First principles studies of hydrogen sulfide adsorption and dissociation on NiAl(110)-(2x2)

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The molecular and dissociative adsorption of H_2S molecule on NiAl(110) surface is examined using density functional theory (DFT). We have considered the five possible adsorption sites given in Fig.1. We have found that the binding geometry depicted in Fig. 2(e) was energetically more favorable than the others. For the dissociative adsorption of H_2S molecule on NiAl(110) phase, it is found that SH molecule is attached almost Ni-Ni site while H atom is located to the surface 2Ni-Al site, with adsorption energy -1.23 eV. The atomic key parameters of considered systems have been compared with theoretical and experimental values (in the gas phase). We have also calculated the reaction path and energy profiles for dissociation of both H_2S into SH-H and SH into S-H on NiAl(110) surface, and it is found that the both reaction is exothermic.

1. Introduction

The necessary energy for the cleavage of hydrogen sulfide to hydrogen production is less than that is needed for the electrolysis of water. Hydrogen sulfide (H_2S) gas puts in an appearance in many industrial processes such as a pollutant in gas feed streams and a by-product in the vulcanization process. Many of the chemical reactions involves its reaction and dissociation on a surface to form elemental sulphur (S) and hydrogen (H), frequently resulting highly poisonous of the surface causing corrosion and embrittlement [1]. Moreover H_2S accumulates its hydrogen atoms on transition metals causing embrittle metals [2]. Furthermore the adsorption of H_2S and its dissociation on surface are important steps to understand poisoning embrittlement. If we improve insight into the fundamental mechanism, we may develop material that either resist sulfur poisoning or adsorb a limited amount of sulfur compounds, without highly blocking their chemical activity. Recently, adsorption of H_2S on different metal surface and alloy has been studied in some detail, especially close packet surface [1-9]. However, to the best of our knowledge there is no theoretical and experimental reports about the adsorption of H_2S on NiAl(110), despite representing a prototypical alloy surface [10-12]. Therefore, we hope this study may be helpful to further improve the understanding of the behavior of H_2S on alloy. Here, we report a density functional study to the characterize of H_2S on the NiAl(110) surface by examining the initial stages of adsorption, which may lead to formation of surface sulfides and hydrogen embrittlement of NiAl, both of which may be undesirable in industrial processes. Moreover, we have presented decomposition pathway of H_2S to SH and H and patway of

sulfuhydryl (SH) to H and S via sequential scission on the NiAl(110) surface.

2. Methodology

All calculations are based on DFT code and the use of Vienna *ab initio* simulation package (VASP) [13-14]. The code is using in a plane-wave basis set. The electron-ion interaction was described by pseudopotential with plane waves up to a kinetic energy cutoff of 30 Ry testing convergence in total energy. Exchange and correlation potentials are diagnosed with (non-local) generalized gradient corrections (GGA) [15] of Perdew and Zunger [16-17]. The Brillouin zone was employed at (6x4x1) Monkhorst-Pack [18] grid of k-points for the (2x2) surface reconstructed unit cell. We designed an artificially constructed periodic geometry along the surface normal. We choosed a five layer slab of NiAl substrate plus a vacuum region equivalent to about eight substrate layers in thickness, consecutive slabs were separated by ~12 Å. The center layer was kept fixed in bulk positions. All the remaining substrate atoms were allowed to relax into their minimum energy position. Molecular adsorption was allowed to relax on one side of the slab. We found equilibrium lattice constant for bulk NiAl 2.90 Å, in agreement well with the experimental measured value of 2.88 Å [19]. This theoretical value was used in calculations.

3. Results and discussion

3.1. Hydrogen sulfide (H$_2$S) adsorption and dissociation NiAl(110)

In all calculations, we used (2x2) surface unit cell with coverage of 0.125 monolayer (ML) [20]. For adsorbed molecule, we consider the hydrogen sulfide overlayer adsorbed only on one side of the slab. This allows us to obtain clean surface data and adsorbed molecule data. Optimized adsorption configurations may correlate both with size and with the electronegativity of the adatoms, i.e., with how strongly an atom will attract electrons from the surrounding atoms. Sulphur (2.58) has the largest electronegativity, followed by H (2.20), Ni (1.91), and Al (1.61). Electrons localize between the elements with the largest electronegativity difference, creating polar covalent bonds [21].

In order to obtain the most energetic binding site of H$_2$S to the NiAl(110) surface, the five high-symmetry sites have been considered as possible site preferences: A, B, C, D and E (in Fig. 1) and for the adsorption energy we used as Ref. [22]

$$E_{ads,x} = E_{x/NiAl(110)}^{tot} - E_x^{tot} + E_{NiAl(110)}^{tot})$$

where, $E_{x/NiAl(110)}^{tot}$ is the energy of the relaxed combine system (X-NiAl(110)), E_x^{tot} is the energy of a gas phase adsorbate and $E_{NiAl(110)}^{tot}$ is the energy of the relaxed clean NiAl(110) surface. The energies $E_{NiAl(110)}^{tot}$ and $E_{x/NiAl(110)}^{tot}$ have calculated in the same size supercell. Equilibrium geometry for the isolated atom have performed in a large boxes (20x20x20) Å for S, H, SH and H$_2$S. In addition, we examined case of adsorption of SH and H in the same supercell for the reaction path of H$_2$S. In this implies we saw that not to been lateral interaction between SH and H for adsorbed didn't gain energy. For the reaction path of SH we took adsorption of S and H in the same supercell. Fig. 2 display adsorption configurations of H$_2$S, and we have summarized their corresponding adsorption energies and atomic key parameters in Table 1. From energetic point of view, e model is energetically more favorable than the d model, by about 0.17 eV/molecule. The adsorption energies for these models are -1.37 eV and -1.20 eV, respectively. Our results are also confirm to H$_2$S/Fe(110) [5] and H$_2$S/Ni(111) [6]. In Table 1, we have also presented the height of S (H) atom over surface Al atom h$_{Al-S}$ (h$_{Al-H}$) and the height of S (H) atom over surface Ni atom h$_{Ni-S}$ (h$_{Ni-H}$).
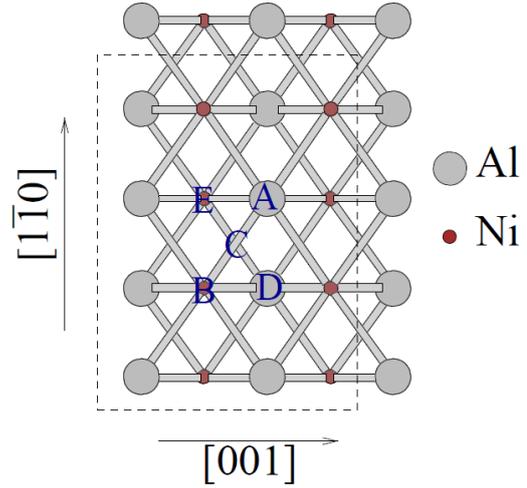
Fig.1. Schematic top view of the possible sites for H$_2$S on the NiAl(110)-(2x2) surface: A (on top of the Al), B (on top of the Ni atom), C (between the Ni atom and Al atom), D (Ni-Ni short bridge) and E (Al-Al short bridge). The dashed lines present the surface unitcell of (2x2).

According to our finding, S and H was found to adsorb on same site (2Ni-Al three fold minimum) of NiAl(110) while H was weakly adsorbed on NiAl(110), which agrees very well with theoretical *ab initio* studies. [20-21]. On the other hand, SH is found to adsorb on the Ni-Ni (but S is found Ni top) with adsorption energy -2.99 eV. In initial structures, the molecular plane of H$_2$S is parallel to the surface and the symmetry axis of H$_2$S is parallel to [001].

Table 1: Adsorption energy of H$_2$S on NiAl(110) E_{ads}, S-H bond length r_{S-H}, the height of S (H) atom over surface Al atom h$_{Al-S}$ (h$_{Al-H}$), the height of S (H) atom over surface Ni atom h$_{Ni-S}$ (h$_{Ni-H}$) and H-S-H bond angle Θ_{HSH}. Adsorption energy (in eV), bond angle (°) and distances (in Å).

Site	a	b	c	d	e
E_{ads}	-0.01	-0.02	-0.07	-1.20	-1.37
r_{S-H}	1.36	1.36	1.37	-	-
h$_{Al-S}$	3.66	3.32	2.62	1.67	1.21
h$_{Al-H}$	2.69	3.55	2.98	3.22	4.00
h$_{Ni-S}$	3.67	3.18	2.32	1.73	1.64
h$_{Ni-H}$	2.70	3.44	2.68	3.28	4.43
Θ_{HSH}	90.9	91.6	90.6	-	-

For H$_2$S molecule, it is found that an optimized bond length (r$_{S-H}$) and H-S-H angle (Θ_{HSH}) are 1.35 Å and 91.8°, respectively, which is very close to experimental values [23] of 1.34 Å and 92.1°. Similarly, optimized bond length of SH molecule is 1.346 Å which is confirm with the experimental value of 1.345 Å [24]. When we compare these results with Table 1 values (a-e), it is seen that changes between all the optimized geometries of H$_2$S is very small to be ignored. But in the model (d) and (e), hydrogen was in gaseous value, H-H bond length was measured 0.75 Å. In summary, we have found that the most favorable position for model e (see Fig. 2) for S is closer to the 2Ni-Al and two H atoms are away from to surface.
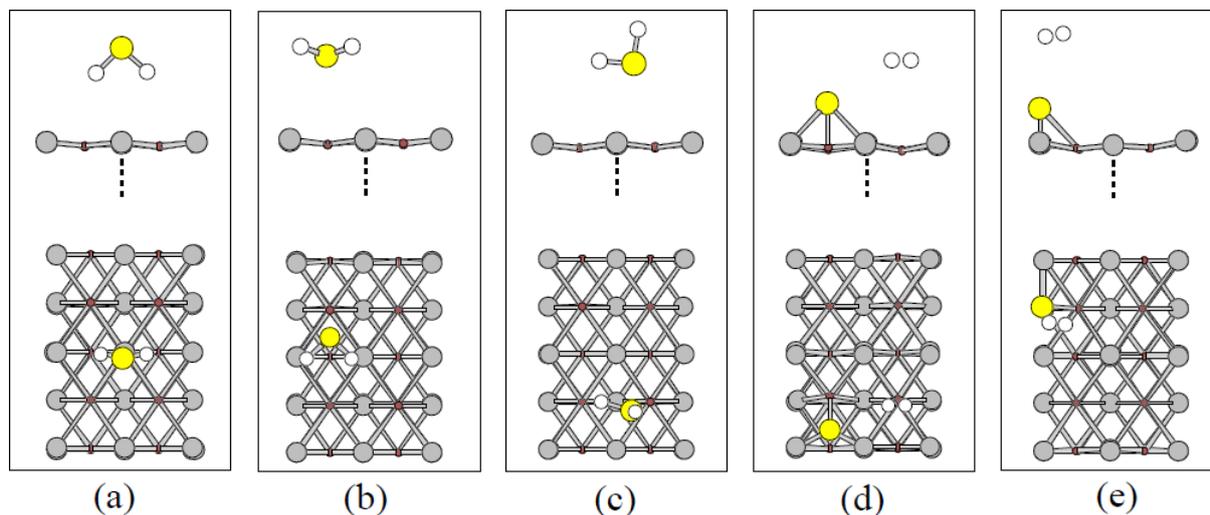
Fig. 2. The most stable adsorption sites for the five possible high-symmetry initial sites in Fig. 1. A, B, C, D and E. Upper panel is the side view, and lower panel is the top view. Ni atoms are in red (small), Al atoms are in grey, S in yellow, and H in white.

In order to explain this circumstance we have plotted density of states (DOS) diagrams in Fig. 3 (a), where the black line corresponds to a clean NiAl(110) while the red line represents H$_2$S/NiAl(110) for stable model (model e). In comparing the DOS of H$_2$S/NiAl(110)-(2x2) surface with that of the clean NiAl(110)-(2x2) surface, it is seen that there is a weak adsorption effect because of similarity in the overall characteristics of the two curves.

To gain more insight into the this adsorption, we have also calculated the partial density of states (PDOS) of H, S atom and the nearest Al and Ni atoms, which is shown in Fig. 3 (b). In this site (the most energetic), we can see that the H s bonding peak appears at 7 eV below the Fermi level. Compared with the S electronic states, the H s electronic state is localized as result of the cleavage of the S-H bond, which indicates that the H atom interacts with the S p states weakly (see also in Fig. 4).

As in Fig 3 (b), the S p and Al s states occupy similar energy regions, especially nearby -8 eV and 1 eV, which means that the S p interacts strongly with the Al s states. Compared with the Al electronic states, Ni s electronic state has similar peak, which means that the s p interacts with the Ni s states strongly.

In addition, the Ni s, p, d states also interact strongly with S s, p states at the 1 eV. In order to verify this result we have drawn partial electronic charge densities for the model e in Fig. 4. We have seen contribution of surface Ni d orbitals (see in left) and also pronounced σ-bonding between the s orbital of surface Al (blue) atoms and p orbital of S (yellow) atom (see in right) by cutting model e at different angles. As seen in figures, there was almost no charge transfer occurred between the molecule and the surface. This situation corresponds to a physisorbed structure.
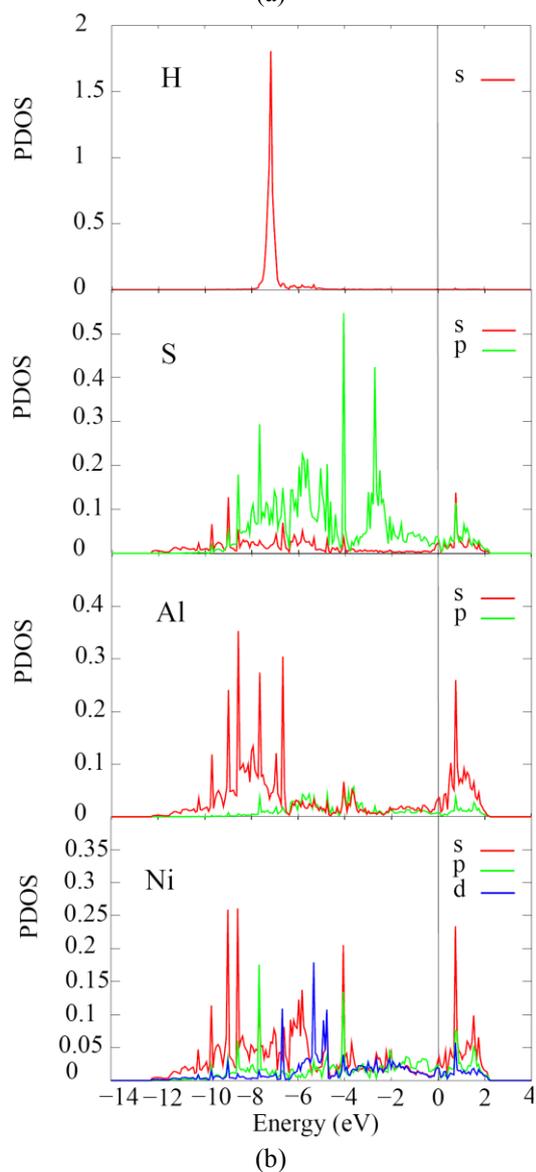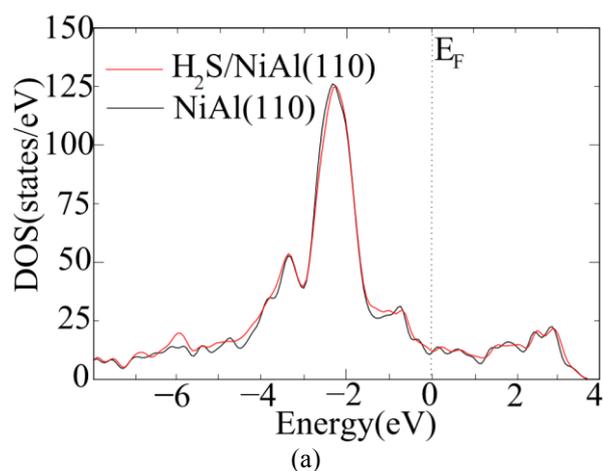
Fig. 3. (a), total density of states (DOS) of H₂S/NiAl(110) and clean NiAl(110), (b) partial density of states (PDOS) of the H₂S molecule (H and S atom) and the surface Al and Ni atom (the binding of the molecule). Fermi level is set to zero.
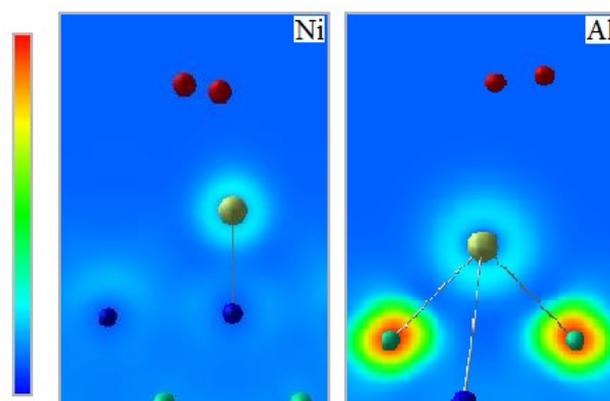
Fig. 4. (left) electronic charge density between Ni and S, (right) electronic charge density between Al and S.
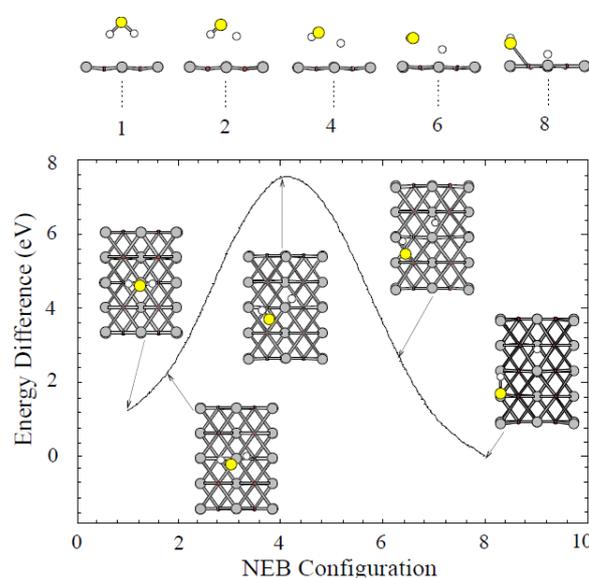
Fig. 5. Minimum-energy paths obtained with NEB calculations for H₂S dissociation to SH and H on the NiAl(110)-(2x2) surface.

The nudged elastic band (NEB) method [25] is carried out to find the transition states and characterize the reaction path for H_2S dissociation to SH and H on the NiAl(110) surface. In this method, a chain of intermediate structures are found by interpolating initial and final configurations. We have converged the migration process between the H_2S and SH-H using eight image points. For the H_2S, we choose first location at the position Al-top, lowest preferred adsorption sites, since it is almost degenerate whereas 2Ni-Al site is stable; S bends 2Ni-Al and H-H in gaseous value. We choose final location corresponding to SH and H adsorbed in their most stable site and the nearby Ni-Ni site for the SH molecule while H occupy a 2Ni-Al site.
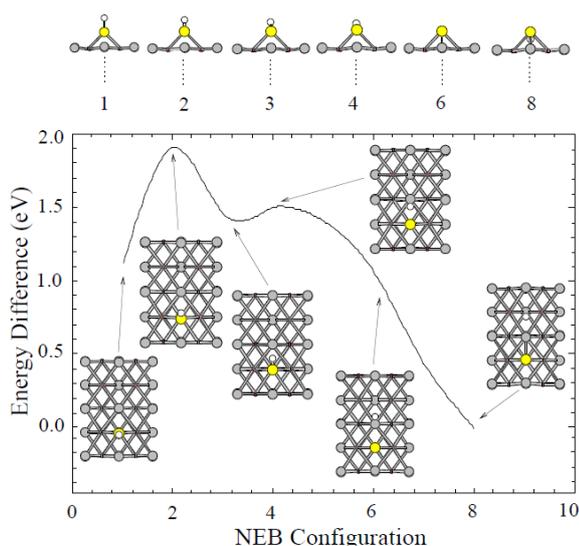
Fig. 6 Minimum-energy paths obtained with NEB calculations for SH on the NiAl(110)-(2x2) surface.

As seen from Fig. 5, the accompanying pictures are labeled with a number corresponding to where they would be located on the energy profile. With the climbing image scheme, the highest-energy image climbs uphill to the saddle point. We calculated energy barrier, 6.30 eV at this the saddle point. H_2S molecule bonds break one S-H bond and one H atom. After passing this energy barrier, the SH (H) moves to the 2Ni-Al (nearby Ni-Ni) site and lowering the energy as much as about 7.52 eV, which is necessary to produce final product. As seen from Fig. 5, the overall reaction is exothermic. In Fig. 2(e), we saw that the structure of H_2S more stable at the 2Ni-Al site than other sites. We can be predicted that the structure of H_2S changes towards this site. H_2S breaks one H-S bond and one H atom towards a nearby surface Ni atom. This situation explained Ni-dominated H adsorption sites on the NiAl(110) surface because the heat of adsorption of atomic hydrogen on pure Ni(110) is bigger than on pure Al(110) [26]. In this reaction path (between H_2S and SH and H), overall energy change is about 1.22 eV as seen in Fig. 5. Our results are in agreement with Alfonso favorable case [6].

3.2. Sulfuhydryl (SH) adsorption and dissociation on NiAl(110)

Sulfuhydryl is extremely unstable and a short-lived intermediate [7]. Firstly we have analyzed the results corresponding to the most stable SH configuration on surface. We have calculated the most energetic position nearby site with threefold coordination, with two Ni and one Al (S adsorbed to the 2Ni-Al and H atom bonded S atom), adsorption energy of SH (-2.99 eV) and optimized bond length (r_{S-H}) of 1.45 Å. In this configuration, SH lies nearly parallelized to surface (see also in Fig. 5 final state). We have also calculated some atomic key parameters, namely, the height of S (H) atom over surface Al atom h_{Al-S} (h_{Al-H}) as 2.18 Å (1.79 Å) and the height of S (H) atom

over surface Ni atom h_{Ni-S} (h_{Ni-H}) as 1.93 Å (2.05 Å) like H_2S.

We showed minimum energy pathway for dissociation SH in Fig. 6. For this middle reaction path we selected initial state adsorbed Ni-Ni site and final state, the most stable site of adsorbed atomic S and H. We saw 1.14 eV energy change in overall reaction step. We saw also first barrier is 0.8 eV and second barrier is about 0.05 eV in S-H scission. As seen from Fig. 6, curve has a one minimum, between first barrier and second barrier. We can say this second transition state is short time process. After passing second transition state distance of S and H increases for both atoms move towards stable site (Ni-Ni) which is necessary ~1.5 eV energy. We can say dissociation of SH is exothermic reaction as H_2S.

4. Conclusions

We have presented the details of the atomic geometry, electronic structure, adsorption energies, relative energies and reaction pathways of the H_2S on the NiAl(110) surface using periodic DFT calculations. The calculations show that H_2S molecule weakly binds nearby 2Ni-Al site, with the molecular bond break. In the lowest energy structure, H atoms prefer gas phase bonding trend, above a bridge site containing Ni and Al atoms, while S bond a threefold hollow site containing two Ni and one Al atom. All of these trends point to quite weakly interactions at this site. In the dissociation of H_2S to desorbed SH and H, we calculated a barrier, as 6.30 eV. Then in the dissociation of SH to desorbed atomic S and H, we calculated a barrier, as 0.80 eV. We saw that both dissociation H_2S and SH are exothermic reaction.

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