE_0^0 is the energy change at 0 K calculated by Eq. (2) and $\Delta G_{T_{\mathrm{corr}}}^0$ represents the finite temperature correction for the standard free energy change [20]. The data listed in Table 1 are taken from our previous paper [20].

Fig. 5 plots the relative energies of the W edge and S edge of unpromoted WS_2 with different sulfur coverages as a function of p_{H_2S}/p_{H_2} ratios at 650 K. On the W edge, the structure with 50% sulfur coverage is the most stable over the entire range of p_{H_2S}/p_{H_2} ratios. On the S edge, the fully sulfided surface is the most stable when the p_{H_2S}/p_{H_2} ratio is higher than 0.15, and the 50% sulfur coverage surface is stable at lower p_{H_2S}/p_{H_2} ratios. For the 50% Ni(Co)-promoted W edge (Fig. 6), the surface with 25% sulfur coverage is the most stable, and for the 50% Ni(Co)-promoted S edge (Fig. 7), the surface with 50% sulfur coverage is the most stable over the range of p_{H_2S}/p_{H_2} ratios. For the 100% Ni-promoted W edge (Fig. 8a), the bare surface is the most stable provided the p_{H_2S}/p_{H_2} ratio is lower than 450;

Table 1
Values of $\Delta G_{T_{\mathrm{corr}}}^0$ at representative temperatures for catalyst sulfidation and hydrotreating reactions

Temperature (K)	$\Delta G_{T_{\mathrm{corr}}}^0$ (eV)
575	0.31
600	0.33
625	0.36
650	0.38
675	0.40



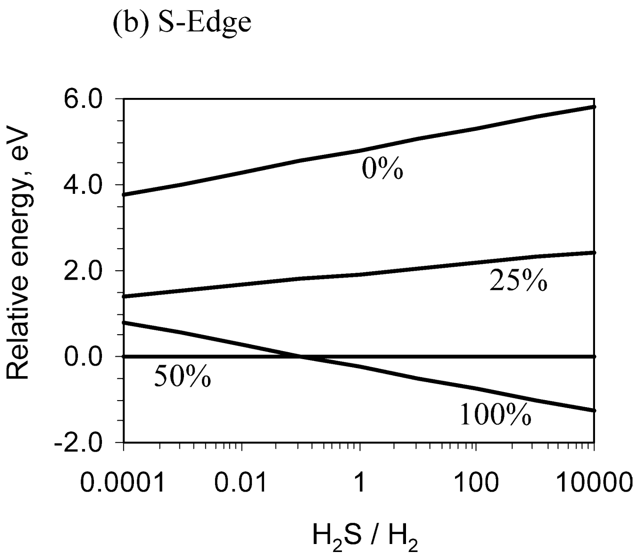
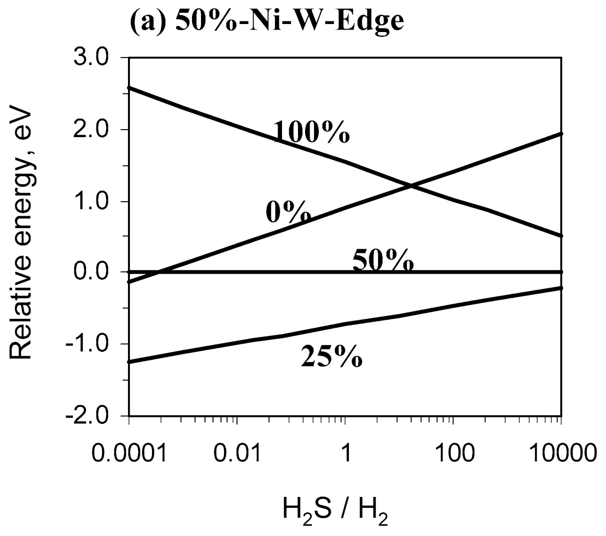


Fig. 5. Relative energies of WS_2 as function of p_{H_2S}/p_{H_2} ratios at 650 K, (a) W edge, (b) S edge. Each line is labeled by the corresponding sulfur coverage on the edge surface, with 50% sulfur coverage is taken as reference.



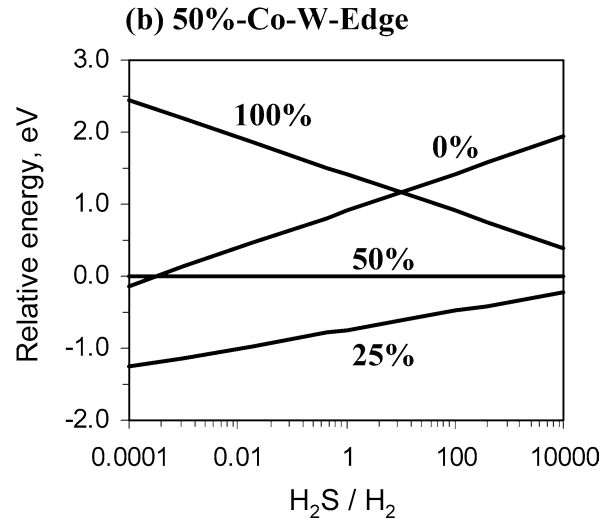


Fig. 6. Relative energies as function of p_{H_2S}/p_{H_2} ratios at 650 K, (a) 50%-Ni-W edge, (b) 50%-Co-W edge. Each line is labeled by the corresponding sulfur coverage on the edge surface, with 50% sulfur coverage is taken as reference.

at higher p_{H_2S}/p_{H_2} ratios, the 50% sulfur coverage surface is stable. For the 100% Co-promoted W edge (Fig. 8b), the bare surface is the most stable at low p_{H_2S}/p_{H_2} ratios (< 1.5), and at higher p_{H_2S}/p_{H_2} ratios the 50% sulfur coverage surface is stable. For the 100% Ni-promoted S edge (Fig. 9a), the stable surface can have 25% (when $p_{H_2S}/p_{H_2} < 0.004$), 50% (when $0.004 < p_{H_2S}/p_{H_2} < 15$), or 100% (when $p_{H_2S}/p_{H_2} > 15$) sulfur coverage depending on the p_{H_2S}/p_{H_2} ratio in the gas phase. For the 100% Co-promoted S edge (Fig. 9b), the structure with 50% sulfur coverage is the most stable over the entire range of p_{H_2S}/p_{H_2} ratios.

Table 2 shows the stable edge structures of various catalysts under reaction conditions, which are similar to the edge structures of corresponding molybdenum catalyst [12–16,20]. For the W edge of unpromoted WS_2, the surface is covered by sulfur atoms bridging tungsten atoms, which corresponds to the 50% sulfur coverage. The tungsten atoms on the 50% sulfur coverage W edge are sixfold coordinated to sulfur atoms, and thus there are no coordinately unsaturated sites on the unpromoted W edge surface. For the 50% Ni(Co)-substituted W edge, where every second tungsten atom is substituted by a nickel or cobalt atom, one sulfur atom bonds to a tungsten atom directly atop, and the promoter atoms are uncovered. The bare nickel or cobalt atoms and surface sulfur anions can act as unsaturated metal sites (Lewis acid sites) and basic sites (or nucleophile), respectively, in catalyzing various hydrotreating reactions [20]. For the 100% Ni(Co)-substituted W edge, the bare surface is the most stable under reaction conditions, which provides the

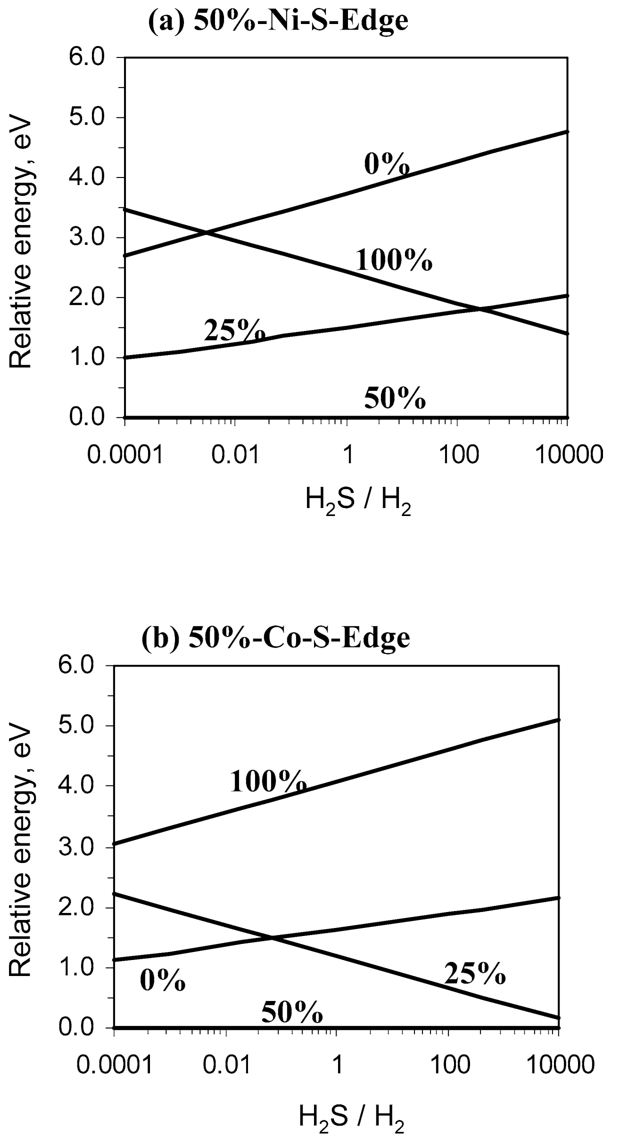


Fig. 7. Relative energies as function of p_{H_2S}/p_{H_2} ratios at 650 K, (a) 50%-Ni-S edge, (b) 50%-Co-S edge. Each line is labeled by the corresponding sulfur coverage on the edge surface, with 50% sulfur coverage is taken as reference.

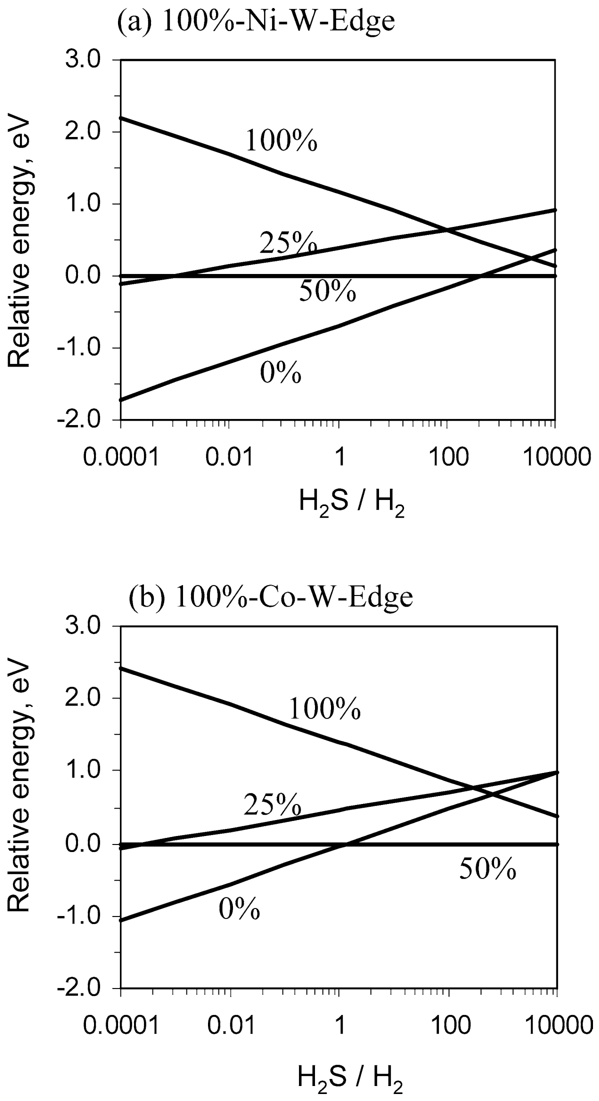


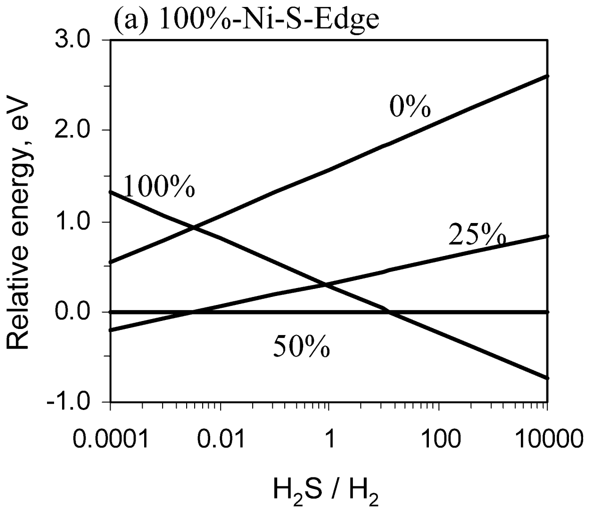
Fig. 8. Relative energies as function of p_{H_2S}/p_{H_2} ratios at 650 K, (a) 100%-Ni-W edge, (b) 100%-Co-W edge. Each line is labeled by the corresponding sulfur coverage on the edge surface, with 50% sulfur coverage is taken as reference.

required space for the adsorption of large aromatic molecules for hydrogenation. On the S edge, all catalysts have the same geometry with sulfur atoms at bridging positions, and each surface metal atom is fourfold coordinated to sulfur atoms. The strength of sulfur–metal bonding decreases in the order: WS_2 > 50% Co-S edge > 50% Ni-S edge > 100% Co-S edge > 100% Ni-S edge. The same trend was previously found for molybdenum catalysts [12,14,20].

3.3. Preferred location of the promoter atoms

When promoter atoms are incorporated into edges of WS_2, one of the edges is energetically preferred over the other due to the difference in chemical environment. Previous studies have shown that nickel prefers the Mo edge and cobalt prefers the S edge for molybdenum catalysts under reaction conditions [16,20]. It has also been pointed out that the stable structures should be considered when discussing the preferred locations for promoter atoms in promoted catalysts [16,17,20]. The same approach is followed in studying the edge preference of nickel and cobalt in tungsten catalysts as we previously used for molybdenum catalysts [20].

In Section 3.2, the most stable edge structures for various catalysts under reaction conditions were identified. For the 50% Ni-W edge, the 25% sulfur coverage is the most stable configuration for the entire range of p_{H_2S}/p_{H_2} ratios (Fig. 6a). For the unpromoted S edge of WS_2, 50% sulfur coverage is stable at low p_{H_2S}/p_{H_2} ratios, and 100% sulfur coverage is stable at high p_{H_2S}/p_{H_2} ratios (Fig. 5b). For the 50% Ni-S edge, the 50% sulfur coverage is the most stable at all p_{H_2S}/p_{H_2} ratios (Fig. 7a). For the unpromoted W edge,



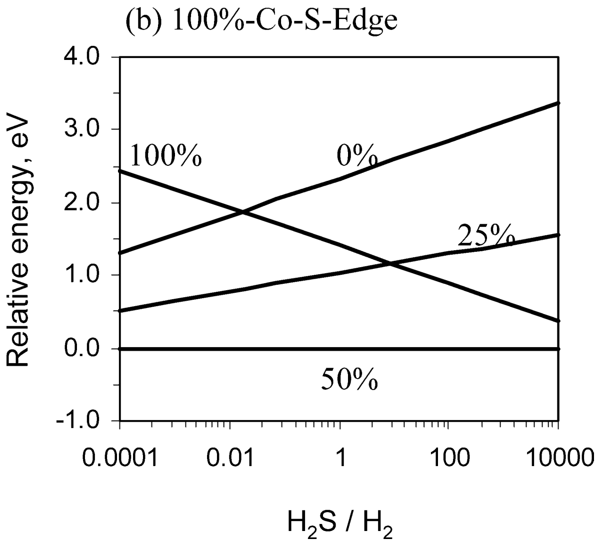
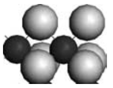
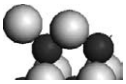
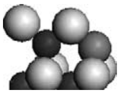
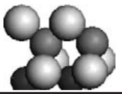


Fig. 9. Relative energies as function of p_{H_2S}/p_{H_2} ratios at 650 K, (a) 100%-Ni-S edge, (b) 100%-Co-S edge. Each line is labeled by the corresponding sulfur coverage on the edge surface, with 50% sulfur coverage is taken as reference.

Table 2
The stable edge-surface structures at 650 K, $p_{H_2S}/p_{H_2} = 0.01$ to 0.1 (black indicates tungsten atoms, light gray indicates sulfur atoms, and dark gray indicates promoter atoms)

	Metal-edge	S-edge
WS_2		
50%-Ni(Co)-promoted WS_2		
100%-Ni(Co)-promoted WS_2		

the 50% sulfur coverage is the most stable at most p_{H_2S}/p_{H_2} ratios (Fig. 5a). Therefore, three possible structures are compared for 50% Ni-substituted WS_2 in Fig. 10. These three structures have the same number of metal atoms, while the number of sulfur atoms differs depending on the stable surface configurations. In Fig. 10, Structure (a) is taken as the reference, and Structures (b) and (c) are related to Structure (a) by the following reactions:

$$\text{Structure (a)} + 2H_2 = \text{Structure (b)} + 2H_2S, \quad (5)$$

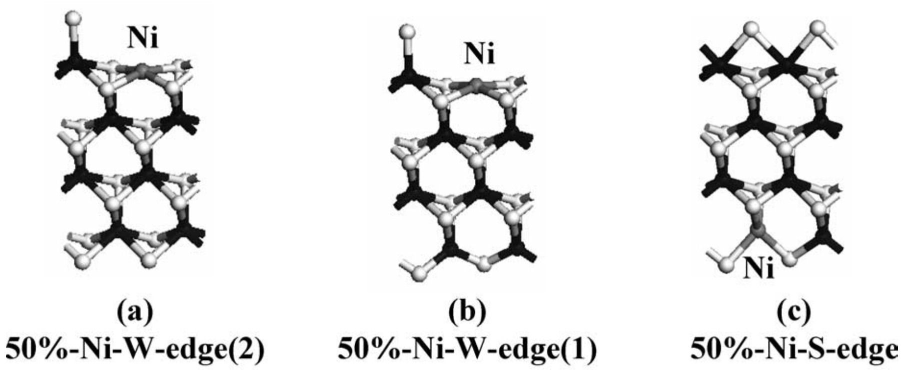
$$\text{Structure (a)} + H_2 = \text{Structure (c)} + H_2S. \quad (6)$$

The relative energies as a function of the p_{H_2S}/p_{H_2} ratio are calculated according to Eq. (3). Fig. 10 shows that the structure with nickel at the W edge is the most stable over a wide range of p_{H_2S}/p_{H_2} ratios. For 100% Ni substitution, the relative energies of six possible structures are compared in Fig. 11. The structure with nickel at the W edge still has a lower energy than that with nickel at the S edge, provided the p_{H_2S}/p_{H_2} ratio is lower than 220. At higher p_{H_2S}/p_{H_2} ratios, the nickel atoms can be stabilized at the S edge by forming a planar configuration with sulfur atoms as shown in Fig. 11 (Structure d). In general, it can be concluded the W edge is preferred for nickel substitution.

The edge preference for the Co substitution is investigated by following the same approach. For 50% Co substitution, three similar structures as those for 50% Ni-substituted WS_2 are compared in Fig. 12. The S-edge substitution is preferred when p_{H_2S}/p_{H_2} ratios are between 0.002 and 6, which encompasses the typical range for sulfidation conditions of hydrotreating reactors. At lower or higher p_{H_2S}/p_{H_2} ratios, W-edge substitution is preferred. For 100% Co substitution, four structures are stable at different p_{H_2S}/p_{H_2} ratios which are shown in Fig. 13. In Structures (a), (b) and (c), the tungsten atoms on the W edge have been substituted by cobalt atoms, and in Structure (d) the S-edge tungsten atoms are substituted by cobalt atoms. The structure with cobalt atoms at the S edge is the most stable at most p_{H_2S}/p_{H_2} ratios (Fig. 13). Therefore, it can be concluded the S edge is the preferred location for cobalt substitution.

3.4. *Stability of promoter atoms at WS_2 edges*

Based on experimental [29] and theoretical [12,14,16] studies, it is believed that promoter atoms incorporate into the MoS_2 structure by substituting molybdenum atoms at edge surfaces. There are several studies that indicate the existence of promoter-incorporated structures at WS_2 edges [9,30–32]. It is generally accepted the NiWS phase is present due to the observed synergistic effect of nickel for improving the activities of tungsten catalysts. However, the promotional effect of cobalt is still debated because of the stability of the CoWS phase relative to cobalt sulfide. A synergistic effect was not observed between cobalt and tungsten in CoW/Al_2O_3 because cobalt forms Co_9S_8 instead of the CoWS structure [9]. By applying chelating agents, Kishan



(a) 50%-Ni-W-edge(2) **(b)** 50%-Ni-W-edge(1) **(c)** 50%-Ni-S-edge

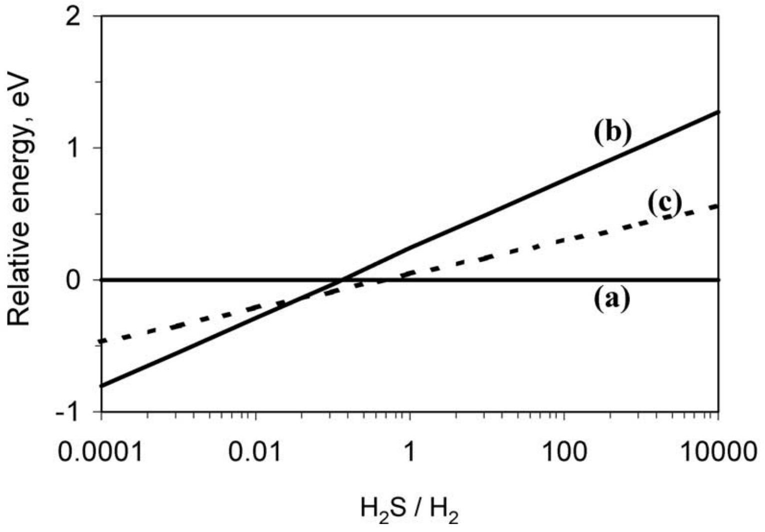


Fig. 10. Relative energies of the 50%-Ni-S edge (dash lines) and 50%-Ni-W edge (solid lines) as a function of p_{H_2S}/p_{H_2} ratios at 650 K, (1) and (2) represent number of sulfur atoms bonding to each tungsten atom on the unpromoted S edge. The sulfur coverage is 25% on the Ni-promoted W edge and 50% on the Ni-promoted S edge.

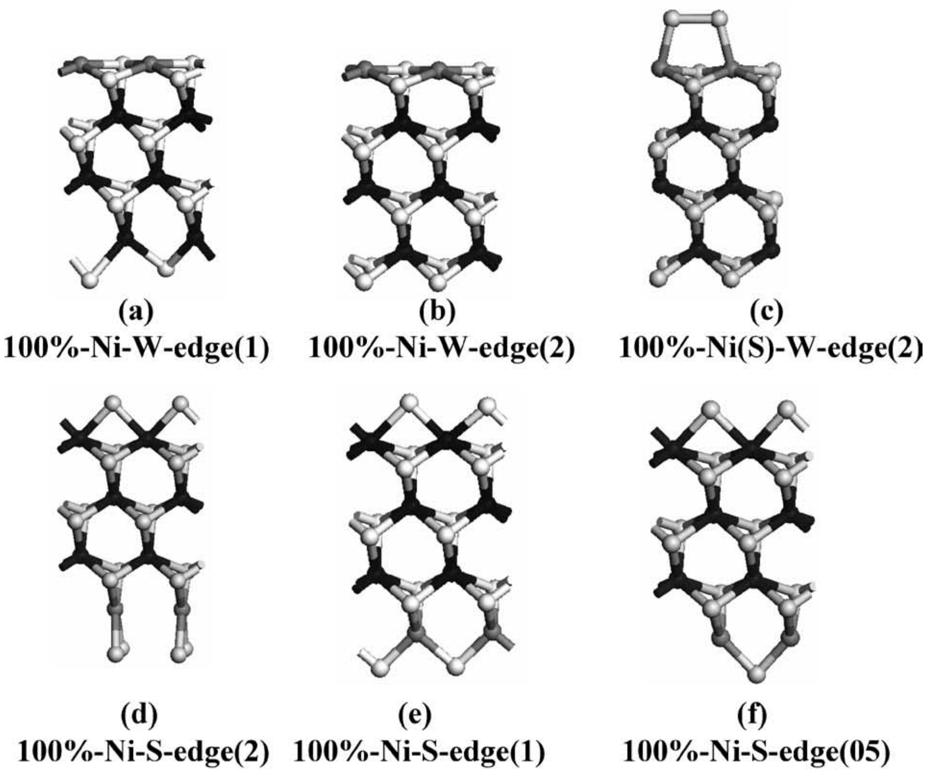
et al. observed a notable synergistic effect of cobalt on tungsten for the HDS of thiophene [32]. They also observed the CoWS phase, in addition to Co_9S_8, after high-temperature sulfidation. To this point, we have assumed that promoter atoms would substitute tungsten atoms at either the W edge or S edge for tungsten catalysts, as discussed in previous sections. In order to clarify if promoter atoms at edge surfaces are more stable than those for individual sulfides, the energetics of the following reaction was calculated:

$$\{\text{Promoter sulfide}\} + \{\text{WS}_2\text{-slab}\} + m\text{H}_2\text{S} = \{\text{Promoted-WS}_2\} + m\text{H}_2, \tag{7}$$

$$\Delta E^0_{0,\text{syn}} = E^0_{0,\text{Promoted WS}_2} - E^0_{0,\text{WS}_2\text{ slab}} - E^0_{0,\text{Promoter sulfide}} + m\left(E^0_{0,\text{H}_2} - E^0_{0,\text{H}_2\text{S}}\right). \tag{8}$$

Negative values for $\Delta E^0_{0,\text{syn}}$ indicate that promoted WS_2 is stable relative to unpromoted WS_2 and individual promoter sulfides, while positive values would suggest the individual promoter sulfides and WS_2 are more stable. The validity of this calculation depends on the stable sulfide structure that is used for each calculation. The difference in relative energies between structures with bare and 50% sulfur coverage W edge is 1.8 eV per edge tungsten atom. This means that by using different structures for WS_2, the reaction enthalpy of Eq. (7) may vary up to 1.8 eV per edge tungsten atom.

When Byskov et al. investigated whether cobalt atoms in the CoMoS structure are more stable relative to Co_9S_8, they used a fully sulfided MoS_2 slab and bulk MoS_2 structure to represent the unpromoted structure, a CoMoS structure with 75% sulfur coverage on the promoted S edge to represent the promoted structure, and CoS to represent the isolated cobalt sulfide [12]. However, our calculations indicate these structures are not stable under reaction conditions. The reaction enthalpy obtained in their study was 1.3 eV per cobalt atom, which is in the range of possible error incurred by using different representative structures. Consequently, the most stable structure must be identified for each term in



(a) 100%-Ni-W-edge(1) (b) 100%-Ni-W-edge(2) (c) 100%-Ni(S)-W-edge(2)

(d) 100%-Ni-S-edge(2) (e) 100%-Ni-S-edge(1) (f) 100%-Ni-S-edge(05)

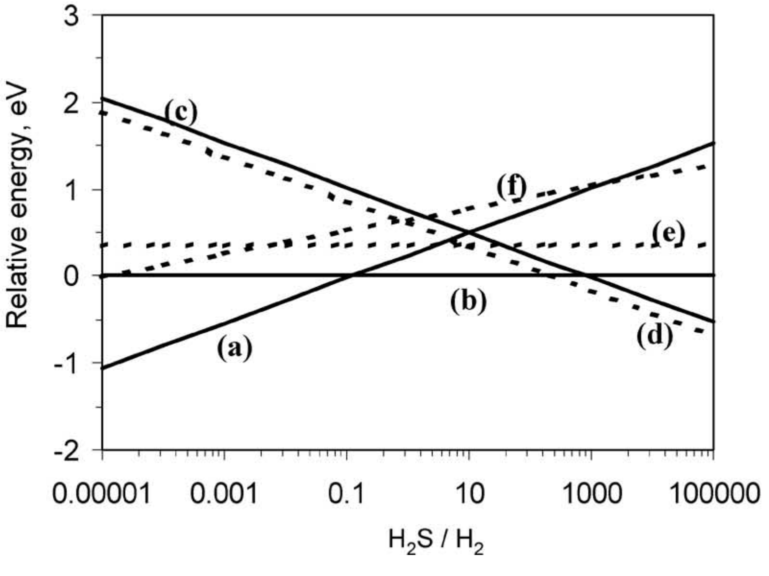
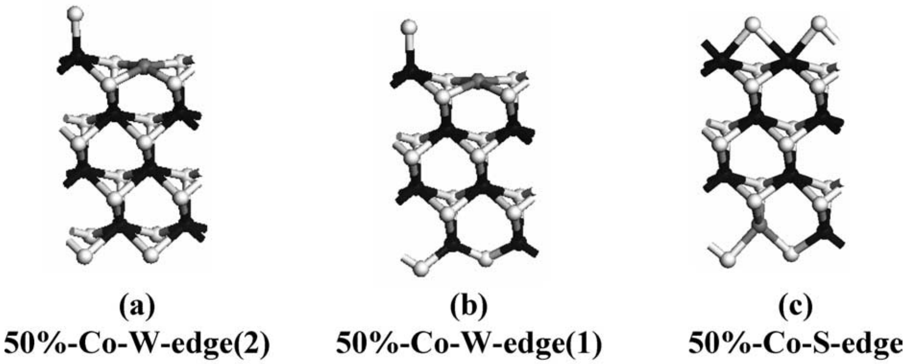


Fig. 11. Relative energies of the 100%-Ni-S edge (dash lines) and 100%-Ni-W edge (solid lines) as a function of p_{H_2S}/p_{H_2} ratios at 650 K, (1) and (2) represent number of sulfur atoms bonding to each tungsten atom on the unpromoted S-edge and Ni-promoted metal edge. The sulfur coverage is 50% on the unpromoted W edge.

Eq. (7) before one can calculate the energetics of promoter incorporation into the WS_2 structure. For separated promoter sulfides, Ni_3S_2 and Co_9S_8 are stable under sulfidation conditions [13,33]. The energies of other sulfides that are stable at low temperature, including NiS and CoS_2, are very close to those of Ni_3S_2 and Co_9S_8, respectively [18]. Therefore, Ni_3S_2 and Co_9S_8 are excellent representative structures for determining the energetics of promoter sulfides. The models for Ni_3S_2 and Co_8S_9 bulk structures are constructed according crystallographic data [28], and fully optimized using the method as described in Section 2.1.

For unpromoted WS_2, the 50% sulfur coverage on both the W edge and the S edge is the most stable at 650 K and p_{H_2S}/p_{H_2} ratios between 0.01 and 0.1 (Fig. 5). For Ni- and



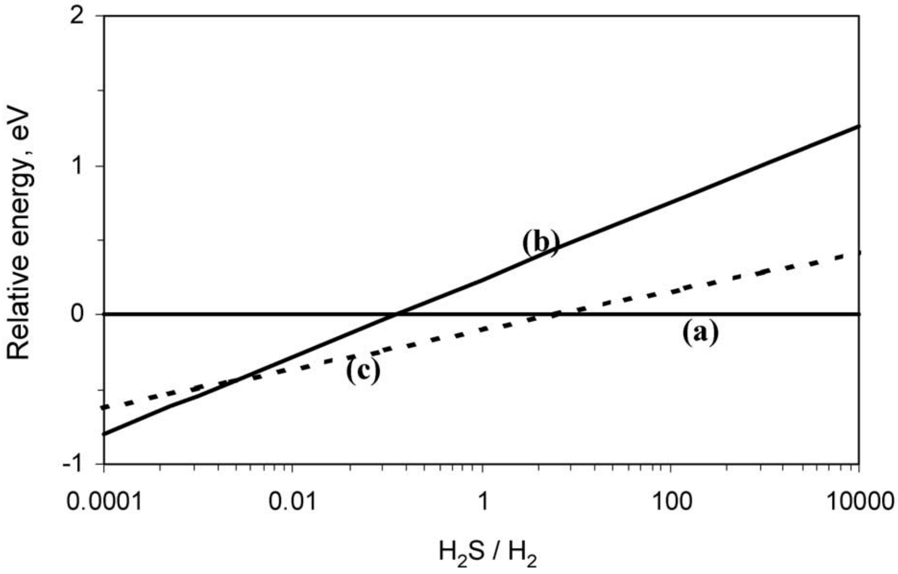
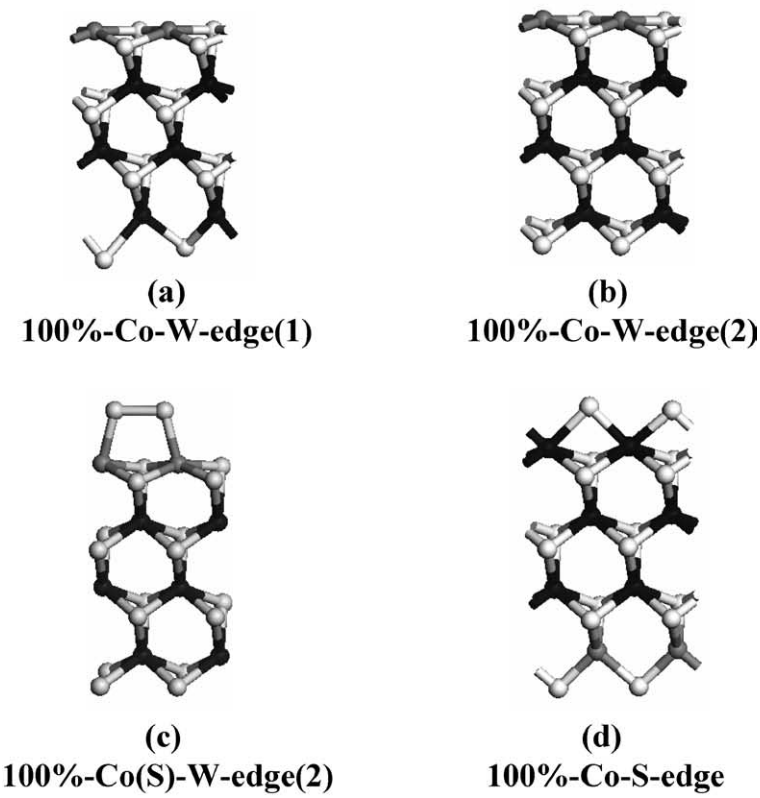


Fig. 12. Relative energies of the 50%-Co-S edge (dash lines) and 50%-Co-W edge (solid lines) as a function of p_{H_2S}/p_{H_2} ratios at 650 K, (1) and (2) represent number of sulfur atoms bonding to each tungsten atom on the unpromoted S edge. The sulfur coverage is 25% on the Co-promoted W edge and 50% on the Co-promoted S edge.

Co-substituted WS_2 edges, the sulfur coverage is zero on the 100%-substituted W edge, and 50% on the 100%-substituted S edge under reaction conditions (Fig. 9). The $\Delta E^0_{0,\mathrm{Syn}}$ for promoter incorporation into WS_2 edges is calculated according Eq. (8) using the stable structures under reaction conditions. Following this calculation, ΔG_{Syn} for Eq. (7) can be calculated according Eq. (3) at 650 K and $p_{H_2S}/p_{H_2} = 0.1$. The results for nickel substitution are listed in Table 3, and those for cobalt substitution in Table 4. These results indicate that nickel on the S edge is less stable than that on the W edge, and that the structure of nickel at the W edge is stable relative to separated Ni_3S_2. In contrast, cobalt incorporation at the S edge is more stable than the W edge or the Co_9S_8 structure.

These results confirm our previous conclusions about the edge preferences of nickel and cobalt. Thermodynamically both nickel and cobalt are stable at WS_2 edges by substituting the edge tungsten atoms. For Ni-promoted tungsten catalysts, nickel can be sulfided at temperatures below 100 °C, while WS_2 cannot be formed from the oxidic state on SiO_2 at temperatures lower than 200 °C [31]. The nickel sulfide formed at low temperatures can redisperse over the WS_2 edge and incorporate with WS_2 to form the NiWS structure at high temperatures. While it is possible for nickel sulfide to combine with WS_2 at high temperatures, cobalt sulfide formed at low temperatures is unlikely to redisperse and combine with the WS_2 to form the CoWS phase [9,31]. One of the probable reasons that the energetically more stable CoWS phase was not formed in CoW/Al_2O_3 [9] and co-impregnated CoW/SiO_2 [32] is that the sulfur–cobalt bond strength in Co_9S_8 is stronger than the sulfur–nickel bond strength in Ni_3S_2 [34]. Higher sulfur–cobalt bond strength in Co_9S_8 makes it very difficult to redisperse to the WS_2 edges once well-structured Co_9S_8 crystallites are formed. There-



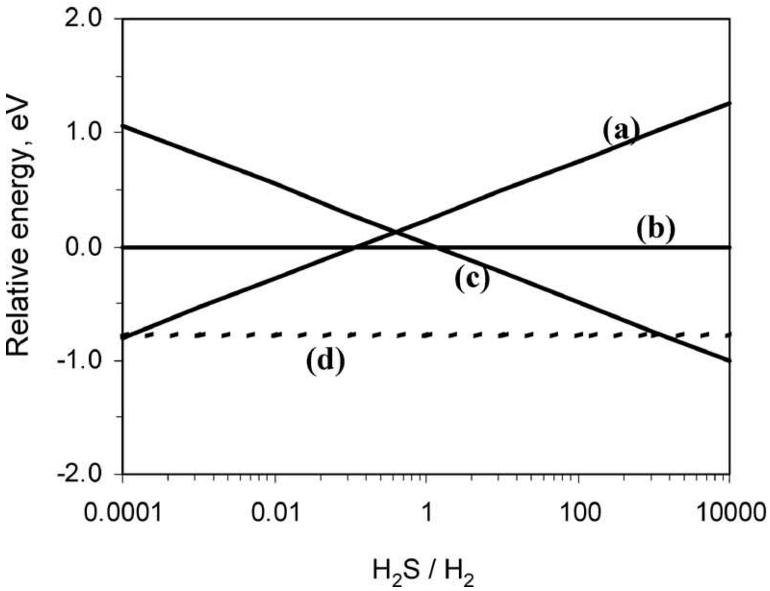


Fig. 13. Relative energies of the 100%-Co-S edge (dash lines) and 100%-Co-W edge (solid lines) as a function of p_{H_2S}/p_{H_2} ratios at 650 K, (1) and (2) represent number of sulfur atoms bonding to each tungsten atom on the unsubstituted edge. The sulfur coverage is 0% on the Co-promoted W edge and 50% on the Co-promoted S edge.

fore, it is the kinetic limitation that prevents the formation of the CoWS phase from separated Co_9S_8 and WS_2.

Using a chelating agent to protect cobalt from sulfidation at low temperatures before formation of WS_2 makes it possible to form the stable CoWS phase instead of Co_9S_8 [32]. The sulfidation of alumina-supported tungsten catalysts are more difficult, which requires temperatures higher than 300 °C for the formation of WS_2 [35]. Using a support, with which tungsten oxide has a weaker interaction will help the sulfidation of tungsten [9]. Another possibility of forming CoWS instead of separated Co_9S_8 and WS_2 is to make WS_2 available at low temperatures during the sulfidation

Table 3
The free energy changes for incorporating one nickel atom into the W edge or S edge of WS_2 at 650 K, $p_{H_2S}/p_{H_2} = 0.1$ (black indicates tungsten atoms, light gray indicates sulfur atoms, and dark gray indicates promoter atoms)

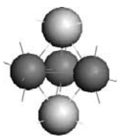
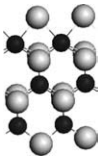
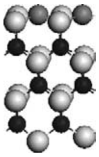
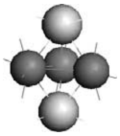
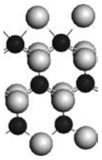
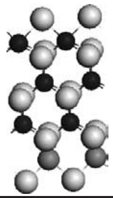
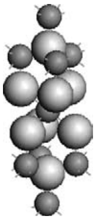
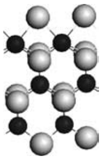
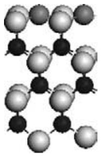
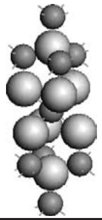
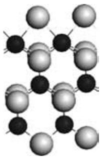
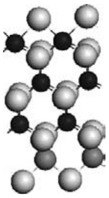
	Ni_3S_2	W_6S_{12}	$Ni_2W_6S_{14}$	ΔG_{syn} (eV/Ni)
W-edge				−0.32
S-edge				−0.14

Table 4
The free energy changes for incorporating one cobalt atom into the W edge or S edge of WS_2 at 650 K, $p_{H_2S}/p_{H_2} = 0.1$ (black indicates tungsten atoms, light gray indicates sulfur atoms, and dark gray indicates promoter atoms)

	Co_9S_8	W_6S_{12}	$Co_2W_6S_{14}$	ΔG_{syn} (eV/Co)
W-edge				−0.15
S-edge				−0.54

of cobalt. For example, when using ammonium tetrathiotungstate as the source of tungsten without calcination, the tungsten is already at a sulfidic state before cobalt is impregnated, as has been done previously for high activity NiW catalysts [35].

4. Conclusions

This paper presents the first systemic study of energetics and surface geometries of unpromoted and promoted tungsten-based hydrotreating catalysts, which will serve as the basis for further theoretical work on tungsten catalysts. Under reaction conditions, 50% sulfur coverages on the unpromoted W edge and S edge are the most energetically stable configurations. The sulfur atoms are located at the bridging positions between the surface tungsten atoms on both the S edge and the W edge. On the stable edge surfaces, the tungsten atoms are sixfold coordinated on the W edge, and are only fourfold coordinated on the S edge. When nickel or cobalt is incorporated into the WS_2 structure, nickel prefers the W edge and cobalt the S edge. When compared to the energetics of the individual promoter sulfides (Co_9S_8 and Ni_3S_2), the promoted edge structures are more stable. The general trends for tungsten catalysts are similar in surface energetics and geometry, but no detailed comparison between molybdenum and tungsten catalysts is made to account for their differences in catalysis in the present paper. This will be the subject of a subsequent paper.

Acknowledgments

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