

Removal of surface sulfur from MoS_x cluster under CO adsorption

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Abstract

Removal of bridging sulfur from the Mo edge of a $\text{Mo}_{20}\text{S}_{43}$ cluster has been investigated at the level of density functional theory. It is found that the reductive removal of bridging sulfur is not favored energetically but becomes favorable under CO adsorption. Due to the strong adsorption, CO can help the reductive removal of surface sulfur, and in turn, the reduced Mo edge can favor and facilitate the hydrogenation process of CO.

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1. Introduction

Molybdenum sulfide (MoS_x) in combination with transition metals as a promoter is a widely used catalyst in CO hydrogenation (HYD) and hydrodesulfurization (HDS) processes for producing cleaner fuels and fuel additives [1]. In contrast to metallic catalysts, MoS_x has the advantage of excellent resistance to sulfur poisoning. To understand the reaction mechanisms, Delmon et al. proposed the “remote-control” model and indicated that the source of activated H atoms can be enriched by a promoter [2], and that these hydrogen atoms can remove surface sulfur to produce coordinatively unsaturated sites (CUS) on Mo, which are essential to HYD and HDS [2a,3].

Theoretically, Raybaud et al. [4], Cristol et al. [5] and Byskov et al. [6] performed systematic calculations on the removal of surface sulfur by hydrogen and Sun et al. [7] summarized their results. They found that the [3–3] surface, where both the $\text{Mo}(1\ 0\ \bar{1}\ 0)$ and $\text{S}(\bar{1}\ 0\ 1\ 0)$ edges are half covered by bridging sulfur, can be formed easily, but that its

further reduction is thermodynamically unfavorable. Li et al. [8] studied the effect of removing surface sulfur for understanding the activation mechanism of HDS/HYD catalysts on the basis of a Mo_7S_{24} cluster model. Paul and Payen [9] studied the vacancy formation mechanism on the surfaces of MoS_x nano-crystallites of active phases in HDS process, and the dynamic equilibrium on these surfaces.

CO adsorption and activation on MoS_x have been investigated experimentally and theoretically. Müller et al. [10], Elst et al. [11] and Peri [12] reported a characteristic broad band at 2070 cm^{-1} with a tail extent to 2000 cm^{-1} in the IR spectra of adsorbed CO on MoS_x . It has been generally believed that this band is attributed to CO adsorbed on two-fold CUS at Mo [13]. Maugé et al. [14] attributed the red-shift from 2143 cm^{-1} of free CO to the surface back donation. Travert et al. [15] performed a systematic computation of CO adsorption on various kinds of MoS_x surfaces, and assigned the observed IR frequencies to different adsorption modes. Recently, Zeng et al. [16] used simplified but still representative stoichiometric and non-stoichiometric Mo_{16}S_x clusters ($x=29, 32, 34$ and 38) for CO adsorption and activation to model the changes of surface structure and composition. They found that end-on CO adsorption modes on the corner and

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edge sites are populated equally at low CO concentration, but the corner sites are predominant at high CO coverage. However, it is possible that at high CO coverage, the composition of these edges might change, and so will act as the catalytic center. They also identified the 2070–2000 cm^{-1} band as the corner and edge CUS at Mo and showed that the S-naked Mo edge adsorbs and activates CO to the largest degree, and should be the potential catalytic center for CO HYD. Indeed, S-naked Mo edges have been considered as one of the most active sites [17,18]. However, due to the strong interaction with bridging sulfur, the formation of such edges is unlikely under H_2 atmosphere.

In this paper, we focus on the formation of the S-naked Mo edge under the influence of both H_2 and CO, setting off from the results of CO adsorption [16], and confirm the catalytic centers on the Mo edge under real CO/ H_2 HYD conditions, using DFT calculation.

2. Models and methods

2.1. Models

The structure of MoS_2 is a closely packed layered sandwich with each Mo atom co-ordinated by six sulfur atoms in a prismatic unit, and Mo atoms in a plane situated between two sulfur planes [19]. Small MoS_2 slabs are responsible for the catalytic activities of HYD [3a,3c,20]. Two primary surfaces, $\text{Mo}(10\bar{1}0)$ and $\text{S}(\bar{1}010)$, are located on a MoS_x slab, as shown in Fig. 1. The active phase of HYD over MoS_x has long been known to be highly dispersed MoS_x crystals in nano-size with boundaries in all-crystallographic directions. More recently, the scanning tunneling microscopy revealed a truncated hexagon form for MoS_x cluster under excess hydrogen [21]. This result indicates that a cluster model similar to a hexagon, rather than a periodic model, should be

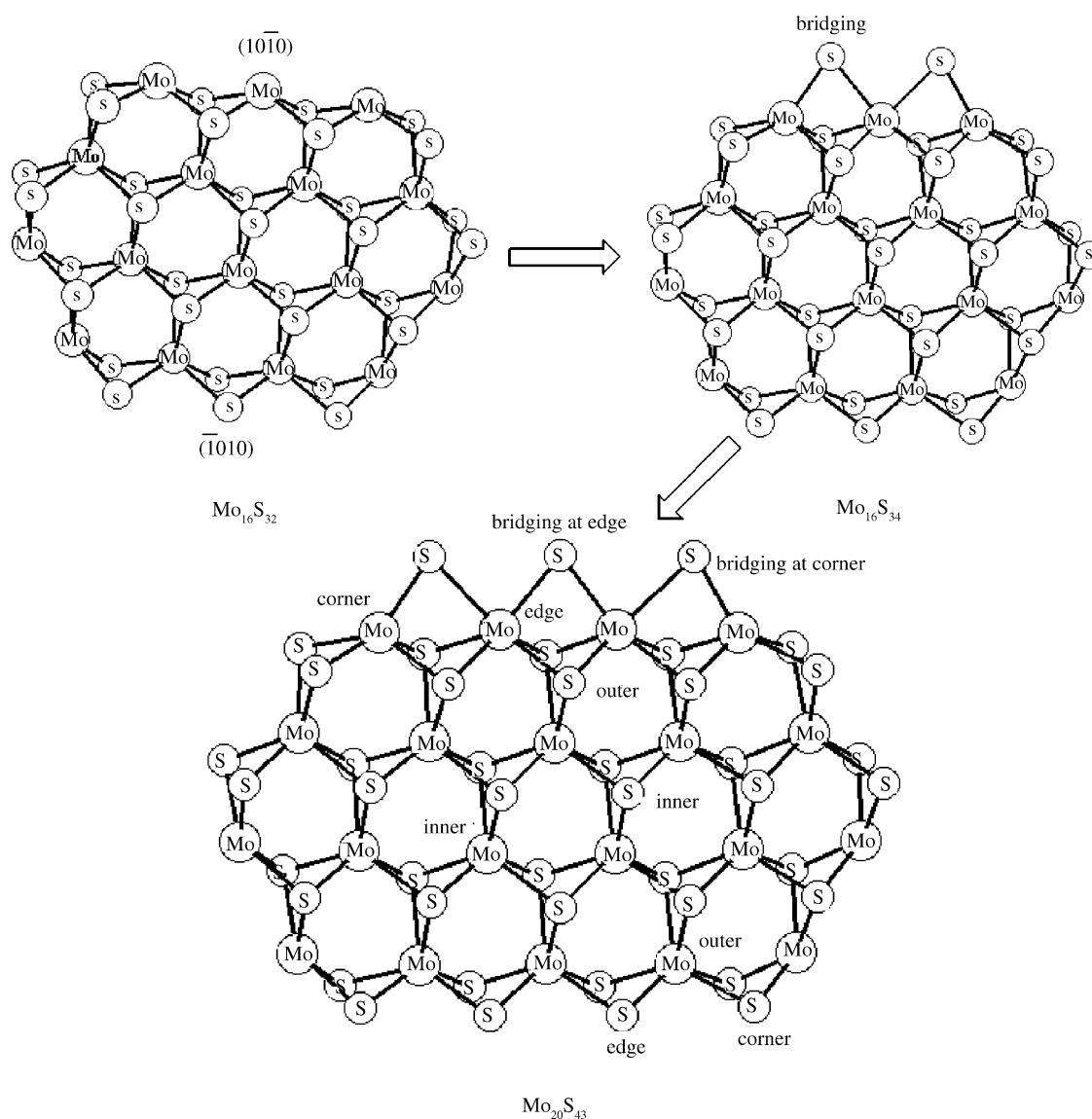


Fig. 1. MoS_x cluster models.

used to simulate the MoS_x phase under H_2 rich CO HYD condition.

To model thiophene adsorption on MoS_2 effectively, a simplified $\text{Mo}_{16}\text{S}_{32}$ cluster (Fig. 1) was employed by Orita et al. [22]. Based on the same cluster, Zeng et al. [16] performed systematic investigations of CO adsorption on each CUS site, and the computed CO stretching frequencies agree well with the experimental data. However, for the Mo edge bearing bridging sulfur, the $\text{Mo}_{16}\text{S}_{34}$ cluster with only one kind of bridging sulfur at the corner site is too small, and this is because real catalysts should have non-adjacent bridging sulfur to the corner sites [23]. For this reason, we extended the cluster into $\text{Mo}_{20}\text{S}_{43}$ bearing bridging sulfur at both edge and corner sites. Since a small cluster, $\text{Mo}_{16}\text{S}_{34}$, gives good results for CO adsorption and activation, the larger one, $\text{Mo}_{20}\text{S}_{43}$, should also be reasonable for CO adsorption.

2.2. Methods

All calculations were done with the program package Dmol [24] in the Material Studio of Accelrys Inc. For structure optimization and energy calculation, the density functional semi-core pseudopotential [25] was used for molybdenum, while the doubled numerical basis set with p- and d-polarization functions was used for all other elements. The gradient functional corrected by Perdew and Wang (PW91 [26]) was used, and real space cutoff of atomic orbital was set at 5.5 Å. The FINE standard for the tolerances of energy, gradient, displacement and self-consistent field convergence criteria of 1×10^{-5} au, 2×10^{-3} au/Å, 5×10^{-3} Å, and 1×10^{-6} au, respectively, was used and the MEDIUM quality mesh size of the program for numerical integration was adopted. The complete linear synchronous transit/quadratic synchronous transit (LST/QST) method was used to locate the transition states. The validity of these methods has been proved [16]. In this paper, we used Gibbs energy (ΔG) as the thermodynamic criterion to judge the favorability of sulfur removal process, e.g. $\mathbf{1} + 3\text{H}_2 = \mathbf{8} + 3\text{H}_2\text{S}$, in the later part. For gaseous components, G values are given by the sum or the calculated electronic energies (E_{elec}) and the Gibbs energy correction using statistic thermodynamic formula. Similarly to the previously work [5,27], we can assume that for condensed phases, the differences between Gibbs energies and enthalpies can be approximated by the difference of their computed electronic energies (E_{elec}). This approximation gives good results, because that corrections from energy to Gibbs energy for the most condensed phases are similar, and can be cancelled or compensated. Thus, ΔG is defined in the following equation:

$$\begin{aligned} \Delta G = & \sum E_{\text{elec}}(\text{condensed products}) \\ & - \sum E_{\text{elec}}(\text{condensed reactants}) \\ & + \sum G(\text{gaseous products}) \\ & - \sum G(\text{gaseous reactants}) \end{aligned}$$

As to the kinetic study, because it concerns some intermediates between condensed phase and gaseous phase, e.g. **3**, **5**, **7**, etc., for which we could not find a good way to give Gibbs energy corrections, we used E_{elec} to depict the kinetic favorability. In short, ΔG is used to judge the thermodynamic probability, and E_{elec} is used to judge the kinetic practicability. We chose 600 K to calculate Gibbs corrections, for it is the CO HYD temperature on the MoS_x edge [28].

3. Results and discussion

3.1. Full CO adsorption on Mo edge

As shown in Fig. 1, all sulfur atoms can be divided into six groups; S_c (corner), S_e (edger), S_o (outer), S_i (inner), S_{be} (bridging two edge Mo atoms) and S_{bc} (bridging corner and edge Mo atoms), and all Mo atoms can be classified into Mo_c (corner), Mo_e (edge), Mo_o (outer), and Mo_i (inner), respectively. Our previous study indicated that the CO adsorption energy on Mo_c of the half covered surface by bridging sulfur is -24.4 kcal/mol, while that on Mo_e is -12.2 kcal/mol [16]. Considering the Gibbs free energy correction (-24.1 kcal/mol) at 600 K, CO adsorption on Mo_c is only slightly favored (-0.3 kcal/mol), while that on Mo_e is not possible (11.9 kcal/mol). Based on these results, the full CO adsorption mode (**2**) with four CO probes on the two separated corners was constructed (Fig. 2), and the calculated ΔG_{ads} of -6.6 kcal/mol shows that Mo_c can also bind CO at high temperature, and the binding free energy for each CO is 1.65 kcal/mol. Thus, we used **2** to model the removal of bridging sulfur on the Mo edge with CO adsorption. As shown in Fig. 2, CO adsorption changes the Mo edge considerably, e.g. the Mo_c – S_{bc} and Mo_e – S_{bc} distances become longer and shorter in **2** compared to those in **1** (2.564 versus 2.266 Å and 2.286 versus 2.623 Å, respectively). On the basis of **1** and **2**, we will discuss the thermodynamics and kinetics of the sulfur removal process from the corner and edge sites with and without CO adsorption.

3.2. Removal of S_b from Mo edge without CO adsorption

The removal of bridging sulfur from $\text{Mo}_{20}\text{S}_{43}$ (**1**) without CO adsorption has been analyzed at first. In all cases, it is reasonable to consider that hydrogen atoms are available, and this is a frequently used and well accepted matter [4–7,29]. The optimized structures and the energy changes are shown in Fig. 3 and Scheme 1.

First, we investigate the thermodynamic probability of this sulfur removal reaction. ΔG of the formal reaction, $\mathbf{1} + 3\text{H}_2 = \mathbf{8} + 3\text{H}_2\text{S}$, is 127.6 kcal/mol, which means that the equilibrium $\text{H}_2\text{S}/\text{H}_2$ pressure ratio is 3.3×10^{-16} , which indicates that little H_2S in the reaction atmosphere is enough to prevent this reaction from happening. This is also why in HDS processes a small amount of H_2S is used to prevent deep reduction by very active hydrogen atoms [3c,30].

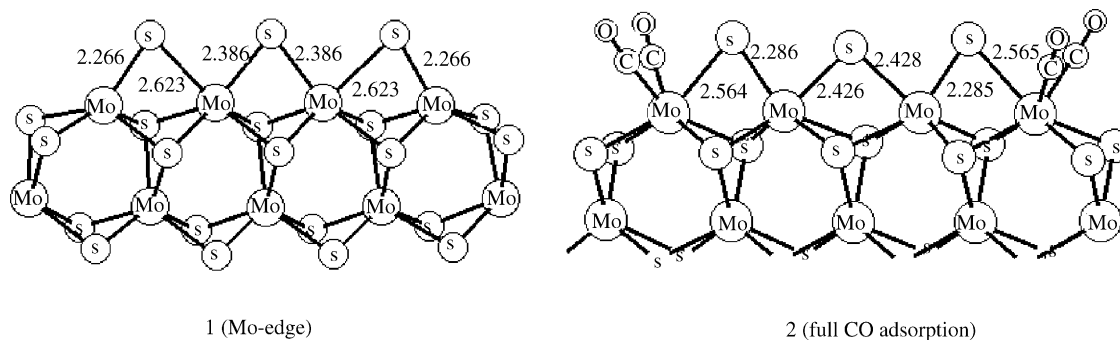


Fig. 2. Structures of bare Mo edge (1) and CO adsorbed Mo edge (2).

It is interesting to compare our result with those in the literature. Using a periodic Mo edge model, Raybaud et al. [4] indicated that removing a surface S from the sulfur bridging Mo edge requires 46.1 kcal/mol per sulfur, and Byskov et al. [6] estimated it at 36.9 kcal/mol for the same process, while we obtained 42.5 kcal/mol. These values are not identical, but are qualitatively consistent and comparable. The

quantitative difference should be due to the used models and methods [7]. On the other hand, Cristol et al. [5] investigated the Gibbs energy changes for different Mo edges by using periodic models, and they also found that the sulfur bridging Mo edge is very stable under high H_2/H_2S ratio, and it is very hard to remove bridging sulfur. This consistency proves that our small cluster model and method are reasonable, and

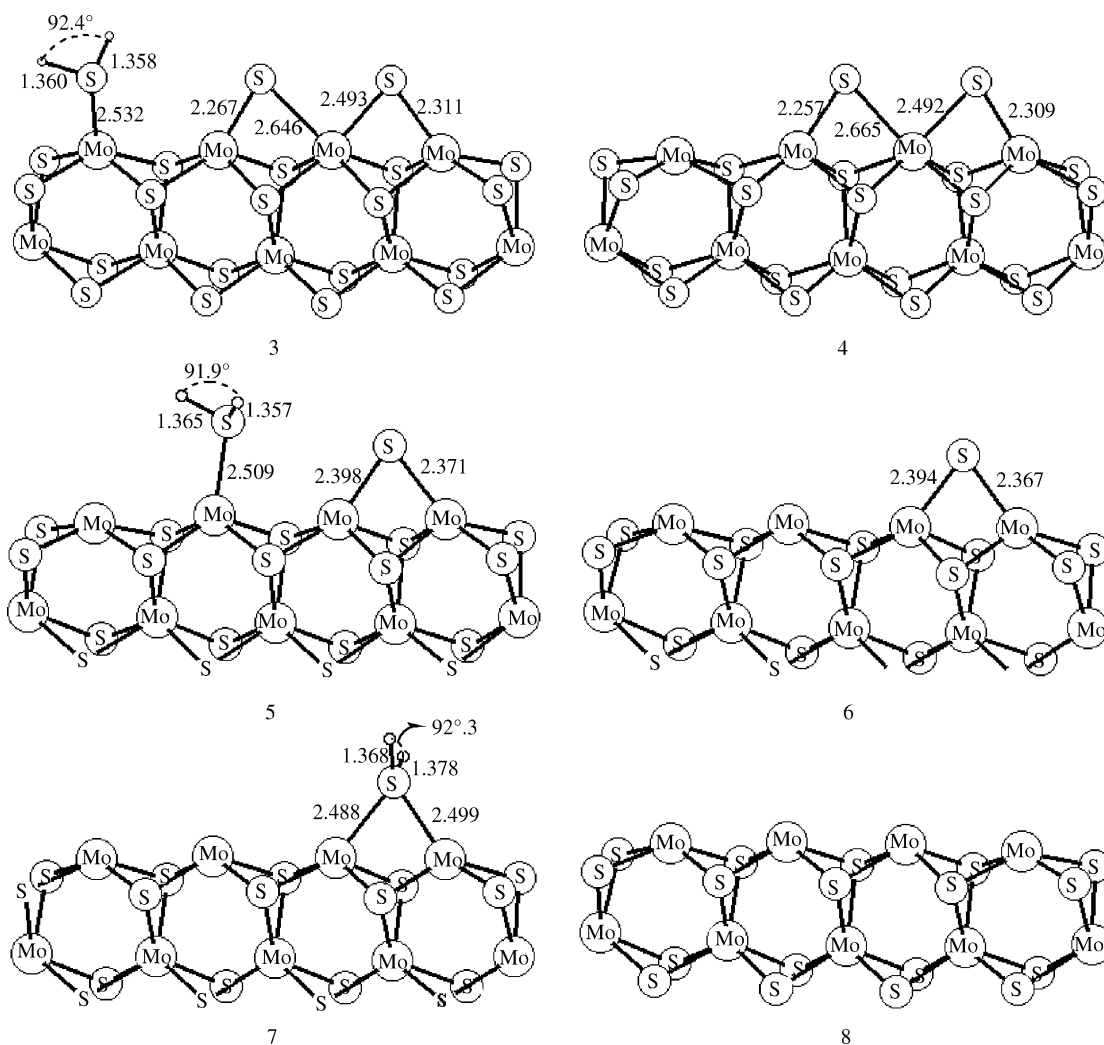
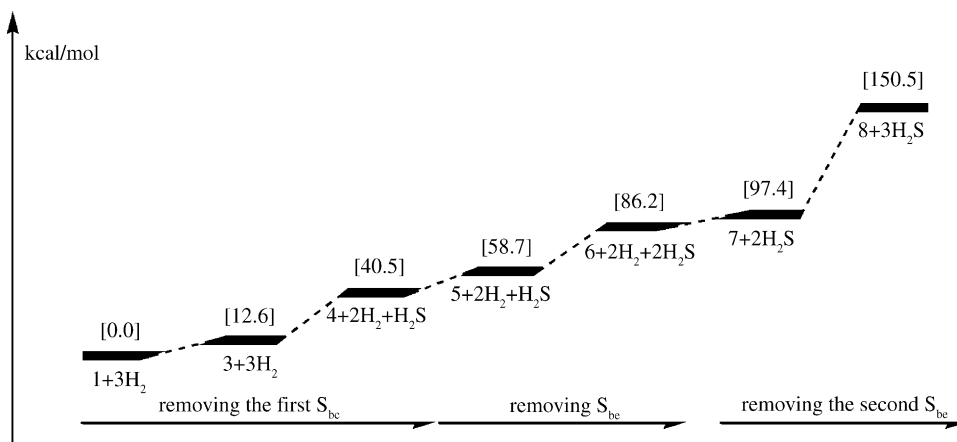


Fig. 3. Structures of removing bridging sulfur from 1.



Scheme 1. Energy profiles (in kcal/mol) for removing bridging sulfur from **1**.

reproduce the results of periodic models well. Thus, using this small cluster to perform further investigation is rational and acceptable.

Structures in Fig. 3 and data in Scheme 1 show the reaction path from the point of kinetics, the energy sum of **1** and three H₂ molecules is chosen as the energy zero point, and all energies are relative data compared to it. In **1**, the S_{bc} is linked to the surface by two S–Mo bonds; one is strong (2.266 Å) and another is weak (2.623 Å), while the S_{be} is linked to the surface by two equally strong S–Mo bonds (2.386 Å). Thus, it is reasonable to consider that one S_{bc} should be removed first. The first intermediate from **1** by adding two hydrogen atoms (formal H₂ addition) on S_{bc} is **3**, in which the sulfur bridge is broken and the formed H₂S is located at the Mo_c site, and the Mo_c–SH₂ distance is 2.532 Å. In **3**, the adsorbed H₂S has similar structural parameters as free H₂S (1.354 Å for H–S and 91.5° for HSH). As shown in Scheme 1, addition of molecular H₂ to **1** resulting in **3** is unfavorable by 12.6 kcal/mol thermodynamically. No transition state for H₂S desorption could be located, and the process is highly endothermic from **3** to **4** by 27.9 kcal/mol.

In **4**, since the S_{be} is pulled by the Mo_e, which has lost a S_{bc}, and the two S_{be}–Mo_e bonds are different (2.257 versus 2.665 Å). The left S_{bc} is still linked to the surface by two fairly strong bonds (2.492 and 2.309 Å). It can be seen that the S_{be}–Mo_e bond (2.665 Å) is the easiest to break, and thus, obviously S_{be} would be the next to escape. Adding two hydrogen atoms on the S_{be} in **4** leads to **5**, where one Mo_e–S_{be} bond is broken, and the formed H₂S is located at the Mo_e site by a S–Mo bond (2.509 Å), and the desorption of this H₂S results in **6**. Addition of H₂ on **4** is unfavorable by 18.2 kcal/mol, and once again, no transition state for H₂S desorption could be located between **5** and **6**, and the dissociation process is highly unfavorable by 27.5 kcal/mol.

Since there is only one S_{bc} on the Mo edge in **6**, it is natural to consider that removing it requires more energy. Adding two hydrogen atoms on the S_{bc} results in **7**. Unlike those two S_b atoms before, no S–Mo bond is broken here, and the formed H₂S is linked to the surface by two fairly strong

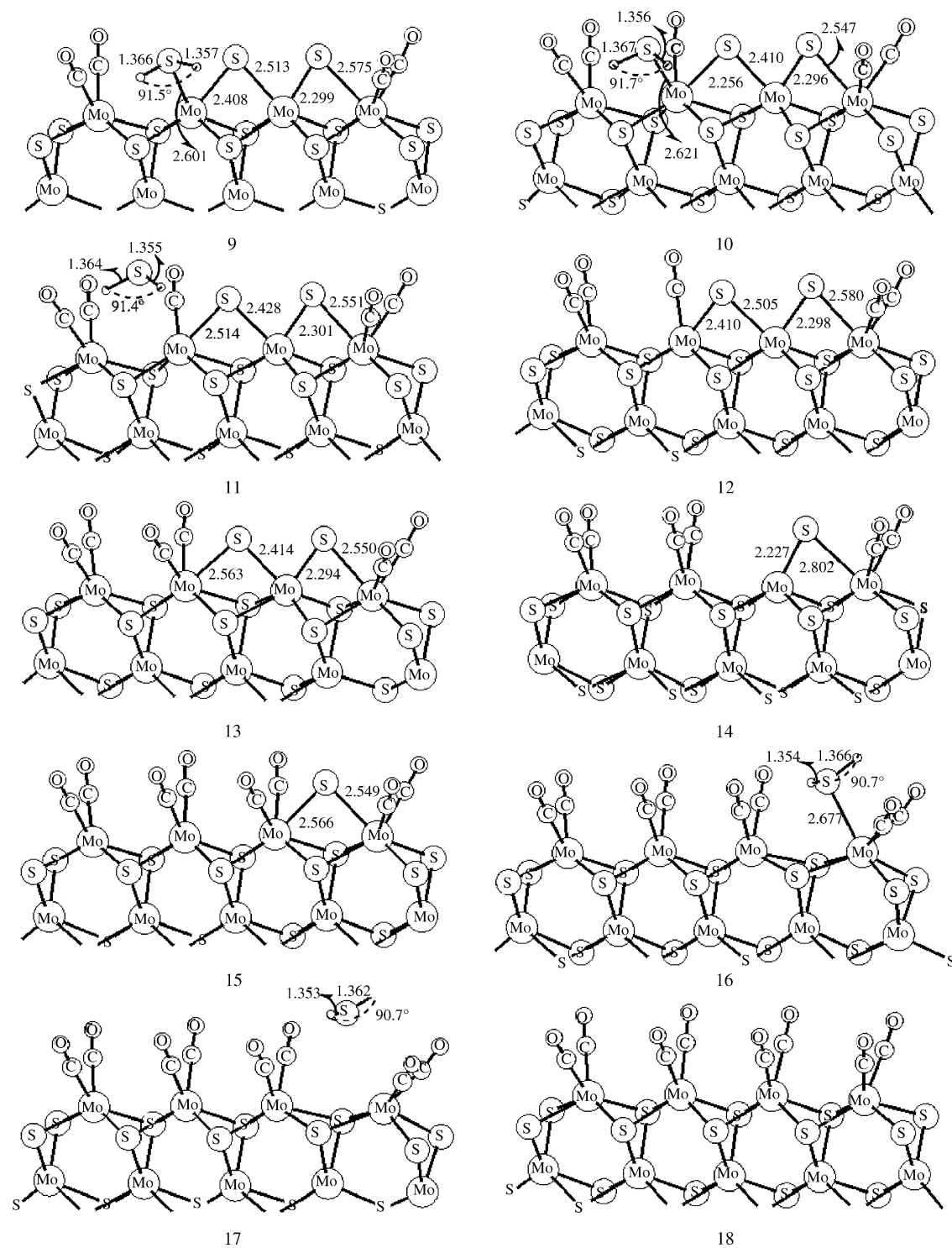
bonds (2.488 and 2.499 Å). Addition of H₂ on **6** is unfavorable by 11.2 kcal/mol. No transition state for H₂S desorption (between **7** and **8**) could be located, and the desorption energy is very high up to 53.1 kcal/mol, because of those two strong S–Mo bonds.

Obviously, the energy line in Scheme 1 increases monotonously, and no transition states could be located in the whole process of removing all bridging sulfur on the Mo edge. Then, the apparent activation energy is the sum of the whole process, which is high up to 150.5 kcal/mol, and formidable enough to prevent the process from happening. The whole formal process, **1** + 3H₂ = **8** + 3H₂S, is unfavorable both kinetically and thermodynamically, and bridging sulfur vacancy is unlikely to appear.

3.3. Removal of S_b from Mo edge under CO adsorption

Since removal of bridging sulfur is not favored both kinetically and thermodynamically, we are interested in the possibility of CO adsorption to help remove bridging sulfur. The main problem is the competitive coordination of CO and H₂S at the Mo edge. The optimized structures and the energy changes for the whole process are shown in Fig. 4 and Scheme 2, and the energy sum of **2**, three H₂ and four CO molecules is chosen as the energy zero point, and all other energies are relative values compared with it.

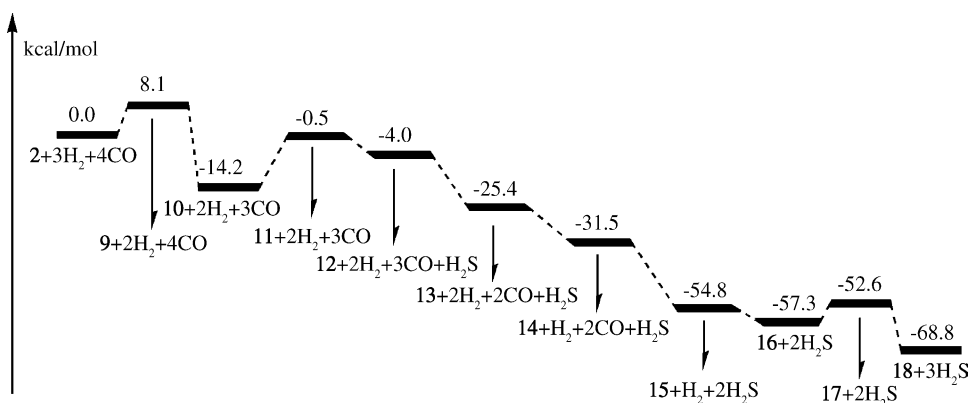
The formal reaction, **2** + 3H₂ + 4CO = **18** + 3H₂S, has a Gibbs energy of 4.6 kcal/mol, which is much smaller than that without CO adsorption, but still positive. Considering the change of entropy, this reaction will take place at lower temperature. At 600 K, the estimated equilibrium constant is 0.02. Taking the syngas composition (14 atm CO and 25 atm H₂) [29] and the fact that formed H₂S has very low partial pressure (<1 atm) into account, the maximal ratio of partial pressure will be approximately 1.7×10^{-9} ($P(\text{H}_2\text{S})^3/P(\text{CO})^4 \times P(\text{H}_2)^3$) (1 atm H₂S supposed), which is much smaller than the equilibrium constant. Thus, the reaction will take place, promoted by the high syngas partial

Fig. 4. Structures of removing bridging sulfur from **2**.

pressure. The CO adsorption structure of **18** is comparable to what we obtained on the S-naked Mo edge previously [16]. The C–O stretching frequencies of **18** are highly coupled and unidentifiable, ranging from 1992 to 2059 cm^{-1} , very close to that of our previous study of 2005–2049 cm^{-1} . This consistency indicates that our research about CO adsorption on

Mo_{16}S_x clusters is reasonable, and can be extended to the adsorption on larger models.

In **2**, S_{bc} is pushed away by two corner CO molecules and the $\text{S}_{bc}\text{--Mo}_c$ bond (2.564 Å) is the longest on the edge. Thus, it is reasonable to think that one S_{bc} should be deleted first. Adding two hydrogen atoms on the S_{bc} of **2** results in

Scheme 2. Energy profiles (in kcal/mol) for removing bridging sulfur from **2**.

9, where the $\text{Mo}_c\text{--S}_{bc}$ bond is broken and the formed H_2S is located at Mo_e . Scheme 2 indicates that the process from **2** to **9** is unfavorable by 8.1 kcal/mol.

According to our investigation of CO adsorption on MoS_x , it is possible that the Mo_e , to which the formed H_2S is linked, can adsorb a CO molecule on the other side, and we put a CO on it to make **9** turn to **10**. This CO adsorption process is favorable by -22.3 kcal/mol thermodynamically. This indicates that only formation of H_2S is not favored energetically and the process accompanied by CO adsorption is favored.

Unlike removing H_2S from **3**, we located a transition state (**11**) for escaping H_2S from **10**, and the activation energy is 13.7 kcal/mol. After surmounting this barrier, **10** becomes **12**, and the formal reaction of H_2S desorption, $\mathbf{10} = \mathbf{12} + \text{H}_2\text{S}$, is unfavorable by 10.2 kcal/mol. However, this endothermic process can be shifted into exothermic by CO adsorption, e.g. from **12** to **13** by -21.4 kcal/mol. The whole process from **10** to **13** is favored by 11.2 kcal/mol.

In **13**, the interaction between the S_{be} and the edge is weaker than that for the left S_{bc} , as indicated by their S--Mo bond lengths (2.563, 2.414 versus 2.550, 2.294 Å), and then, the S_{be} should be the next sulfur to escape. By adding two hydrogen atoms on the S_{be} in **13**, the formal H_2S desorbs automatically without any barrier and results in **14**. Furthermore, coordination of two CO molecules to **14** to form **15** is highly exothermic by -23.3 kcal/mol.

Adding two hydrogen atoms on S_{bc} in **15** results in **16**, where the $\text{S}_{bc}\text{--Mo}_e$ bond is broken and the formed H_2S is located at the Mo_c site by a 2.677 Å $\text{S}_{bc}\text{--Mo}_c$ bond. There is a transition state (**17**) for the final H_2S desorption, and the barrier for the desorption is only 4.7 kcal/mol, and the desorption energy from **16** to **18** is -11.5 kcal/mol.

Obviously, removing bridging sulfur from **2** shows a totally different energetic picture under CO adsorption compared with **1**. The energy line is generally decreasing, and the severest barrier is only 13.7 kcal/mol, which is very easy to pass at 600 K. Thus, CO adsorption can surely help remove bridging sulfur, based on both thermodynamics and kinetics.

In general, we consider that CO helps remove bridging sulfur in two ways. First, adsorbed CO occupies the most stable

coordination position (nipping the Mo plane), and weakens the interaction between bridging sulfur and the Mo edge (longer $\text{S}_b\text{--Mo}$ bonds in Fig. 4), and then S_b can escape more easily. Second, CO will fill the S_b vacancies up, once they are formed, and this CO adsorption is generally exothermic, and lowers surface Mo potential.

According to in situ diffuse reflectance infrared Fourier transform studies of CO HYD on MoS_x [28], soon after the beginning, some C–O stretching frequencies near 2100 cm^{-1} disappeared, and red-shifted to a lower band, which means that the CO activation is stronger. We have identified that the 2100 cm^{-1} peak is from the adsorbed CO on the corner site adjacent to bridging sulfur of a triangular cluster structure [31]. On this basis, one might assume that there will be not only one kind of species of the nano-sized MoS_x particles, and an assembly of MoS_x in different sizes and shapes along with their dynamic equilibrium of their surface structures and compositions should be possible. Furthermore, the disappearance of 2100 cm^{-1} might be attributed to the removal of the bridging sulfur near the corner help from both CO and H_2 . Experimentally, Travert and Mauge observed that the band at 2110 cm^{-1} appears even at the lowest CO coverages and is very symmetric, and assigned this band to monocarbonyl CO adsorption on the Mo edges of supported MoS_2 . They questioned the formation of triangular clusters on supports and the germinal CO adsorption on the corresponding corner sites [32]. Surely, this point is still a conjecture and needs further study.

4. Conclusion

DFT calculations were carried out to investigate the removal of bridging sulfur on the Mo edge of a $\text{Mo}_{20}\text{S}_{43}$ cluster with and without CO adsorption. The goal of this investigation is to understand sulfur removal process under CO influence, which is important to catalyzed CO hydrogenation.

Consistent with previous studies, removal of bridging sulfur atoms from a bare Mo edge is unfavorable thermo-

dynamically and kinetically, and H₂S adsorption rather than desorption is favored. Once some S_b vacancies on these edges are available, H₂S will fill it up immediately, and this is the role of a small amount of H₂S to prevent deep reduction in hydrogenation.

However, under the influence of CO adsorption, the bridging sulfur removal becomes favorable both kinetically and thermodynamically. CO coordination reduces not only the activation barrier, but also the reaction Gibbs energy, and can enable the S-naked Mo edge to present and then, to catalyze CO HYD process.

Acknowledgements

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