The adsorption and dissociation of H$_2$S on Cu(100) surface: A DTF study

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Density functional theory was used to investigate the adsorption of H$_2$S and H/HS, H/H/S on Cu(100). The pathways and transition states of H$_2$S dissociation were also studied. Results show that H$_2$S prefers the top site, while H, S and HS prefer the hollow site during the adsorption process. H$_2$S, HS and S can chemisorb on Cu(100) through the S–Cu bond due to the hybridization of the s, p orbit of S and the d orbit of Cu. The order of the adsorption energy for three forms is as follows: H/H/S, H/HS and H$_2$S. In addition, the dissociation of H$_2$S molecule on Cu(100) is thought to be an exothermic process. The activation energy of the first and second S–H bonds in H$_2$S are low and similar (approximately 10.15 kcal/mol). In the dissociation of H$_2$S, Cu atoms attract electrons from H–S bond which leads the bond-breaking.

1. Introduction

Copper and copper alloys have been widely applied in the industrial, military and civilian fields, due to their good mechanical properties and corrosion resistance. However, corrosion can attack these alloys aggressively in the environment containing hydrogen sulfide (H$_2$S) [1–3]. The presence of H$_2$S induces the degradation of copper or copper alloy components in the electronic and electromechanical devices, which cause enormous economic losses even major accidents.

The corrosion of copper in the hydrogen sulfide containing environment has been studied for many years [4–11]. S.P. Sharma [4] and J.L. Sansregret [5] investigated the reaction of copper and copper oxide with H$_2$S. Results indicated that dry H$_2$S attacks copper at a linear reaction rate, and the reaction product i.e. the film formed on the copper surface is Cu$_2$S. Copper oxide film formed in the air (several hundred Å thick) provides a good barrier against the attack of H$_2$S in the low relative humidity environment but not in the high relative humidity environment. Furthermore, oxides formed in the pure oxygen environment can provide better protection than those formed in the air. Charles T. Campbell et al. [6] explored the interaction of H$_2$S with Cu(111) using XPS, AES, ISS and LEED techniques. Results showed that at 120 K, H$_2$S adsorption is not complete, and by 200 K, desorption occurs on some of the H$_2$S molecules, and the rest of molecules dissociate into adsorption atoms and stably bond on the top site of the Cu(111) surface. T.T.M. Tran et al. [7] studied the atmospheric corrosion of copper in the hydrogen sulfide (H$_2$S) environment with different sulfide concentrations. Results showed that copper oxides and sulfides form on the metal surface, and cationic diffusion through the cuprous oxides and sulfides is the rate-determining step. Although the sulfidation of Cu leading to the formation of Cu$_2$S, i.e. the dissociation of H$_2$S has been clarified by above reported work, the geometries and dissociation pathways of H$_2$S on the copper surface are still not clear, due to the difficulty in observing this fast process experimentally.

First principle calculation has been proved to be a promising technique to study interfacial molecular–metal interaction [12–19] since it allows direct observation of some atomic scale phenomena which is extremely difficult to achieve through traditional experimental techniques. D.E. Jiang et al. [12,13] systematically studied the adsorption, dissociation and dissociation of H$_2$S on Fe surfaces through first principles. They found that the barriers to break the first and second S–H bonds in H$_2$S are low and about the same, ~0.25 eV, suggesting that deposition of S via H$_2$S is kinetically and thermodynamically facile, consistent with experiments. P. N. Abufager et al. [14] studied the adsorption and dissociation of H$_2$S on Cu(111) and Au(111). The results showed that the adsorption of H$_2$S is a non-activated process on both surfaces, and the barrier of the first H–S dissociation on Cu(111) is lower than that on Au(111). Y.M. Choi et al. [15] explored the interaction of H$_2$S with Ni- and Cu-based anodes by periodic DFT calculations in order to understand the adsorption and decomposition mechanisms of H$_2$S on metal surface. Results showed that the formation of initial molecular complexes on a Cu surface is energetically unfavorable (Ead ~ 0 eV), suggesting that Cu is more sulfur-tolerant than Ni. Qianlin Tang et al. [16] studied the water adsorption on the flat and stepped Cu surfaces using the first-principles DFT method and slab models. They found that water interacts with Cu mainly through the 1b1 MO, and on (110) and stepped surfaces Cu 4s–1b1 interaction contributes significantly to the stabilization of adsorbed water. A linear relationship is found between the calculated adsorption energy for monomeric water and the energy shift of the 1b1 MO of water. Using similar method, Marcos May et al. [17], Rouging Zhang et al. [18] and Alfonso et al. [19] studied the

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interaction of atomic S and Cu (111) surface, the adsorption and dissociation of H$_2$S on Cu$_2$O(111) surfaces, the adsorption and dissociation of H$_2$S on Cu(111) surface, respectively.

Although the adsorption behavior of H$_2$S on copper surface has been reported, the understanding of initial formations of adsorbates on the surface are still not adequate, especially the further analysis on the electronic structure which is crucial to a chemical process. The present work investigated the adsorption and dissociation of H$_2$S on the low miller indices surface Cu(100) for the first time to further understand the behavior of H$_2$S on Cu(100) surface. In this work, three adsorption systems were calculated with periodic density function theory (DFT): 1) isolated adsorption of H$_2$S molecule; 2) co-adsorption of H and HS; 3) co-adsorption of H, H and S atoms. The dissociation pathway and the transition states of the dissociation of H$_2$S on Cu(100) were studied as well.

2. Calculated models and details

2.1. Surface model

The adsorption properties of Cu(100) was investigated using the supercell approach [20,21]. Periodic boundary condition was applied to the central supercell in order to reproduce periodicity throughout the whole calculation space. The Cu(100) $- 3 \times 3$ supercell model including five atomic layers and corresponding three different adsorption sites (top, bridge and hollow) are employed, as shown in Fig. 1 (the top view of Cu(100) surface). A vacuum layer of 1.5 nm along the z-direction perpendicular to the surface (x and y being parallel) is employed to prevent spurious interactions between the repeated slabs. The bottom three layers of the slab were frozen to the bulk positions, while the top two layers were relaxed. The adsorbed H$_2$S, HS, S and H were also allowed to relax in all of the geometry optimization calculations.

2.2. Calculation methods

In this work, DFT was applied to perform all of the calculations. The exchange-correlation functional of generalized gradient approximations (GGA) was used, which can give very much better results for adsorbrates chemisorbed on the Cu(100) surface, deformation charge density $\Delta \rho(r)$ was calculated. The transfer of electron density between two atoms was analyzed. $\Delta \rho(r)$ is defined as

$$\Delta \rho(r) = \rho_{\text{total}}(r) - \sum \rho_{\text{atom}}(r)$$

Fig. 1. Top view of the adsorption sites on Cu(100): on-top site (T), two-fold bridge site (B), and four fold hollow site (H).

3. Results and discussion

3.1. H$_2$S adsorption on Cu(100)

For the adsorption of the H$_2$S molecule on the Cu(100) surface, there are two initial structures according to the orientation of the H$_2$S molecule on the three adsorption sites i.e. parallel or perpendicular to the surface. The calculated results show that H$_2$S molecules remain stable instead of dissociation in each structure. Among the six initial structures, four structures show tilted adsorption on top site, while the other two are perpendicularly adsorbed on the bridge and hollow site. Moreover, the adsorption energies of the former four structures are all about $-11$ kcal/mol, which are larger than that on the bridge site ($-8.44$ kcal/mol) and the hollow site ($-3.67$ kcal/mol). This means that the tilted adsorption on top site is more stable. Among those structures the most stable configuration [32] with the adsorption energy of $-11.53$ kcal/mol is shown in Fig. 2. In this structure, the bonding length of H-$S$ and S-Cu are 0.1361 nm and 0.2385 nm, respectively, while the bonding angle of H-$S$-$H$ is 91.4°. It should be also noted that the H-$S$ bonding length is longer than that in the unabsorbed H$_2$S molecule (0.1356 nm), which indicates that the
intensity of H – S becomes weaker and the H – S bond is activated during the adsorption.

The total electron density and deformation electron density of the most stable structure are shown in Fig. 3a and b, respectively. Obviously, mixing of the electron density occurs between S atom in H2S molecule and Cu atom of the surface (Fig. 3a), which indicates that the adsorbate chemically adsorbs on the Cu slab. Deformation electron density (Fig. 3b) exhibits that the electron density is depleted from S and Cu atoms (red area), and accumulates between S and Cu atoms (blue area), which indicates that some electrons move from S and Cu atoms to the region between each other, forming the covalent bond S – Cu. Therefore, H2S molecule could chemisorb on the Cu surface through the S – Cu bond.

In order to understand detailed electronic property of the S – Cu bond, the partial density of states (PDOS) of S and Cu atoms was analyzed (Fig. 4). Fig. 4a shows that the Cu d orbit shifts towards negative energy level after adsorption by the shift of the strongest peak from $-1.75$ eV to $-2.46$ eV. Meanwhile, some peaks ($-2.05$ to $-5.02$ eV) become weak, while some new peaks ($-15.70$ and $-8.01$ eV) appear after H2S adsorbing on the Cu surface. Thus, it is proposed that the d orbit contributes to the formation of S–Cu bond and electrons in the d orbit become more stable after adsorption. Fig. 4b displays PDOS of S s and p orbits. Apparently, some peaks of s and p orbits locate at the same energy level ($-15.70$, $-6.68$, $-6.51$, and $-6.27$ eV), which indicates that the hybridization occurs between the orbits of s and p. It also demonstrates that H–S bond does not break due to the hybridization of s and p orbits. In a comparison of Fig. 4a and b, it can be seen that some peaks of d orbit of Cu and s orbit of S atom locate at the same energy level ($-15.7$, $-8.0$, $-6.7$, $-6.5$, $-6.3$ eV), and some peaks of d orbit of Cu and p orbit of S atom locate at the same energy level ($15.7$, $-6.7$, $-6.5$, $-6.3$ eV), which indicates the hybridization of s p orbit of the S atom and d orbit of Cu atom contributes to the formation of covalent bond S – Cu.

3.2. H/HS co-adsorption on Cu(100)

The H/HS co-adsorption system contains eighteen initial structures comprised of two adsorbates (H and HS), three adsorption sites (top, bridge and hollow site) and two postures of HS (parallel or perpendicular to the surface). All the initial structures were calculated to obtain the most stable adsorption configuration. After optimization, it can be found that the adsorption energies of H/HS co-adsorption structures are larger ($\sim -117.50$ kcal/mol) than those of the H2S adsorption structures ($\sim -11.53$ kcal/mol), indicating that the H/HS co-adsorption is more stable. Among the eighteen structures, ten structures exhibit the same adsorption configuration, with H and HS perpendicularily adsorbing on the hollow site. In the rest of eight structures, H and HS adsorb on the bridge site. As for the adsorption energy, two above mentioned adsorption configuration are $\sim -125$ kcal/mol and $\sim -123.06$ kcal/mol, respectively, which means that the hollow site are more stable for two adsorbates.

The most stable adsorption configuration [32] among the eighteen structures is shown in Fig. 5. The adsorption energy of this configuration is $-125.43$ kcal/mol, which is much larger than that of the stable H2S adsorption configuration ($-11.53$ kcal/mol). It also can be seen that HS adsorbs on the Cu through the interaction of S atom with four neighboring Cu atoms. The length of four S–Cu bonds is 0.2334, 0.2349, 0.2351, and 0.2355 nm, respectively, which are shorter than that of S–Cu bonding length in the most stable H2S adsorption configuration (0.2385 nm). It is proposed that the H/HS co-adsorption is more stable than the H2S adsorption due to the larger adsorption energy and shorter S–Cu bonding length. However, the length of the H – S bond in the H/HS co-adsorption (0.1374 nm) is longer than that in H2S adsorption and the free H2S molecule, which indicates that the H – S bond is more active in the H/HS co-adsorption.

The total electron density and deformation electron density of the most stable configuration are shown in Fig. 6. Obviously, electron density of Cu surface mixes with electron density of S, indicating that HS chemically adsorbs on the Cu slab. It also can be seen that the mixing area of S and Cu atoms is much bigger than that in H2S adsorption, which suggests that the interaction between HS and Cu is stronger than that between H2S and Cu. The deformation electron density (Fig. 6b) shows that four S–Cu bonds in the HS/S co-adsorption are similar with S–Cu bond in the H2S adsorption. The accumulation of electrons between S and Cu atoms (blue area) and the depletion from S and Cu atoms (red area) also indicate the formation of S–Cu covalent bond. Additionally, there are totally four S–Cu bonds formed in HS adsorption on the hollow site, while only one bond formed in H2S adsorption. Therefore, the interaction between HS and Cu is stronger than that in H2S adsorption.

The PDOS of Cu d orbit and S s p orbit is shown in Fig. 7. Overall, the variation of Cu d orbit before and after adsorption in the H/HS adsorption is consistent with that in the H2S adsorption (Fig. 3). After
adsorption, except for the appearance of some new peaks, Cu d orbit also shifts towards negative energy level, which indicates the interaction of S and Cu atoms. However, there are also some differences in the variation of Cu d orbit before and after adsorption between H/HS and H2S adsorption systems. The shift of the strongest peak (from $-1.75$ eV to $-2.60$ eV) in the H/HS adsorption systems is bigger than that in the H2S adsorption systems (from $-1.75$ eV to $-2.46$ eV). In addition, the decrease of some peaks value ($-1.43$ to $-3.91$ eV) is larger than H2S adsorption. These results demonstrate that the adsorption of H/HS is stronger than that of H2S on Cu(100). From comparison between PDOS of S s p and Cu d orbits, it can be seen that some peaks of d orbit of Cu locate at the same energy level with s orbit of S atom ($-14.7$ eV) and p orbit of S atom ($-14.7$, $-8.1$ eV), indicating S–Cu bond due to the mixing of S s p orbit with Cu d orbit. In addition, there are much fewer hybridized peaks between s and p orbits of S atom in the H/HS adsorption than that in the H2S adsorption, which indicates that the hybridization between s and p orbits becomes weaker. Considering the formation of H2S through s p hybridization of S atom, it can be proposed that the weakening of s p hybridization is due to the detaching of H atom from H2S molecule.

### 3.3. H/H/S co-adsorption on Cu(100)

For the H/H/S co-adsorption, there are also eighteen initial structures determining by three adsorbates (H, H and S) and three adsorption sites. Calculation results show that there are ten structures optimized to the same configuration in which three adsorbates are adsorbed on the hollow site. In the other eight similar configurations, two adsorbates are adsorbed on the hollow site, and the other one adsorbs on the bridge site. In addition, the former ten configurations have similar adsorption energy (about $-224$ kcal/mol) which is larger than the latter eight configurations ($-220.67$ to $-222.72$ kcal/mol). This means that the former ten configurations are more stable than the latter eight configurations, and three adsorbates tend to adsorb on the hollow site.

The most stable configuration [32] of H/H/S co-adsorption system is shown in Fig. 8. The adsorption energy of this configuration is $-224.54$ kcal/mol which is larger than that of H/HS adsorption systems ($-117.50$ to $-125.43$ kcal/mol) and the H2S adsorption system ($-3.67$ to $-11.53$ kcal/mol).

It also can be seen that S atom in this adsorption interacts with four neighboring Cu atoms, which is similar to that in the H/HS co-adsorption. However, the length of each S–Cu bond in the H/H/S co-adsorption (0.2275, 0.2279, 0.2302 and 0.2308 nm respectively), is even shorter than that in H/HS co-adsorption, suggesting that S atom in the H/H/S co-adsorption system has the strongest interaction with Cu in the three adsorption systems. In addition, two H atoms in the H/H/S co-adsorption system both fall into the hollow site. However, there is not chemical bond forming between Cu atom and H atom, which is similar to that in the H/HS co-adsorption.

The total electron density and deformation electron density are shown in Fig. 9. It can be seen that the electron density of S atom (Fig. 9a) mixes with that of Cu atoms around it, which is similar to that in the H/HS adsorption system. However, the mixing area in the H/H/S co-adsorption is much larger compared with that in the H/HS adsorption. Therefore, the interaction between S and Cu is thought to be stronger than that between HS and Cu. Similarly, the deformation electron density of S–Cu (Fig. 9b) showing that the electrons accumulate (blue area) between S and Cu atoms also indicates that the S–Cu bond is covalent.

The PDOS of S and Cu atoms in the H/H/S co-adsorption is shown in Fig. 10. It can be seen that the results are similar to the H2S and H/HS adsorption systems regarding the shift and appearance of PDOS peaks. The shift of Cu d orbit towards the negative energy level after adsorption and the appearance of some new peaks after H/H/S adsorbing on the Cu...
surface suggests that the interaction of S – Cu bond is contributed from the variation of Cu d orbit.

Meanwhile, both the shift of the strongest peak (from −1.75 eV to −2.64 eV) and the decrease of some peaks (−2.05 to −3.15 eV) are largest among the three adsorption systems, which indicates that the S – Cu bond in the H/H/S co-adsorption is the strongest. S – Cu bond is also due to the mixing of S s p orbit with Cu d orbit through the similar analysis with the former two adsorption systems. In addition, the number of hybridized peaks of S s p orbit is less than that in H/HS co-adsorption system, indicating that the hybridization between s and p become much weaker, which might result from the totally dissociation of H$_2$S molecular.

3.4. Dissociation of H$_2$S molecule on Cu(100)

Based on the discussion of H$_2$S, H/HS and H/H/S adsorption systems, it can be seen that the interaction between adsorbates and Cu(100) are through the formation of S – Cu covalent bond, i.e. the hybridization of s and p orbits in the S atom with d orbit in the Cu atom. Regarding to the adsorption energy of three adsorption systems, the interaction of Cu with H/H/S is strongest, then H/HS and H$_2$S. Therefore, it can be proposed that there is strong thermodynamic driving force for the dissociation of H$_2$S molecule on the Cu(100) surface.

After determining the most stable adsorption configurations of H$_2$S, H/HS and H/H/S systems, the minimum energy pathway (MEP) for H$_2$S dissociation on the Cu(100) surface was determined using the nudged elastic band (NEB) method. The MEP pathway is considered as follows: H$_2$S → HS + H → S + H + H. In the NEB method, the initial reactants and the final reactions were determined beforehand based on the most stable adsorption configuration in each adsorption system. Therefore, the path starts with H$_2$S tilted to the surface on the top site, develops to the H/HS which both adsorbing on the hollow sites, and ends up with two H atoms and S atoms falling into the three fold sites. The transition states [32] of the first and second dissociation step (defined as TS1 and TS2 respectively) are shown in Fig. 11. The deformation electron density of H – S bond in TS1 and TS2 was calculated (Fig. 12). The energy profile for the dissociation of H$_2$S on Cu(100) is shown in Fig. 13.

3.4.1. The first dissociation step

In TS1, the Monitoring Bond shows that H – S bond breaks over the Cu atom which the initial H$_2$S adsorbs on. It can be seen that the distance between the dissociated H and S atoms is 0.1741 nm, which is longer than the initial H – S bond length (0.1361 nm). In addition, the undissociated H – S bond length also becomes longer (0.1365 nm) compared with the initial state. Meanwhile, with the dissociated H
and S atoms moving closer to the Cu surface, both the S–Cu and H–Cu bond length become smaller (to 0.2330 nm, and 0.1679 nm, respectively). After TS1, the dissociated H and HS fall into the hollow sites (H/HS co-adsorption). The movement of H and HS leads to the decrease of the system energy. At the moment, the bond length of the undissociated H–S is 0.1374 nm, a little longer than that in TS1. The barrier of the first dissociation step is low (10.17 kcal/mol), indicating that it’s easy to break the first H–S bond. The reaction energy of the first steps is $-21.09$ kcal/mol, indicating that the first step is an exothermic reaction.

Compare the deformation electron density of H–S bond (Fig. 12) in TS1 with H$_2$S adsorption (Fig. 3b), some electrons move away from the H–S bond region in the TS1, and accumulate to the space between H and Cu atoms (blue area), which results in the increase of H–Cu bond and the weakening of the H–S bond in the first step. Moreover, electron density depletion is also seen in the region of S–Cu bond.

### 3.4.2. The second dissociation step

In the second step of dissociation, the S atom and the dissociated H atom almost stay in the hollow site, while the movement of the other H atom is significant. In TS2, the undissociated H–S bond in the first step breaks and new H–Cu bond forms by the Monitoring Bond. The distance between the second dissociated H and the S atoms is 0.1829 nm, much longer than the length of the initial H–S bond (0.1374 nm). In addition, the length of the new H–Cu bond is 0.1575 nm. After TS2, the second H continues moving towards the nearby hollow site, and finally falls there. The barrier energy of the second step is 10.13 kcal/mol, which is similar to that of the first step. The reaction energy is $-20.59$ kcal/mol, indicating that the second step is also an exothermic reaction.

The deformation electron density in the TS2 shows the similar variation as in the TS1. Some electrons move away from the H–S bond region, and accumulate to the space between H and Cu atoms.

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**Fig. 8.** The most stable configuration of H/H/S co-adsorption on Cu(100).

**Fig. 9.** The total electron density (a) and deformation electron density (b) of the most stable H/H/S adsorption configuration.

**Fig. 10.** The PDOS of the Cu orbit (a) and S orbit (b). The green line and black line in the figure (a) refer to the d orbit of the clean Cu and the adsorbed Cu, respectively.
Based on the above analysis, Cu attracts electrons in the H–S bond, which results in the weakening of the H–S bond. Due to the weakening of H–S bond, H atom dissociates from the S atom. The same dissociation also happens on the second H atom. In addition, the Cu surface’s adsorption of adsorbates reduces the system energy, which made the reactions carry out smoothly. Therefore, it can be proposed that Cu surface plays a very important role in the two dissociation processes.

In previous DFT works, the dissociation of H2S on Cu (111) was examined. Alfonso [19] showed that the barriers for the first and second dissociation are 0.43 and 0.40 eV (9.91 and 9.22 kcal/mol), and Abufager et al. [14] show that those are 0.45 and 0.55 eV (10.37 and 12.68 kcal/mol), comparing well with our results. However, the adsorption energy of H2S on Cu(111) is −0.26 eV (5.99 kcal/mol) for Alfonso [19] and −0.23 eV (5.30 kcal/mol) for Abufager et al. [14], much lower than −11.53 kcal/mol in the present work. To elucidate whether this significant difference is due to the different surfaces or due to an insufficient k-point density in the Brillouin zone, we have simulated H2S adsorption on top site, H/HS adsorption on hollow sites and H/H/S adsorption on hollow sites with a 7 × 7 × 1 k-point grid. And the pathway and transition states of H2S dissociation were also searched with a 7 × 7 × 1 k-point grid. The results show that the adsorption energies of H2S, H/HS and H/H/S 7 × 7 × 1 k-point grid are −10.58, −29.13 and −45.07 kcal/mol, and the barriers of the dissociation are 11.98 and 11.33 kcal/mol. The changes of adsorption energies and barriers are small compared with the calculation error of the software (~2.3 kcal/mol). Therefore we believe that the surfaces play an important role in the adsorption of H2S on Cu metal. Atom arrangement may be very different from one surface to another, leading the change of electronic configuration and active sites of surface. This may be the reason why there are significant different adsorption energies between Cu(100) and Cu(111). The dissociation of H2S on Fe surface is also reported from a previous DFT investigation. The barriers are 0.25, 0.28 eV (5.76, 6.45 kcal/mol) on Fe(100) [12] and about 0.10, 0 eV (2.31, 0 kcal/mol) on Fe(110) [13]. The barriers on Fe(100) are much lower than those on Cu(100) in this manuscript, indicating that the dissociation occurs more easily on Fe surface. In addition, the alloying is also an important factor. D.E. Jiang et al. [33] showed that FeAl surfaces raise the barriers for H2S dissociation compared with pure Fe surface, and Fe3Si surfaces are as vulnerable as Fe surfaces to H2S dissociation. Overall, the surface plays an important role in the adsorption and dissociation of molecular on metal. And lots of comprehensive and parallel works are urgently needed to discover how the metal surface affects the adsorption and dissociation.

In the present work, H2S, H/HS and H/H/S adsorption systems were investigated through the calculation of stable configurations, binding geometries, electron properties and PDOS in each system by density functional theory. In addition, the minimum energy path for H2S dehydrogenation of Cu(100), i.e. dissociation was calculated by the nudged elastic band method. The following conclusions are obtained:

1. In the three adsorption systems, HS, S, and H adsorbed on the hollow site, while H2S is adsorbed on the top site. In all systems, the S atoms can form covalent bond with neighboring Cu atoms due to the hybridization of S s, p orbit and Cu d orbit.
2. The electric interaction of H2S with Cu surface is weak, HS have a stronger interaction with Cu surface, and dissociative S adsorption is the strongest. Regarding the adsorption energy of three systems, the adsorbates can be arranged in the as follows: H/HS co-adsorption > H/HS co-adsorption > H2S adsorption.
3. The dissociation of H2S on Cu(100) surface is exothermic, which contain two steps: H2S→HS+H and HS→H+S+2H. The barrier energy of the dissociation in the first and second steps is 0.17 and 10.13 kcal/mol, respectively, which means two H–S bonds are easy to be broken.
4. The two dissociation steps, Cu atoms attract electrons from H–S bond forming the H–Cu bond, which lead to the dissociation of H2S. And the Cu surface's adsorption of adsorbates reduces the system energy, which made the reactions carry out smoothly.
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Appendix A. Supplementary data

Supplementary data to this article can be found online athttp://dx.doi.org/10.1016/j.susc.2013.10.014.

References

[32] See Supplementary Material for the coordinates of atoms locations in all structures.

Fig. 13. Energy profile for the dissociation of H2S on Cu(100). All energies (kcal/mol) are relative to the total energy of the isolated H2S and the clean surface.