

Surface Structure and Stability of MoS_x Model Clusters

Xiao-Dong Wen,[†] Tao Zeng,[†] Yong-Wang Li,[†] Jianguo Wang,[†] and Haijun Jiao^{*,†,‡}

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, P. R. China, and Leibniz-Institut für Organische Katalyse an der Universität Rostock e.V., Albert-Einstein-Strasse 29a, 18059 Rostock, Germany

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Density functional theory (DFT) computations have been carried out to study the structure and stability of MoS_x clusters with the change of sulfur coverage at both Mo and S edges. DFT shows that adding sulfur to the Mo edge is always exothermic. However, deleting corner sulfur from the S edge is exothermic for 67 and 50% sulfur coverages, while deleting edge sulfur from the S edge is endothermic for 33 and 0% sulfur coverages. On the basis of the computed free energies along a wide range of H₂S/H₂ ratios, it is found that there are two stable structures with 33 and 50% sulfur coverages on the Mo edge by having 100% sulfur coverage on the S edge and one stable structure with 67% sulfur coverage on the S edge by having 0% sulfur coverage on the Mo edge. Under fully sulfiding atmosphere or at a very high H₂S/H₂ ratio, triangle MoS_x structures with 100% sulfur coverage on the Mo edge are computed to be more stable than those with 100% sulfur coverage on the S edge, in agreement with the observation of scanning tunneling microscopy. In addition, the effects of cluster sizes on the surface structures are discussed.

1. Introduction

Molybdenum sulfides (MoS_x) are widely used as catalysts in oil refinery for hydrogenation (HYD), hydrodesulfurization (HDS), and hydrodenitrogenation (HDN) reactions for producing cleaner fuels.^{1–5} On the basis of extensive experimental and theoretical studies, it is generally accepted that the catalytic activity is associated with the coordinatively unsaturated Mo sites (CUS) on the edge of MoS_x clusters. Bulky MoS₂ shows a single-layered structure consisting of close-packed triangular double layers of S with each Mo atom coordinated by six S atoms in a trigonal-prismatic unit,⁶ and there is only a weak van der Waals interaction between the consecutive S–Mo–S layers. This enables MoS_x to have the same physical properties such as graphite as a solid lubricant.

Recently, Lauritsen et al.⁷ have provided new insights into the morphology and atomic-scale structure of MoS_x nanoclusters in HDS catalysts by scanning tunneling microscopy (STM) and found that the morphology of MoS_x nanoclusters as catalysts may in fact be very complex. Clusters adopt their shapes according to synthetic conditions, for example, triangles under heavy sulfiding conditions or truncated hexagons under more sulforeductive conditions resembling HDS conditions.

To understand catalytic activities, different models have been used to describe the edge structure of MoS_x catalysts. For example, Byskov et al.^{8–10} used a chain model containing a single S–Mo–S slab constructed from two MoS₂ prisms, while Raybaud et al.,^{11–15} Cristol et al.,^{16–20} and Sun et al.²¹ used larger models containing two S–Mo–S sheets exposing Mo and S edges, alternatively. However, both the chain model and the two-sheet model are repeated periodically along directions perpendicular to the edge surfaces, and they represent real

catalyst structures only partially. This is because real catalysts have boundaries in all directions, while periodic models show only edges. Therefore, cluster models with corners and edges on the catalyst surface represent the catalyst structures more realistically and should describe the catalytic activity more precisely. Due to lack of computer resources in the past, it has been not possible to model the catalytic activity for much larger clusters. With increased progress in computer technology and quantum chemistry in the past decade, many studies in this direction have been done, for example, Mo₂S_x,^{22,23} a-Mo₃S₆,²⁴ b-Mo₃S₆,^{25,26} Mo₃S₉,²⁷ a-Mo₃S₁₄,²⁵ b-Mo₃S₁₄,²⁸ Mo₄S₁₂,²⁸ Mo₅S₁₀,²⁵ Mo₅S₁₂,²⁹ Mo₇S₁₄,²⁸ Mo₉S₁₈,³⁰ Mo₁₀S₁₈,^{31–33} Mo₁₂-S₂₄,^{30,34,35} Mo₁₆S₃₂,^{36,37} Mo₁₈S₃₆,³⁰ Mo₁₉S₃₈,³⁸ and Mo₂₇S₅₄,^{39,40} by using semiempirical methods^{22–25,28–31,38,39} and density functional theory methods.^{26,27,32–37,40} They have been proposed to mimic a MoS_x surface or particles.

An important step in HYD, HDS, and HDN is the adsorption and activation of hydrogen on the catalyst surface, and the role of the adsorbed and activated hydrogen is the removal of surface sulfur to form CUS on both S and Mo edges first for the adsorption of sulfur-containing organic compounds and then for their hydrogenation as well as hydrogenolysis afterward.^{1,2} Lauritsen et al.^{7,41} found that the Mo edge can be sulfided to form a S₂ dimer configuration under fully sulfiding atmosphere (573 K) and sulfur vacancies can be formed at atomic hydrogen (600 K) on the S edge.

Through the use of periodic slab models, Byskov et al.^{8,9} and Raybaud et al.¹⁴ investigated the equilibrium sulfur coverage on MoS_x edge surfaces and found that sulfur atoms bind more strongly to molybdenum atoms at the S edge than at the Mo edge and indicate that it is energetically unfavorable to obtain a sulfur coverage lower than 50% on the MoS_x edge surfaces. Although it is possible to determine the energy and structure of the Mo edge and S edge with chemical potentials of sulfur, these models are not possible for the energy calculation of the Mo edge or S edge independently and this is because the

* To whom correspondence should be addressed. E-mail: Haijun.Jiao@ifok-rostock.de.

[†] Chinese Academy of Sciences.

[‡] Leibniz-Institut für Organische Katalyse an der Universität Rostock e.V.

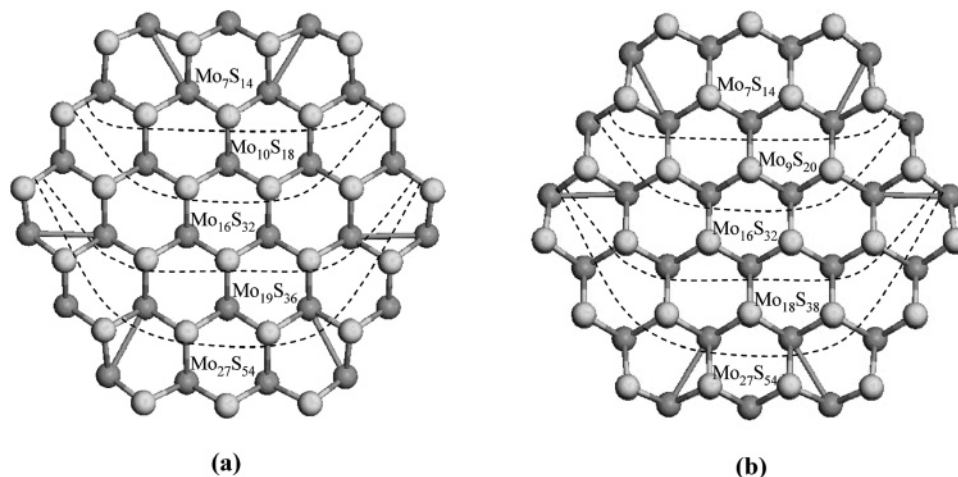


Figure 1. MoS_x cluster models: (a) clusters with 0% sulfur coverage on the Mo edge (Mo₇S₁₄, Mo₁₀S₁₈, Mo₁₆S₃₂, Mo₁₉S₃₆, and Mo₂₇S₅₄); (b) clusters with 100% sulfur coverage on the S edge (Mo₇S₁₄, Mo₉S₂₀, Mo₁₆S₃₂, Mo₁₈S₃₈, and Mo₂₇S₅₄).

calculation for the periodic slab models always yields the average surface energy of both types of edges. To overcome this difficulty, Schweiger et al.⁴² calculated surface energies of the individual edges of MoS₂ single-layer sheets using large cluster models and demonstrated that the Mo edge is energetically the most stable surface under realistic HDS conditions. Although these calculations can simulate a Mo edge or S edge independently, it is difficult to show the interaction between Mo and S edges in cluster models. In addition, these results exhibit only one type of edge in triangular-shaped clusters with 0%, 50%, and 100% sulfur coverage, respectively.

Since different sulfur coverages on the catalyst surface show different types of CUSs, it is interesting to have a look into the role of the adsorbed hydrogen on the catalyst surface. It is found that surface sulfur can be removed by atomic hydrogen,⁴³ and the consequence is that the higher the atomic hydrogen concentration, the higher the concentration of CUS and therefore the higher the HDS activity. Despite extensive experimental studies, the detailed mechanism of formation and exact structures of the active CUS still remain unclear and they continue to be the subject of investigations in many respects.^{3,4,44}

Through the use of a periodic model, Bollinger et al.⁴⁵ studied the electronic structures of MoS₂ nanoparticles and the hydrogen adsorption on both Mo and S edges. It is found that hydrogen adsorption on the S edge with the formation of two $-SH$ groups represents the most stable conformation and that on the Mo edge is also possible with a half S coverage on it. On the basis of calculated free energy including H₂ and H₂S, Bollinger et al. found that hydrogen is expected to be adsorbed at both the Mo and S edges in the form of $-SH$ groups under HDS condition and concluded that the availability of activated hydrogen is an important prerequisite for the HDS process. However, Cristol et al.⁴⁶ found that the industrial condition of reactors (total pressure below 100 bar, with a H₂S/H₂ ratio lower than 0.01) corresponds to domains without stable adsorbed hydrogen atoms and also without stable vacancies for the adsorption of sulfur-containing organic molecules. Recently, Sun et al.⁴⁷ report that the population of the structure with sulfur vacancies increases with a decreasing H₂S/H₂ ratio by using a periodic model.

A significant advantage of using a periodic model to study the MoS₂ surface is the low computation cost for large MoS_x clusters. However, we need to keep in mind that the highly dispersed supported MoS_x catalysts have predominant sizes within 10–30 Å.^{38,48,49} This indicates that there should be two, three, or four Mo atoms (or S pairs) on a corresponding edge

plane, and the electronic properties of each Mo atom (or S pairs) at different positions of the edge planes should be different.³¹ Therefore, the use of MoS₂ clusters with sizes close to real MoS₂ particles instead of the periodic model should be more realistic.

In this paper, Mo₇S₁₄, Mo₉S₂₀, Mo₁₀S₁₈, Mo₁₆S₃₂, Mo₁₈S₃₈, Mo₁₉S₃₆, and Mo₂₇S₅₄ clusters are used to calculate S coverage on the Mo edge and S edge, independently, with thermodynamic arguments. The present approach using cluster models discusses the effect of temperature and the H₂S/H₂ ratio on the stability of the edge structures. In addition, the interaction between Mo and S edges under the variation of sulfur coverage is analyzed with the change of Mo₂₇S_x clusters. The stability of triangular MoS_x clusters has been discussed.

2. Model and Methods

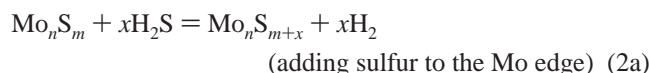
All calculations were performed with the program package DMol³ in the Materials Studio 2.2 of Accelrys Inc. The physical wave functions are expanded in terms of accurate numerical basis sets.⁵⁰ The doubled numerical basis set with p-polarization function for hydrogen and d-polarization functions for other elements is used, while effective core potential is used for molybdenum. The generalized gradient corrected functional by Perdew and Wang (PW91)⁵¹ is used, and the medium-quality mesh size is used for numerical integration. The tolerances of energy, gradient, and displacement convergence are 2×10^{-5} au, 4×10^{-3} au/Å, and 5×10^{-3} Å, respectively. As given in the Supporting Information, the increase of the force threshold changes the bond parameters only marginally (within 0.001 Å). The real space cutoff of atomic orbitals is set at 5.5 Å, and a Fermi smearing of 0.0005 is used for orbital occupancy.

To model the nanometer-sized crystallites observed experimentally, clusters in Figure 1 are used, and the initial coordinate for Mo₂₇S₅₄ is taken from the handbook of crystal structures. For the nomenclature, we used the convention in Chart 1, that is, 100% sulfur coverage corresponding to two S atoms per Mo atom on the Mo edge, then adsorption of two, three, four, and six S atoms on the Mo edge of clusters, which gives 33, 50, 67, and 100% sulfur coverage, respectively. For the S edge, 100% sulfur coverage corresponds to six bridge S atoms. Consequently, two, three, and four S atoms on the S edge show 33, 50, and 67% sulfur coverage, respectively. Chart 1 also shows the most stable edge structure of different sulfur coverage on the Mo edge and S edge. Here, we used five MoS_x models with two corner (Mo_c) and one edge (Mo_e) molybdenum atoms with 0% sulfur coverage by having 100% sulfur coverage on

the S edge (Figure 1a, Mo₇S₁₄, Mo₁₀S₁₈, Mo₁₆S₃₂, Mo₁₉S₃₆, and Mo₂₇S₅₄) and five MoS_x models with four corner (S_c) and two edge (S_e) sulfur atoms with 100% sulfur coverage by having 0% sulfur coverage on the Mo edge (Figure 1b, Mo₇S₁₄, Mo₁₀S₁₈, Mo₁₆S₃₂, Mo₁₉S₃₆, and Mo₂₇S₅₄).

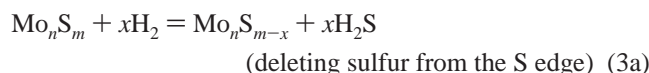
Relative energies of the surfaces with different sulfur coverage are calculated according to similar methods as described in the literature.^{9,14,15,17,18} The free energy change for adding n sulfur atoms on the reference surface at temperature (T) and the H₂S/H₂ ratio can be calculated with eq 1, where ΔE_0 is the standard energy change at 0 K and $\Delta G_0(T)$ is the corrected free energy changes at T and varies for 0.31 eV at 575 K to 0.40 eV at 675 K. To determine the energetically preferred Mo edge or S edge with different sulfur coverage, eqs 2 and 3 are used. In eq 2a (adding sulfur to Mo edge), Mo _{n} S _{m} and Mo _{n} S _{$m+x$} represent MoS₂ models with 0% sulfur coverage and other sulfur coverage on the Mo edge, respectively, while in eq 3a (deleting sulfur from the S edge), Mo _{n} S _{m} and Mo _{n} S _{$m-x$} represent MoS₂ models with 100% sulfur coverage and other sulfur coverage on the S edge, respectively

$$\Delta G = \Delta E_0 + x\Delta G_0(T) - xRT \ln(\text{H}_2\text{S}/\text{H}_2) \quad (1)$$



$$\Delta E_0(\text{Mo}) = [E(\text{Mo}_n\text{S}_{m+x}) + E(x\text{H}_2)] - [E(\text{Mo}_n\text{S}_m) + E(x\text{H}_2\text{S})] \quad (2b)$$

$$\Delta G_0(\text{Mo}) = \Delta E_0(\text{Mo}) + x\Delta G_0(T) - xRT \ln(\text{H}_2\text{S}/\text{H}_2) \quad (2c)$$



$$\Delta E_0(\text{S}) = [E(\text{Mo}_n\text{S}_{m-x}) + E(x\text{H}_2\text{S})] - [E(\text{Mo}_n\text{S}_m) + E(x\text{H}_2)] \quad (3b)$$

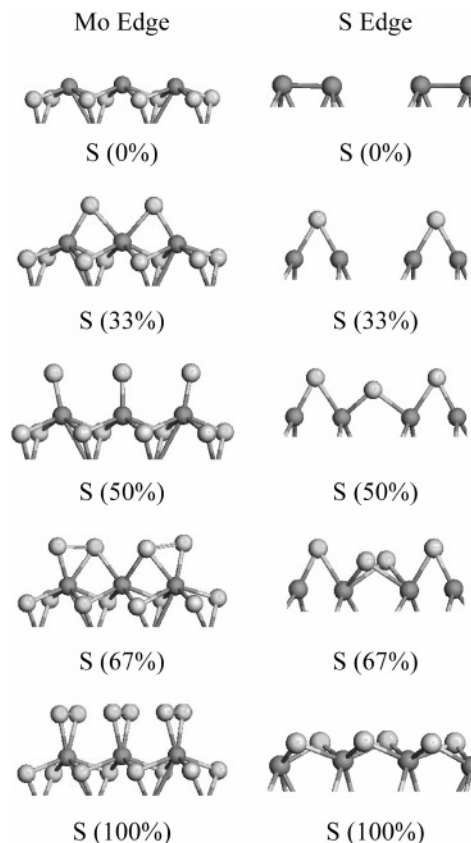
$$\Delta G_0(\text{S}) = \Delta E_0(\text{S}) - x\Delta G_0(T) + xRT \ln(\text{H}_2\text{S}/\text{H}_2) \quad (3c)$$

3. Results and Discussion

3.1. Structures and Energies of MoS_x Edges. (a) Sulfur Coverage on the Mo Edge. The relative energies (ΔE_0 , eq 2b) of the MoS_x model as a function of sulfur coverage on the Mo edge are shown in Figure 2. For the Mo edge of all clusters, the 0% sulfur coverage surface is taken as reference. As shown in Chart 1, the two bridge S atoms have 33% sulfur coverage, three terminal S atoms have 50% sulfur coverage, two S₂ units in bridge conformation have 67% sulfur coverage, and the Mo edge fully covered with S₂ units has 100% sulfur coverage. The optimized structures and total electronic energies are given in the Supporting Information.

When sulfur is added to the bare Mo edge (0% sulfur coverage), our results show that the process is exothermic up to sulfur coverage of 100% for all cluster sizes and indicate that the sulfiding Mo edge is favored thermodynamically, in agreement with the results from periodic slab models.^{8,9,14,17} More importantly, Figure 2 also shows the effects of cluster size and coverage. Generally, Mo₇S_x and Mo₁₀S_x clusters have rather smaller relative energies, indicating their sizes are too small, while Mo₁₆S_x, Mo₁₉S_x and Mo₂₇S_x clusters show relatively constant behaviors. At 33% and 67% sulfur coverages, Mo₁₆S_x, Mo₁₉S_x, and Mo₂₇S_x clusters have nearly the same relative energies, their differences to 100% sulfur coverage are also small, and the largest differences are found at 50% sulfur

CHART 1. Most Stable Surface Structures of the Mo and S Edges with Different Sulfur Coverages



coverage. Both Mo₁₆S_x and Mo₁₉S_x clusters can model MoS_x reasonably by taking the Mo₂₇S_x cluster as a reference.

In addition, the equilibrium of sulfur coverage can be changed by the H₂S/H₂ ratio. To understand this, we have studied the relative free energies (ΔG_0 , eq 2c) of different sulfur coverages (33, 50, 67, and 100%) as a function of the H₂S/H₂ ratio in the range of 0.0001–10 000 at 675 K, and this reveals the cluster stability at different H₂S/H₂ ratios. As shown in Figure 3 and regardless the size of clusters, the most stable clusters at a very low H₂S/H₂ ratio range have 33% sulfur coverage, while clusters at a high H₂S/H₂ ratio with 100% sulfur coverage represent the most stable structures. This indicates that at high H₂ or H₂S partial pressure, only one sulfur coverage is possible and other

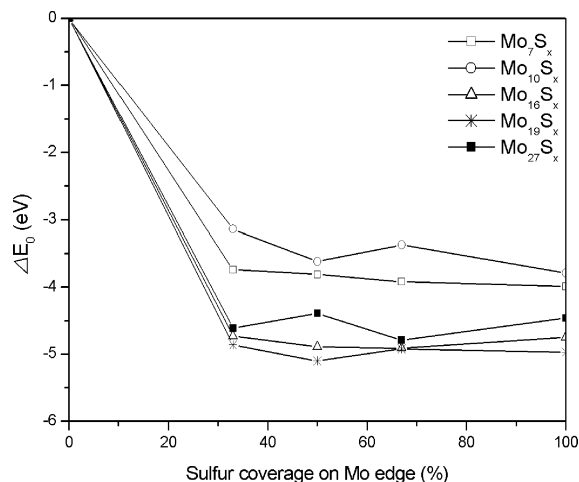


Figure 2. Relative energies (ΔE_0) of MoS_x clusters with different sulfur coverage on the Mo edge (0, 33, 50, 67, and 100%). The Mo edge with 0% is taken as reference (dotted line) for all clusters.

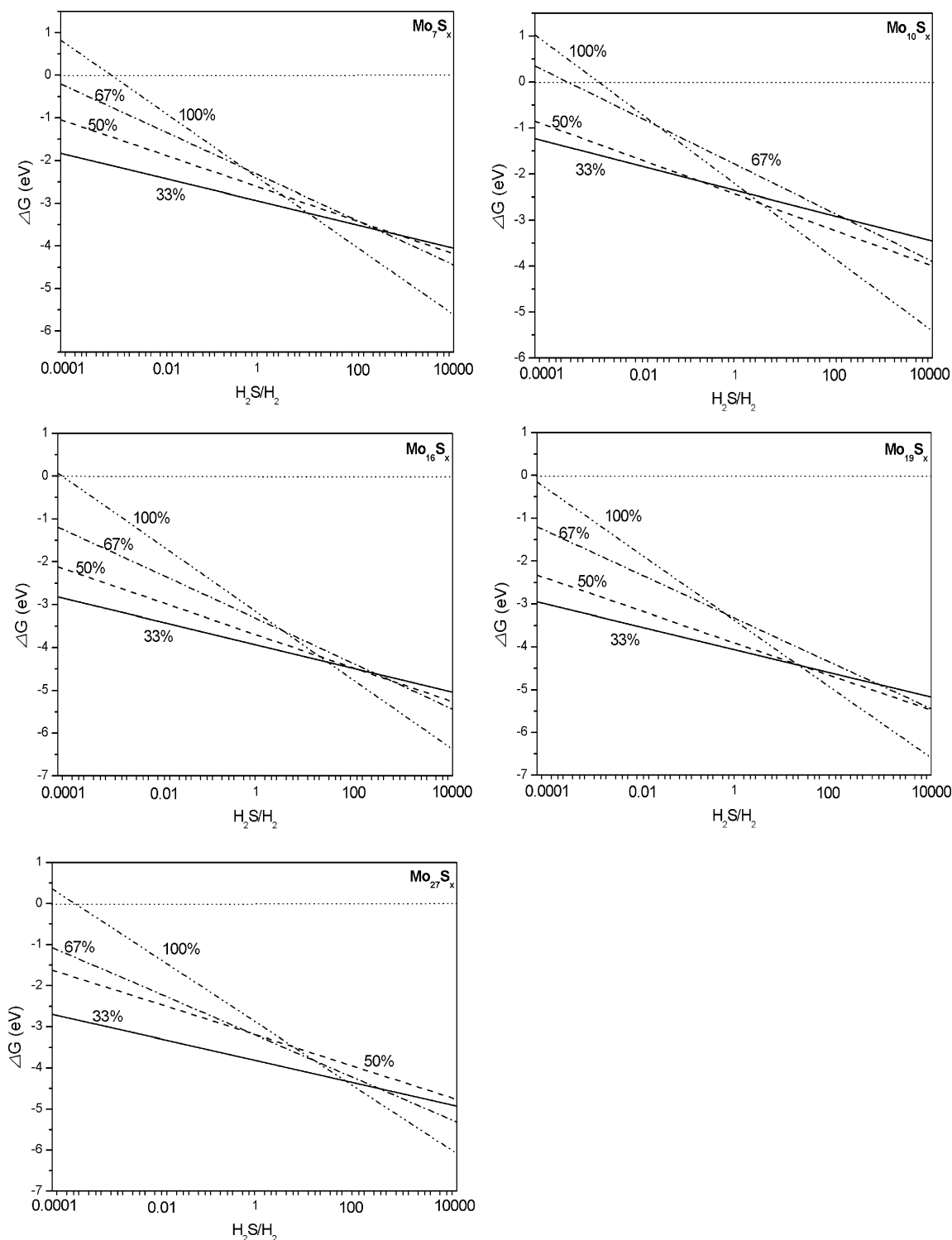


Figure 3. Relative free energies (ΔG_0) of MoS_x clusters with different sulfur coverages on the Mo edge as a function of the $\text{H}_2\text{S}/\text{H}_2$ ratio at 675 K. The Mo edge with 0% is taken as reference (dotted line) for all clusters.

coverages are less likely. The largest $\text{H}_2\text{S}/\text{H}_2$ ratio effect is found for 100% sulfur coverage, while that of 33% sulfur coverage is the smallest, as indicated by the slopes of these two lines in Figure 3.

Apart from these two extreme cases, there are cases for the $\text{H}_2\text{S}/\text{H}_2$ ratio ranges having equilibrium between various coverages and the equilibrium positions depend on the cluster sizes. For example, the cross point for the equilibrium between 33 and 100% sulfur coverage for Mo_7S_x cluster is at $\text{H}_2\text{S}/\text{H}_2 = 60$, while that for 33, 50, and 100% sulfur coverage for Mo_{10}S_x is around $\text{H}_2\text{S}/\text{H}_2 = 0.5\text{--}40$. For Mo_{16}S_x , Mo_{19}S_x , and Mo_{27}S_x ,

the equilibrium positions for the coexistence of various coverages are at a $\text{H}_2\text{S}/\text{H}_2$ ratio of 70–100. This similarity indicates that the simplification of Mo_{27}S_x into Mo_{16}S_x and Mo_{19}S_x is reasonable to model the Mo edge.

(b) Sulfur Coverage on S Edge. The relative energies (ΔE_0 , eq 3b) of MoS_x cluster as a function of sulfur coverage on the S edge are shown in Figure 4. The optimized structures and total electronic energies are given in the Supporting Information. The most stable surface structures are shown in Chart 1. For the S edge of all clusters, the 100% sulfur coverage surface is taken as reference. The two bridge corner sulfurs are formed in

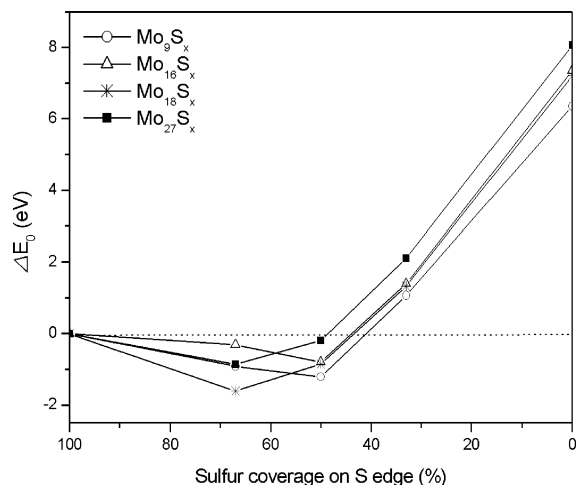


Figure 4. Relative energies (ΔE_0) of MoS_x clusters with different sulfur coverages on the S edge (0, 33, 50, 67, and 100%). The S edge with 100% sulfur coverage is taken as reference (dotted line) for all clusters.

TABLE 1: Calculated Relative Electronic Energies (ΔE_{rel} , eV) for Structures with 67% Sulfur Coverage on the S Edge under Removal of Corner Sulfur (S_c) and Edge Sulfur (S_e)

cluster	S_c and S_c	S_c and S_e	S_e and S_e
Mo7	0.00	1.36	
Mo9	0.00	0.52	4.07
Mo16	0.00	0.12	3.43
Mo18	0.00	1.35	4.61
Mo27	0.00	1.07	4.04

33% sulfur coverage. For 50% sulfur coverage, the S edge is covered with bridge sulfur atoms. For 67% sulfur coverage, removing two corner sulfur atoms forms the most stable configuration. For comparison, we have also computed the relative energies of structures from removing one corner and one edge sulfur, as well as two edge sulfur atoms for 67% sulfur coverage. As shown in Table 1, the structures of removing one corner and one edge or two edge sulfur atoms are higher in energy than those of removing two corner sulfur atoms. These indicate that the formation of corner vacancies is thermodynamically more favorable than that of the edge vacancies. This suggests that corners should play key roles in the HDS process. This agrees well with these results by using cluster models.⁴² Since structures with 0 and 33% sulfur coverage cannot be formed for Mo₇S_x, we will not pay further attention to the sulfur coverage for this cluster model.

The process of sulfur removal is discussed on the fully sulfided S edge (100% sulfur coverage). As shown in Figure 4, it is energetically favorable for all clusters to have 67 and 50% sulfur coverage on the S edge, while the formation of 33 and 0% sulfur coverages is endothermic. For Mo₁₈S_x and Mo₂₇S_x, the relative energies of 67% sulfur coverage are higher than those of 50% sulfur coverage, and the formation of 67% sulfur coverage is therefore more favorable than that of 50% sulfur coverage on these two clusters. For Mo₉S_x and Mo₁₆S_x, however, the formation of 50% sulfur coverage is more favored than that of 67% sulfur coverage, respectively.

However, our findings do not agree fully with the results obtained by using periodic slab models, which show that the removal of sulfur from the S edge is *always* endothermic and the energy requirement increases as the sulfur coverage decreases. This difference can be reduced or eliminated by considering the relative energies of the less stable clusters from removing one corner sulfur and one edge sulfur or two edge sulfur atoms (Table 1). The thermodynamics can be shifted from

highly endothermic (removal of edge sulfur only) to less endothermic or even exothermic (removal of corner and edge sulfurs) and to highly exothermic (removal of corner sulfur only), respectively.

On the basis of the fact that periodic models have only edge sulfur, it is not surprising that the removal of only edge sulfur is *always* endothermic. Considering the removal of only edge sulfur, there is no discrepancy between cluster models and periodic models. The only difference is that cluster models have corner sulfur, while periodic models do not. This explains nicely the avoidable discrepancy between and periodic models in the thermodynamics of the sulfur removal process.

To understand the influence of the H₂S/H₂ ratio into the stability of sulfur coverage, the relative free energies (ΔG_0 , eq 3c) of MoS_x clusters with 0, 33, 50, and 67% sulfur coverages as functions of the H₂S/H₂ ratio at 675 K are calculated. As shown in Figure 5, the calculated relative free energy for 0% sulfur coverage is very positive in the whole range of the H₂S/H₂ ratio, but that of 33% sulfur coverage is only slightly positive at 0.0001 H₂S/H₂ ratio and increases with increasing H₂S/H₂ ratios. This indicates that the formation of 33% sulfur coverage on the S edge can only be obtained at a very low H₂S/H₂ ratio, while that of 0% sulfur coverage on the S edge is practically impossible for molecular H₂. In contrast, those of 50 and 67% sulfur coverages have negative relative free energies, which increase with increasing H₂S/H₂ ratios and become positive at a high H₂S/H₂ ratio. At a high H₂S/H₂ ratio, the only stable cluster should be that with 100% sulfur coverage at the S edge. It is also very interesting to show the effect of cluster sizes. At a very low H₂S/H₂ ratio, both Mo₉S_x and Mo₁₆S_x with 50% sulfur coverage on the S edge are the most stable structures, while both Mo₁₈S_x and Mo₂₇S_x with 67% sulfur coverage represent the most stable clusters. Therefore, the Mo₁₈S_x cluster can model the Mo₂₇S_x cluster for the S edge, while Mo₉S_x and Mo₁₆S_x are too small.

Comparison between the Mo and S edges shows that at a very low H₂S/H₂ ratio the most stable cluster on the Mo edge has 33% sulfur coverage but the most stable cluster on the S edge can have both 50 and 67% sulfur coverages. At a very high H₂S/H₂ ratio, the only stable cluster has 100% sulfur coverage at both Mo and S edges. At a medium H₂S/H₂ ratio, it is possible to have stable clusters with different sulfur coverage in coexistence. Therefore, it is possible to control the sulfur coverage of the most stable clusters by varying temperature and the H₂S/H₂ ratio.

3.2. Structures and Energies of Mo₂₇S_x Clusters. After analyzing sulfur coverage on the individual Mo and S edges, we were also interested in the structures and energies as a function of sulfur coverage on both edges at the same time. For this purpose, we used the Mo₂₇S₅₄ cluster in Figure 1 as a starting point. In Mo₂₇S₅₄, there are three S edges and three Mo edges and the change of sulfur coverage is (a) adding sulfur to the Mo edge at four different sulfur coverages on the S edge or (b) deleting sulfur from the S edge at four sulfur coverages on the Mo edge. On this basis, there are 17 stable structures (Mo₂₇S_x), and the calculated energies and the optimized structures are shown in the Supporting Information.

(a) Adding Sulfur to the Mo Edge at Defined Sulfur Coverage on the S Edge. Figure 6a shows the change of the relative energies of different sulfur coverages at the Mo edge (0, 33, 67, and 100%) with four sulfur coverages at the S edge (33, 50, 67, and 100%) and 0% sulfur coverage at the Mo edge (Mo₂₇S₅₄) as reference. It is noted that the structures with 50% sulfur coverage at the Mo edge are stable only for 100% sulfur

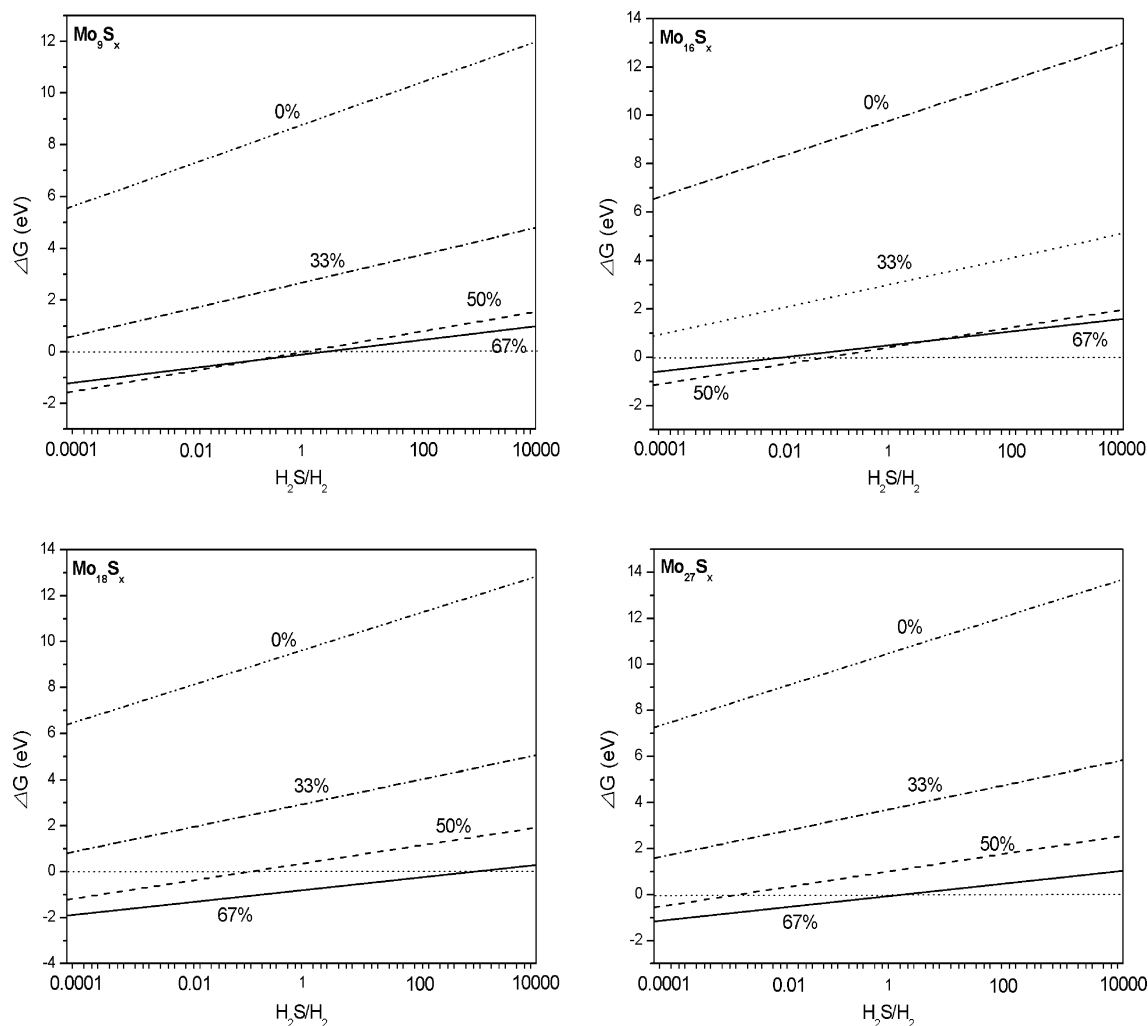


Figure 5. Relative free energies (ΔG_0) of MoS_x clusters with different sulfur coverages of the S edge as a function of the $\text{H}_2\text{S}/\text{H}_2$ ratio at 675 K. The S edge with 100% is taken as reference (dotted line) for all clusters.

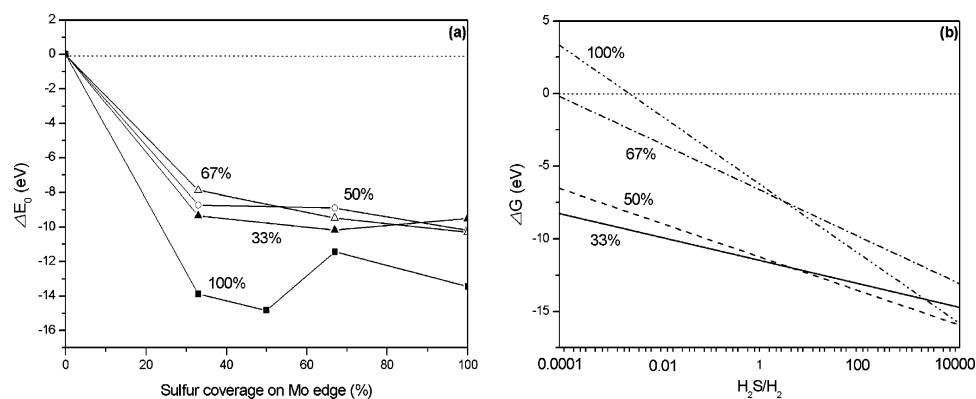


Figure 6. (a) Relative energies (ΔE_0) of Mo_{27}S_x clusters with four sulfur coverages on the Mo edge (0, 33, 67, and 100%) at defined sulfur coverage on the S edge (0, 33, 50, 67, and 100%). (b) Relative free energies (ΔG_0) of a Mo_{27}S_x cluster with different sulfur coverages on the Mo edge at 100% sulfur coverage and on the S edge as a function of the $\text{H}_2\text{S}/\text{H}_2$ ratio at 675 K. The Mo edge with 0% sulfur coverage is taken as reference (dotted line).

coverage at the S edge, and other structures with 50% sulfur coverage at the Mo edge and sulfur coverages (33, 50, and 67%) on the S edge are unstable. Thus, we will not pay further attention to 50% sulfur coverage on the Mo edge for the Mo_{27}S_x cluster model apart from that with 100% sulfur coverage at the S edge. Regardless, the sulfur coverage on the S edge shows clearly that adding sulfur to the Mo edge is *always* exothermic. The most stable structures of 33, 50, 67, and 100% sulfur

coverage on the Mo edge are those with 100% sulfur coverage at the S edge, while other structures are significantly less stable.

On the basis of eq 2b, we have calculated the thermodynamic effect (ΔE_0) of the stepwise increase of sulfur coverage on one Mo edge and on three Mo edges. These results are listed in Table 2. It shows clearly that adding sulfur to the Mo edge is always exothermic, as also discussed above. It is also interesting to note that there is practically no energy difference (ΔE) from

TABLE 2: Calculated ΔE_0 (eV) for Adding Sulfur on Mo Edge^a

Mo edge	ΔE_0^b (one edge)	ΔE_0^b (three edges)	ΔE^c
33% sulfur	-4.61	-13.88	-0.02
50% sulfur	-4.39	-14.83	-0.55
67% sulfur	-4.79	-11.43	+0.98
100% sulfur	-4.46	-13.44	-0.02

^a With 100% sulfur coverage on the S edge. ^b Using eq 2. ^c $\Delta E = [\Delta E_0 \text{ (three edges)}]/3 - \Delta E_0 \text{ (one edge)}$.

adding sulfur to one Mo edge and to three Mo edges at 33 and 100% sulfur coverages, respectively. At 50% sulfur coverage, the energy difference (ΔE) from one Mo edge to three Mo edges becomes more negative, while it becomes positive at 67% sulfur coverage, indicating the long-range effect of the added sulfur on the surface.

On this basis, we have investigated the effect of the H₂S/H₂ ratio (0.0001–10 000) on four sulfur coverages on the Mo edge with 100% sulfur coverage the S edges and the Mo edge with 0% sulfur coverage as reference. As shown in Figure 6b, there are three surface structures that are the most stable, and at a very low H₂S/H₂ ratio, the most stable structure has 33% sulfur coverage on the Mo edge, while at a high H₂S/H₂ ratio, the surface structure with 50% sulfur coverage on the Mo edge becomes more stable. At a very high H₂S/H₂ ratio, surface structures with 50 and 100% sulfur coverages on the Mo edge are stable. Our results show that the process of full sulfidation will happen under a fully sulfiding atmosphere. It is also interesting to note the possible coexistence of structures with 33 and 100% sulfur coverages at a H₂S/H₂ ratio of about 2000 and the structures with 33 and 50% sulfur coverages at a H₂S/H₂ ratio of about 6.

(b) Removal of Sulfur from the S Edge at Defined Sulfur Coverage of the Mo Edge. Apart from the variation of sulfur coverages on the Mo edge, we are also interested in the changes of sulfur coverage on the S edge. Figure 7a shows the change of the relative energies of four sulfur coverages on the S edge (33, 50, 67, and 100%) with defined sulfur coverages on the Mo edge (0, 33, 67, and 100%) and 100% sulfur coverage on the S edge (Mo₂₇S₅₄) taken as reference. At 0% sulfur coverage on the Mo edge, the formation of structures with 67 and 50% sulfur coverages on the S edge is exothermic, while that with 33% sulfur coverage is endothermic. At 67% sulfur coverage on the Mo edge, the formation of structures with 67% sulfur coverage on the S edge is exothermic, while that with 50 and

TABLE 3: Calculation ΔE_0 (eV) for Deleting Sulfur on the S Edge^a

S edge	ΔE_0 (one edge)	ΔE_0 (three edges)	ΔE
67% sulfur	-0.86	-2.89	-0.10
50% sulfur	-0.19	-0.82	-0.08
33% sulfur	2.11	5.93	-0.13

^a With 0% sulfur coverage on the Mo edge. ^b Using eq 3. ^c $\Delta E = [\Delta E_0 \text{ (three edges)}]/3 - \Delta E_0 \text{ (one edge)}$.

33% sulfur coverages is endothermic. At 100 and 33% sulfur coverages on the Mo edge, the formation of all structures with the variation of sulfur coverage on the S edge is endothermic.

On the basis of eq 3b, we have calculated the thermodynamic effect (ΔE_0) of the stepwise deleting of sulfur coverage from one S edge to three S edges. These results are listed in Table 3. As discussed above, the formation of 67 and 50% sulfur coverages on the S edge is exothermic, while that of 33% is endothermic. However, it is interesting to note that the energy difference (ΔE) for deleting sulfur on three S edges is somewhat more favored thermodynamically than that on one S edge, indicating the long-range effect. However, this effect is much smaller than that from adding sulfur to the Mo edge at 50 and 67% sulfur coverages.

On the basis of this finding, we also investigated the effect of the H₂S/H₂ ratio (0.0001–10000) on different sulfur coverages of the S edge by having the Mo edge with 0% sulfur coverage and the S edge with 100% sulfur coverage as reference. It shows clearly in Figure 7b that the most stable structure has 67% sulfur coverage at the S edge and 0% sulfur coverage on the Mo edge. Considering the typical working condition for HDS ($T = 650$ K and $H_2S/H_2 = 0.01$), 67% sulfur coverage on the S edge and 0% sulfur coverage on the Mo edge is the most stable structure.

Combining points a and b, it is clearly seen that there are some structures that are the most favored for Mo₂₇S_x clusters, that is, one with 100% sulfur coverage on the S edge and 33 or 50% sulfur coverages on the Mo edge and one with 67% sulfur coverage on the S edge and 0% sulfur coverage on the Mo edge. It is noted that 0 and 33% sulfur coverages on the Mo edge correspond to 2-fold and 1-fold CUS, respectively, while 67% sulfur coverage at the S edge corresponds to 1-fold CUS. Thermodynamically, it is not possible to have sulfur coverage higher than 50% on the Mo edge (apart from at a very high H₂S/H₂ ratio for 100% sulfur coverage) and to have sulfur coverage lower than 67% on the S edge at the atmosphere of molecular hydrogen.

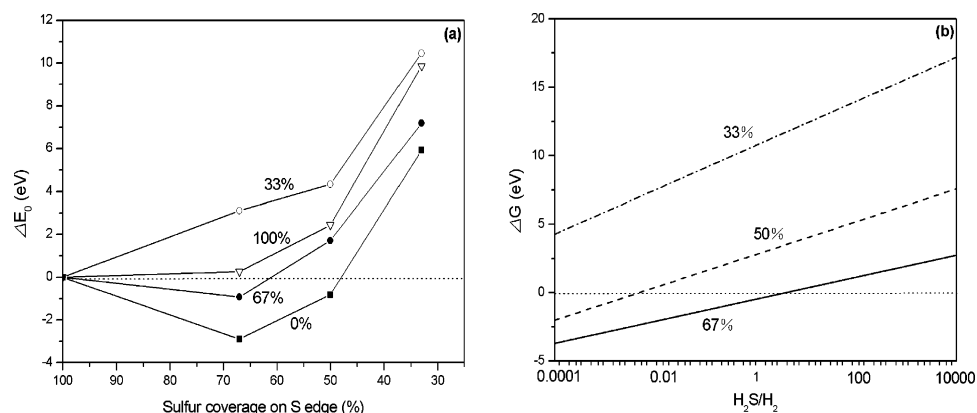


Figure 7. (a) Relative energies (ΔE_0) of Mo₂₇S_x clusters with four sulfur coverages on the S edge (33, 50, 67, and 100%) at defined sulfur coverage on the Mo edge (0, 33, 67, and 100%). (b) Relative free energies (ΔG_0) of a Mo₂₇S_x cluster with different sulfur coverages on the S edge at 0% sulfur coverage and on the Mo edge as a function of the H₂S/H₂ ratio at 675 K. The S edge with 100% sulfur coverage is taken as reference (dotted line).

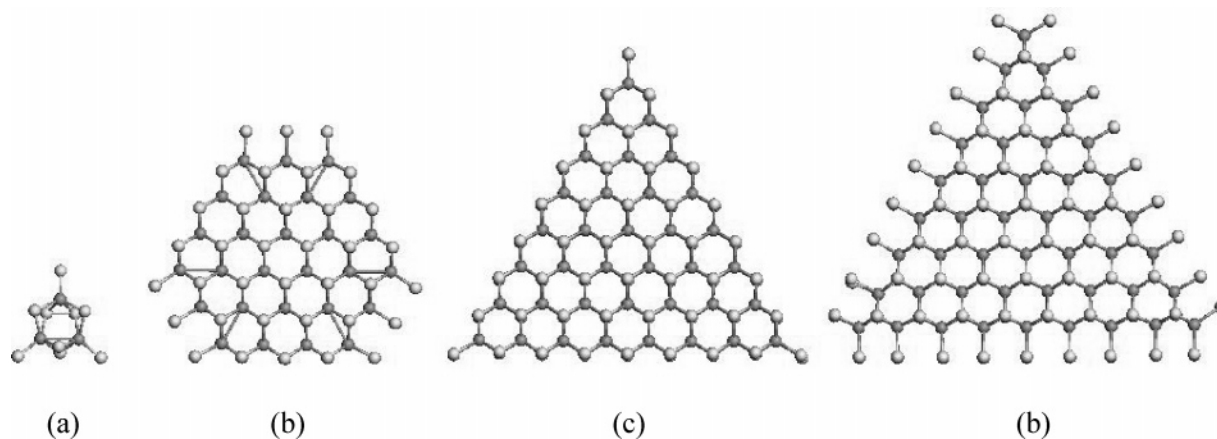
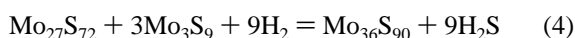
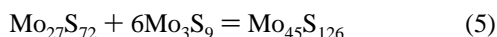


Figure 8. Sketch map of a forming triangular cluster from a hexagonal cluster: (a) Mo_3S_9 cluster, (b) fully sulfided hexagon-shaped cluster ($\text{Mo}_{27}\text{S}_{72}$), (c) triangular-shaped cluster terminated by S edges ($\text{Mo}_{36}\text{S}_{90}$), and (d) triangular-shaped cluster terminated by Mo edges ($\text{Mo}_{45}\text{S}_{126}$).

3.3. Structure of Triangle Clusters. On the basis of our above discussion and on that finding of triangular structures by STM,⁷ we have proposed that there is a growth process of triangular MoS_x clusters with increasing $\text{H}_2\text{S}/\text{H}_2$ ratio to a fully sulfiding atmosphere. Under a fully sulfiding atmosphere, the hexagonal $\text{Mo}_{27}\text{S}_{54}$ cluster is fully sulfided into $\text{Mo}_{27}\text{S}_{72}$, as shown in Figure 8. In addition, two triangular MoS_2 clusters terminated by S edges ($\text{Mo}_{36}\text{S}_{90}$) and Mo edges ($\text{Mo}_{45}\text{S}_{126}$) are optimized. Since Mo_3S_9 clusters are considered to be formed simultaneously during the preparation process of a catalyst,⁵² fully sulfided clusters will grow up once Mo_3S_9 clusters appear in the course, and the triangular MoS_x may be formed, as shown in eqs 4 and 5



$$\Delta E_0 = -9.83 \text{ eV} \quad (-3.28 \text{ eV}/\text{Mo}_3\text{S}_9)$$



$$\Delta E_0 = -31.30 \text{ eV} \quad (-5.22 \text{ eV}/\text{Mo}_3\text{S}_9)$$

It is expected that both types of triangular MoS_2 clusters can be formed by Mo_3S_9 clusters, as shown in eqs 4 and 5 with highly exothermic reaction enthalpies of -3.28 and -5.22 eV per Mo_3S_9 unit. Therefore, the triangular MoS_x terminated by the S edges and Mo edges are favorable. However, the triangular $\text{Mo}_{45}\text{S}_{126}$ terminated by Mo edges with 100% sulfur coverage is more favorable thermodynamically than the triangular $\text{Mo}_{36}\text{S}_{90}$ terminated by the sulfur edge with 100% sulfur coverage. Therefore, triangular MoS_x clusters terminated by fully sulfided Mo edges can be more easily observed at a high $\text{H}_2\text{S}/\text{H}_2$ ratio. Indeed, Lauritsen et al.^{7,41} have observed the structure of triangular MoS_x nanoclusters at a fully sulfiding atmosphere by STM and concluded that triangular MoS_x clusters are terminated by Mo edges fully covered with S_2 dimers. On the basis of the calculated surface energies for the individual edges of the triangular MoS_2 cluster, Schweiger et al.⁴² showed that triangularly shaped particles with a mostly exposed Mo edge can grow under very high pressures of H_2S , and the triangularly shaped MoS_2 clusters terminated by Mo edges (100%) are stable under fully sulfiding atmosphere. These findings indicate the perfect agreement of our results with the experiment and those of theoretical calculations by using other cluster models.

5. Conclusions

The structure and stability of different sized MoS_x clusters with a set of sulfur coverage on both the Mo edge and the S

edge have been computed systematically at the level of density functional theory. On the basis of the computed relative energies, simplified Mo_{16}S_x and Mo_{19}S_x clusters can model the sulfur coverage on the Mo edge as effectively as Mo_{27}S_x , while a simplified Mo_{18}S_x cluster is needed to model the sulfur coverage on the S edge. Other smaller clusters are insufficient.

The computed relative energies also show that formation of sulfur coverage on the Mo edge by adding sulfur is always exothermic. In contrast, formation of sulfur coverage on the S edge by removing or deleting sulfur is exothermic for 67% and 50% sulfur coverage, while endothermic for 33% and 0% sulfur coverage. This finding is in contrast with the results from periodic model calculations, which show that sulfur removal from the S edge is *always* endothermic. This discrepancy is caused by the difference between periodic and cluster models, since the periodic model has only edge sulfur, while the cluster model has both corner and edge sulfurs and removal of the corner sulfur is much easier than that of the edge sulfur. This suggests that corners might play a key role in the catalytic process.

In addition, the relative free energies of different edge surfaces of MoS_x clusters as a function of $\text{H}_2\text{S}/\text{H}_2$ ratio (0.0001–10 000) at 675 K are discussed. It is demonstrated that there are two stable structures with 33 and 50% sulfur coverage on the Mo edge along the range of the $\text{H}_2\text{S}/\text{H}_2$ ratio and they can also coexist in equilibrium. At a very high $\text{H}_2\text{S}/\text{H}_2$ ratio, 100% sulfur coverage on both the Mo edge and S edge is possible.

Along the $\text{H}_2\text{S}/\text{H}_2$ ratio range, the only stable structure has 67% sulfur coverage on the S edge. These results have been further confirmed by changing the sulfur coverage on both the Mo and S edges at the same time by using a Mo_{27}S_x model.

Under fully sulfiding atmosphere, it is found that the triangular structure with 100% sulfur coverage on the Mo edge is more favored thermodynamically than that with 100% sulfur coverage on the S edge, in agreement with the triangles observed experimentally in the STM.

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Supporting Information Available: Total electronic energies and optimized structures for all MoS_x clusters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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