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DFT study on the sulfurization mechanism during the desulfurization of H2S on the ZnO desulfurizer

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Abstract

The sulfurization mechanism of H2S on the ZnO(1010) surface during the desulfurization of coal gas was investigated by using periodic density functional theory (DFT) calculations. The adsorption of H2S, SH, atomic S, and atomic H, as well as the coadsorption of SH and an H atom, and the coadsorption of S and two H atoms, were initially examined to identify energetically favorable intermediates. Potential energy profiles for three paths of H2S—ZnO(1010) interactions producing H2 and H2O were obtained, respectively. Our results show that H2S is preferred to dissociatively adsorb on the ZnO(1010) surface, followed by dehydrogenation process to form sulfur species. Molecular-level calculations demonstrate that H2O formation via the H2S—ZnO interaction is the most probable reaction pathway both kinetically and thermodynamically. ZnO has double functions during the desulfurization of H2S. One is as a catalyst to accelerate the dissociation of H2S, while the other is as the reactant participating in the reaction of H2S with ZnO to form H2O.

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1. Introduction

Sulfur compounds including H2S need to be reduced to low levels in natural gas, chemical synthesis gas and coal-derived fuel gas due to their negative effects on environment and chemical processing [12]. Metal oxides as candidate desulfurization sorbents have been investigated as desulfurizers for the removal of H2S [3–7]. Of the various oxides available, ZnO is known as a highly efficient desulfurizer [8–11]. A fundamental understanding of the interaction of H2S with ZnO is important by reason that ZnO can reduce the concentration of H2S to a few parts per million [12–14].

Sulfurization is the first process in desulfurization, which determines the desulfurization efficiency. Adsorption is the precondition of sulfurization. Experimental results show that H2S adsorption progresses via the chemical reaction of sulfide formation. In this system, a reaction takes place between the gas-phase reactant and the solid surface [15,16]: H2S + ZnO → H2O + ZnS. A more detailed study shows that ZnO is able to dissociate H2S at very low temperatures [17]. Adsorption of molecules on this oxide at approximately 100 K produces only Zn-bonded HS species, which decompose into S atoms at temperatures between 300 and 400 K. The reaction between H2S and ZnO at elevated temperatures of 400 K to 500 K produces H2O and ZnS: H2S(gas) + ZnO(solid) → H2O(gas) + ZnS(solid) [18,19]. Furthermore, the apparent kinetics of H2S removal by ZnO has been investigated via thermogravimetric analysis [20], and an activation energy of 19.32 kJ·mol−1 has been obtained. An activation energy of 30.31 kJ·mol−1 for the reaction between H2S and ZnO was obtained by Westmoreland et al. [21]. To date, experimental data on the sulfurization process, including each elementary step, are insufficient. Therefore, theoretical calculations will be helpful in elucidating the mechanism of this process. With the development of quantum chemistry, the density functional theory (DFT) method has already been extensively used to provide qualitative and quantitative insights into the structure of active surfaces, as well as into the surface reactions [22–24]. Rodriguez et al. [12] studied the adsorption and dissociation of H2S on the ZnO(0001) surface using first-principles density-functional calculations (DFT-GGA) and a periodic supercell, which showed that the strong bonding of H2S and its S-containing dissociated species (HS and S) on the ZnO(0001) surface facilitate the dissociation. Casarin et al. [25] studied H2S adsorption on the ZnO(1010) surface by using a local DFT coupled with the molecular-cluster approach, including molecular and dissociative adsorptions. They found that the dissociative chemisorption of H2S on the relaxed ZnO(1010) is highly favored. Desulfurizer is a special material, which has double roles during the desulfurization of H2S. One is that desulfurizers have catalytic capacity to dissociate H2S. The other is that desulfurizers participate in the desulfurization reaction as a reactant. However, only the adsorption processes of H2S on ZnO surfaces have been studied, the detailed interaction between H2S and the ZnO surface remains unclear, and the formation

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mechanism of the probable products is unknown. More importantly, the two roles of ZnO in the desulfurization process have not yet been elucidated.

In this study, the ZnO(1010) surface is chosen as the study surface because it is electrostatically stable and is shown to be the main surface of ZnO [26]. The adsorption of H2S and dissociated species on the ZnO(1010) surface, as well as the coadsorption of different dissociated species are discussed. The first-principles DFT and self-consistent periodic calculation are applied to systematically investigate the adsorption energies and adsorption geometries systematically. Meanwhile, the interaction of H2S with the ZnO(1010) surface is discussed to obtain the sulfuration mechanism of ZnO, which is important to illustrate the desulfurization process of ZnO. The two roles of ZnO during the desulfurization process of ZnO are discussed to obtain the sulfuration mechanism of ZnO, which is important to illustrate the desulfurization process of ZnO.

2. Computational modes and methods

2.1. Calculation methods

We have performed periodic density functional calculations using the Dmol³ program [27,28]. The PW91 gradient-corrected GGA functional of Perdew and Wang [29,30] was employed, which can give much better dissociation energies [31] and adsorption energies [32]. It is now widely used in molecular calculations. The double-numeric quality basis set with polarization functions (DNP) was used. The size of the DNP basis set was comparable to that of Gaussian 6–31 G **. The inner electrons of Zn atoms were kept frozen and replaced by an effective core potential (ECP), and other atoms in this study were treated with an all-electron basis set. Brillouin-zone integrations were performed using a 4×2×1 Monkhorst-Pack grid [33]. A Fermi smearing of 0.005 hartree and a 0.13 Å cut-off were used to improve the computational performance. Spin polarization was considered in all calculations. The tolerances of energy, force, and displacement convergence were 2×10⁻⁵ hartree, 4×10⁻³ hartree/Å, and 5×10⁻⁷ Å, respectively. All calculations were performed on an HP Proliant DL 380 G5 server system.

2.2. Surface models

The ZnO(1010) surface was modeled using a 6-layer slab and a p(2×2) supercell. The slab was periodically repeated in the x-y directions with a 1 nm vacuum region between the slabs in the z-direction. The optimized ZnO(1010) surface is shown in Fig. 1. The O and Zn atoms on the first layer are labeled, and hexagonal channels are composed of atoms in the first and second layers. In all calculations, the bottom two layers of the slab were kept fixed at their bulk-like positions, whereas the remaining atoms in the top four layers, as well as the adsorbed molecules or atoms, were allowed to relax. Considering that the effect of layers on the surface and the electronic coupling between adjacent slabs, an 8-layer slab model and a larger model p(3×2) supercell were used in calculating the adsorption energy of H2S on the ZnO(1010) surface. Our results show that the energy differences were only 1.29 and 3.12 kJ·mol⁻¹, corresponding to the 6-layer slab with p(2×2) supercell, respectively.

The adsorption energies, E_{ads}, are calculated as follows:

\[ E_{ads} = E_{tot(ads)} + E_{tot(slab)} - E_{tot(ads/slab)} \]  

(1)

where \( E_{tot(ads)} \) is the total energy of the free adsorbate in the gas phase, \( E_{tot(slab)} \) is the total energy of the bare slab, and \( E_{tot(ads/slab)} \) is the total energy of the slab with adsorbate in its equilibrium geometry. By this definition, a positive \( E_{ads} \) value corresponds to an exothermic adsorption. Furthermore, the more positive the \( E_{ads} \) is, the stronger the adsorption is.

Transition state (TS) search was performed at the same theoretical level with the complete linear synchronous transit/quadratic synchronous transit (LST/QST) method [34]. In this method, the LST maximization was performed, followed by an energy minimization in the directions that conjugate to the reaction pathway to obtain an approximated TS. The approximated TS was used to perform QST maximization, followed by another conjugated gradient minimization. The cycle was repeated until a stationary point was located. TS confirmation is performed on every transition state structure to confirm that they lead to the desired reactants and products using the nudged elastic band (NEB) method.

The reaction energy (\( \Delta E \)) and the activation energy (\( E_a \)) are defined as follows:

\[ \Delta E = E_{(p)} - E_{(R)} \]  

(2)

\[ E_a = E_{(TS)} - E_{(R)} \]  

(3)

where \( E_{(p)} \) is the energy of the product in each reaction, \( E_{(R)} \) is the energy of the reactant in each reaction, and \( E_{(TS)} \) is the energy of the transition state in each elementary reaction.

3. Results and discussion

3.1. Calculations of H2S molecule and ZnO

The accuracy of the computational method used in this study has been tested by describing the properties of H2S molecule in gas phase and the lattice constants of bulk ZnO. The bond length and bond angle of molecular H2S calculated by our approach are 0.1354 nm and 91.34°, which are in good agreement with the experimental values of 0.1336 nm and 92.12° [35], respectively. The calculated lattice parameter for bulk ZnO is \( a = b = 0.3306 \) nm and \( c = 0.5236 \) nm in comparison with the experimental value of \( a = b = 0.3249 \) nm and \( c = 0.5205 \) nm [36]. The largest deviations in the calculated values from the experimental ones are only 1.75% and 2.32%, respectively. The calculated lattice constants are also in good agreement with other similar GGA results [37]. The calculated ZnO bond length is 0.2036 nm in bulk, which shortens by 0.0148 nm to become 0.1885 nm in the surface. The Zn atom relaxes inward, whereas the O atom expands, resulting in a buckling of the surface layer and tilting angle (\( \theta \)) is 9.899°, which is consistent with previously reported GGA-PW91 results [38], as well as the experimental results of Duke et al. [39]. They concluded from their best low-energy electron diffraction analysis that the top-layer Zn ion is displaced downward by \( \Delta d(Zn) = -0.005 \pm 0.01 \) nm and likewise the top-layer oxygen by \( \Delta d(O) = -0.005 \pm 0.01 \) nm, leading to a 12° ± 5° tilt of the Zn-O dimmer. Above results obtained in these tests make us confident in pursuing the next step of our investigations.

3.2. Adsorption of single species on the ZnO(1010) surface

The adsorbed structures of single species involved in the desulfurization of H2S are shown in Fig. 2, and the main bond lengths and the adsorption energies are listed in Table 1.
3.2.1. H2S adsorption

When H2S is placed on the top of Zn1 with S atom, two H atoms face O3 and O4 in the initial structure, the optimized structure is H2S(a) (in Fig. 2). We can see that the H2S molecule is dissociatively adsorbed on the ZnO(1010) surface, consistent with the experimental observations [17]. The adsorption energy is 131.58 kJ·mol⁻¹, and the S—H1 bond is elongated to 0.2211 nm corresponding to 0.1354 nm of H2S in gas phase. The other adsorption structure is molecular, H2S(b), in which two H atoms are toward O1 and O2. The adsorption energy is 51.00 kJ·mol⁻¹, which is lower than that of H2S(a). The dissociative adsorption of H2S is thus clearly favorable. Casarin et al. [25] have also studied H2S adsorption on the ZnO(1010) surface with the cluster model. They found that H2S is preferred to dissociatively adsorb on the ZnO(1010) surface. The experimental studies by Galtayries et al. [5] show the same results about the dissociative adsorption of H2S on the Cu2O(111) surface using X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopies (ISS). However, both the molecular and dissociative interactions are investigated during H2S adsorption by Casarin et al. [40]. Only the molecular adsorption of H2S on the perfect Cu2O(111) surface is obtained in our recently study [41], and the dissociative adsorption of H2S occurs predominantly on the oxygen-vacancy surface. H2O is similar in structure to H2S, but has a different adsorption state. The results show that a H2O is fully molecularly adsorbed on the ZnO(1010) surface with p(2×2) supercell, however partial dissociation may be possible at elevated temperatures or coverage of H2O molecules [42–44].

3.2.2. SH adsorption

Initially, two stable configurations [SH(a) and SH(b)] of SH adsorption on the ZnO(1010) surface are obtained. In SH(a), the S atom is bond to two Zn atoms of surface in the adjacent hexagonal channels via the bridge bond mode, while the H atom lies toward O1 and O2. The adsorption energy is 142.21 kJ·mol⁻¹. SH(b) is similar to the SH(a), with nearly similar S—Zn bond lengths and adsorption energies. The only difference between the two structures is that the H atom in

![Fig. 2. The geometric structures of H2S, SH, S and H on the ZnO(1010) surface optimized by the GGA-PW91 functional.](image)
The properties of single species adsorbed on the ZnO(1010) surface with different adsorption modes calculated from the GGA-PW91 functional.

<table>
<thead>
<tr>
<th></th>
<th>r(S–Zn1)</th>
<th>r(S–H1)</th>
<th>r(S–H2)</th>
<th>r(S–Zn2)</th>
<th>r(S–O3)</th>
<th>r(S–O1)</th>
<th>r(H–O)</th>
<th>E_{ads}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S(a)</td>
<td>0.2323</td>
<td>0.2211</td>
<td>0.1156</td>
<td>0.4397</td>
<td></td>
<td></td>
<td></td>
<td>131.58</td>
</tr>
<tr>
<td>H$_2$S(b)</td>
<td>0.2557</td>
<td>0.1368</td>
<td>0.1154</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>51.00</td>
</tr>
<tr>
<td>SH(a)</td>
<td>0.2441</td>
<td>0.1358</td>
<td>0.1154</td>
<td>0.2439</td>
<td></td>
<td></td>
<td></td>
<td>142.21</td>
</tr>
<tr>
<td>SH(b)</td>
<td>0.2443</td>
<td>0.1358</td>
<td>0.2439</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>140.14</td>
</tr>
<tr>
<td>SH(c)</td>
<td>0.2299</td>
<td>0.1376</td>
<td>0.4258</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>121.74</td>
</tr>
<tr>
<td>S(a)</td>
<td>0.2374</td>
<td>0.1825</td>
<td></td>
<td>0.0975</td>
<td></td>
<td></td>
<td></td>
<td>198.86</td>
</tr>
<tr>
<td>S(b)</td>
<td>0.2353</td>
<td>0.2348</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>123.16</td>
</tr>
<tr>
<td>S(c)</td>
<td>0.2253</td>
<td>0.1748</td>
<td></td>
<td>0.0975</td>
<td></td>
<td></td>
<td></td>
<td>265.14</td>
</tr>
<tr>
<td>H(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0975</td>
<td></td>
<td></td>
<td>75.81</td>
</tr>
<tr>
<td>H(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0975</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: the unit of bond length is nm, and the unit of $E_{ads}$ is kJ·mol$^{-1}$.

3.3. Coadsorption of dissociated species on the ZnO(1010) surface

In order to investigate the desulfurization process of H$_2$S on the ZnO(1010) surface, it is necessary to investigate the coadsorption of dissociated species of H$_2$S, namely, the coadsorption of SH and H, as well as the coadsorption of S, H and O, respectively. The main bond lengths and coadsorption energies are listed in Table 2.

3.3.1. SH and H coadsorption

As above mentioned, two stable adsorption structures of SH on the ZnO(1010) surface are obtained. Based on these two configurations, two coadsorption configurations of SH and H on the ZnO(1010) surface were investigated, see SH+H(a) and SH+H(b) in Fig. 3. It can be seen that H atom is located at the O-top site on the ZnO(1010) surface, and SH is bonded to two Zn atoms of the surface in the adjacent hexagonal channels. There is only a difference of 4.60 kJ·mol$^{-1}$ in coadsorption energy.

3.3.2. S, H and H coadsorption

As shown in Fig. 3, the most stable coadsorption structure is that two H atoms are on the two O atoms of surface in two adjacent hexagonal channels, and the S atom adsorb on two Zn atoms in the adjacent hexagonal channels via the bridge bond mode, while the adsorption mode of single S atom is the most unstable. S+2 H(a) is especially noted, the original structure is S atom bridging Zn and O based on S(a), and two H atoms placed on the O-top sites. After optimization, the S atom adsorbs on two adjacent Zn atoms with bridge bond mode. S+2 H(b) have similar structure, the difference is that S and two H atoms coadsorb on two adjacent Zn–O bonds in S+2 H(a), while in S+2 H(b), the coadsorbed S and H atoms are placed on two adjacent hexagonal channels. The difference of coadsorption energy is 49.62 kJ·mol$^{-1}$. S+2 H(c) is the optimized structure of the most stable adsorption of single S atom S(c) combining with two H atoms, the coadsorption energy is 656.19 kJ·mol$^{-1}$, which is the most unstable in the three coadsorption configurations.

Table 2

The properties of dissociated species coadsorbed on the ZnO(1010) surface with different adsorption modes calculated from the GGA-PW91 functional.

<table>
<thead>
<tr>
<th></th>
<th>r(S–Zn1)</th>
<th>r(S–H2)</th>
<th>r(S–Zn2)</th>
<th>r(S–O3)</th>
<th>r(H1–O3)</th>
<th>r(H2–O4)</th>
<th>E_{ads}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH + H(a)</td>
<td>0.2467</td>
<td>0.1358</td>
<td>0.2455</td>
<td>0.0974</td>
<td>0.2737</td>
<td>507.34</td>
<td></td>
</tr>
<tr>
<td>SH + H(b)</td>
<td>0.2453</td>
<td>0.1355</td>
<td>0.2456</td>
<td>0.0975</td>
<td>0.2737</td>
<td>511.94</td>
<td></td>
</tr>
<tr>
<td>S + 2 H(a)</td>
<td>0.2307</td>
<td>0.2310</td>
<td>0.1808</td>
<td>0.0999</td>
<td>0.0999</td>
<td>851.55</td>
<td></td>
</tr>
<tr>
<td>S + 2 H(b)</td>
<td>0.2393</td>
<td>0.2393</td>
<td>0.0977</td>
<td>0.0977</td>
<td>656.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S + 2 H(c)</td>
<td>0.2244</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: the unit of bond length is nm, and the unit of $E_{ads}$ is kJ·mol$^{-1}$.
Fig. 3. The coadsorption structures of dissociated species of H$_2$S on the ZnO(10\(\overline{1}0\)) surface optimized by the GGA-PW91 functional.

Fig. 4. The structures of transition states and products obtained by the GGA-PW91 functional.
3.4. Reaction mechanism of H$_2$S—ZnO(1010) interactions

To characterize the probable reaction pathways of H$_2$S on the ZnO(1010) surface, we applied energetically the most stable adsorption configuration H$_2$S(a) as the reactant. According to the reaction process, the coadsorption configuration SH + H(a), the coadsorption configuration S + 2 H(b) and S + 2 H(c) are selected as intermediates. Fig. 4 shows the optimized structures of the transition states and products, their partial bond lengths are listed in Table 3. Fig. 5 shows the potential energy profiles for the interaction of H$_2$S with the ZnO(1010) surface. The relative energy of each configuration to the reactant is also listed, and the reaction energies ($\Delta E$) and activation energy ($E_a$) of each elementary reaction can be obtained according to Eqs. (2) and (3). In Path 1, H$_2$S is dissociatively adsorbed on the ZnO(1010) surface without a tight transition state. This is the first dehydrogenation process. However, H$_2$S is weakly molecularly bound to the CeO$_2$(111) surface with a binding energy of 14.65 kJ·mol$^{-1}$, then a little energy barrier of 7.95 kJ·mol$^{-1}$ is needed for the first dehydrogenation by the DFT calculation [24]. On the CeO$_2$(111) surface, an energy barrier of 52.40 kJ·mol$^{-1}$ is needed to overcome [41]. The bond dissociation energy of H—S is about 381.40 kJ·mol$^{-1}$ [49] in gas, indicating that ZnO has the catalytic effect on the dissociation of H$_2$S. It is the first role of ZnO during the desulfurization of H$_2$S. S atom bonds to Zn with single bond, which is unstable according to the above calculation of SH adsorption. The S atom in SH changes the adsorption mode via TS1 leading to SH + H(a) with a small activation energy of 35.66 kJ·mol$^{-1}$. In this configuration, the S atom bridges two Zn atoms in two adjacent hexagonal channels. The SH species is an important reactive intermediate, which has also been investigated by FT-IR in the interaction of H$_2$S with Fe$_2$O$_3$ [50]. This step of SH changing the adsorption mode is endothermic by 6.13 kJ·mol$^{-1}$. The bond length of S—Zn1 elongates from 0.2323 nm in dissociative H$_2$S molecule via 0.2327 nm in TS1 to 0.2467 nm in SH + H(a), while the S—Zn2 bond shortens from 0.4397 nm in H$_2$S(a) via 0.3335 nm in TS1 to 0.2455 nm in SH + H(a). Then the second dehydrogenation step takes place from SH + H(a) to S + 2 H(b). H$_2$ transfers from S to O4 by overcoming a reaction energy barrier of 51.47 kJ·mol$^{-1}$ at TS2, producing S + 2 H(b) with a reaction energy of 20.75 kJ·mol$^{-1}$ compared to SH + H(a). The energy barriers of 35.17 kJ·mol$^{-1}$ and 82.70 kJ·mol$^{-1}$ are needed for the second dehydrogenation of H$_2$S on the CeO$_2$(111) surface [24] and Cu$_2$O(111) surface [42], respectively. At the transition state TS2, the breaking S—H and forming O—H bonds in TS2 are 0.1642 and 0.1397 nm, respectively. Finally, S + 2 H(b) can undergo an H$_2$ forming process giving P1. However, the TS confirmation calculation shows that an intermediate similar to SH + H(a) existed in this step, which suggests that an H$_2$ molecule can be directly formed by SH + H(a). The formation of P1 via TS3 from SH + H(a) is investigated, and an activation energy of 318.99 kJ·mol$^{-1}$ is needed, suggests that this pathway is less favorable. In P1, the distances between H1 and O3, and between H2 and O4 are 0.3025 and 0.3296 nm, which show that the interaction between the formed H$_2$ and the ZnO surface is negligible; The S atom is adsorbed on two Zn atoms in the adjacent hexagonal channels via the bridge bond mode, which is the most unstable structure of single S adsorption. Thus, other pathways are investigated, and the results are discussed in the subsequent paragraphs.

Path 2 has steps which are different from Path 1. H$_2$S(a) undergoes dehydrogenation steps to S + 2 H(b) via the intermediate SH + H(a). Starting from S + 2 H(b), the S atom changes the adsorption mode from bridging two adjacent Zn atoms to bonding to a Zn—O bond via the bridge bond mode, leading to S + 2 H(c) via TS4 with a reaction barrier of 219.97 kJ·mol$^{-1}$, which is 99.02 kJ·mol$^{-1}$ lower than that of the SH + H(a) → P1 step. The breaking S—Zn2 and forming S—O1 bonds are 0.3708 nm and 0.2318 nm in TS4, respectively. S + 2 H(c) is converted

Fig. 5. Potential energy profiles for the interaction of H$_2$S and ZnO(1010) surface. The energies are relative to that of the adsorption structure of H$_2$S calculated from the GGA-PW91 functional.
to P2 leading to final products H2 and S adsorbing on the ZnO(1010) surface via a transition state TS5 involving the bonds H1−O3 and H2−O4 cleavage. TS5 is predicated to be 199.45 kJ·mol−1 higher in energy than S+2H(c), which is 119.54 kJ·mol−1 lower than that of the SH+H(a)→P1 step.

In Path 3, all of the steps are identical to those in Path 2 except for the last step. H2 is eliminated from S+2H(c) in Path 2, whereas in Path 3, two HO surface species in S+2H(c) can undergo H-migration via TS6 with a small reaction barrier of 97.55 kJ·mol−1, leading to the formation of a H2O-containing P3 product via an exothermic process of 55.77 kJ·mol−1. H2O is also investigated as the final product in the interaction of H2S with other metal oxides, such as Fe2O3 [48], CoO [51], Cu2O [5]. In this step, the distance between H1-O3 increases from 0.0978 nm in S+2 H(c) via 0.1249 nm in TS6 to 0.5147 nm in P3. Due to the formation of an H2O species, an oxygen vacancy is generated in the surface. The oxygen vacancies on the WO3 surface during the interaction of H2S and WO3 have also been investigated via XPS, as well as via ultra-high vacuum (UHV) and ultraviolet photoelectron spectroscopy (UPS) [52,53]. During the formation of H2O, ZnO acts as a reactant via ultra-high vacuum (UHV) and ultraviolet photoelectron spectroscopy (UPS). The formation of H2O, ZnO acts as a reactant in the reaction of H2S with ZnO, which is the second role of ZnO during the desulfurization of H2S.

From Fig. 5, we can see that the total reaction energy of the H2O-forming path is 166.47 kJ·mol−1, which is the lowest among all three paths. This result shows that the H2O-forming path is the most thermodynamically favorable. From the kinetic point of view, the activation energy of the step (SH+H(a)→P1) is 318.99 kJ·mol−1, which is the highest in Path 1. Therefore, this step is the rate determining step in Path 1. While in Path 2 and 3, the same rate determining step (S+2 H(b)→S+2 H(c)) is overcome, the activation energy is 219.97 kJ·mol−1, which is 99.02 kJ·mol−1 less than that of Path 1. In addition, a high energy of 421.69 kJ·mol−1 is needed in TS5 for Path 2. So the H2O-forming process is the most favorable reaction pathway for the H2S−ZnO interaction both kinetically and thermodynamically. The results are similar to those obtained from the interaction of H2S with the CeO2(111) surface, which shows that the H2O-forming pathway is also energetically more favorable than the H2S-forming pathway [24].

3.5. Comparison of different functionals

To investigate the influence of different functionals on the study results, the adsorption energy of H2S on the ZnO(1010) surface and the potential energies in the H2O-forming pathway have been calculated using the GGA-PW91, GGA-BLYP (generalized gradient approximation with the Becke-Lee-Yang-Parr), and LDA-PWC (local spin density approximation with the Perdew–Wang correlational) functionals.

The adsorption energies of H2S on the ZnO(1010) surface are 131.58, 108.34 and 171.62 kJ·mol−1 at the GGA-PW91, GGA-BLYP, and LDA-PWC functional levels, respectively. It can be seen that the energy difference between the GGA-PW91 and GGA-BLYP functionals is little, whereas the LDA-PWC adsorption energy is 40.04 and 63.28 kJ·mol−1 higher than those of GGA-PW91 and GGA-BLYP, respectively. Obviously, the LDA approximation often overestimates the adsorption energy [54]. As the energetically favorable path, the H2O-forming pathway during the interaction of H2S and ZnO(1010) surface has been selected to determine the influence of different functionals. Every equilibrium structure has been optimized, and the transition states are searched at the GGA-BLYP and LDA-PWC levels, which can be seen in the supplemental materials. A comparison of the potential energies at the three functional levels is shown in Fig. 6. We can see that the three functionals have little influence on the bond lengths of all structures. The different functionals yield nearly similar results for the relative reaction energy. The rate determining step for all functionals is S+2 H(b)→S+2 H(c), and the activation energies at the GGA-PW91, GGA-BLYP and LDA-PWC levels are 219.97, 192.56 and 227.48 kJ·mol−1, respectively.

In summary, the different functionals have influence on the adsorption energy. In particular, LDA approximation often overestimates the adsorption energy. However, the effects of these functionals on the relative reaction energy are negligible.

4. Conclusions

Using the DFT method, a periodic slab model study has been carried out to investigate the adsorption of three types of sulfur-containing species (H2S, SH and atomic S) and atomic H, as well as the coadsorption of SH and H, and of S and two H. The interaction of H2S with ZnO(1010) was also investigated. The results show that the dissociative adsorption of H2S molecule on the ZnO(1010) surface is preferred, which is in agreement with experimental observations [17]. The most stable configuration for SH adsorption on the ZnO(1010) surface is that the S atom is bonded to two adjacent Zn atoms of the surface via the bridge bond mode. The S atom bridging a Zn−O bond is the most stable configuration for single S atom adsorption. The H atom is preferentially adsorbed on the O-top site on the ZnO(1010) surface.

In the coadsorption structure of SH and H, the adsorption sites are the same as the sites of SH and H adsorption separately. In the coadsorption
structure of S and ZH2, the most stable structure is that the S atom is adsorbed on two adjacent Zn atoms via the bridge bond mode, and two H atoms are located on the O-top sites. However, this adsorption mode of single S atom is the most unstable.

Finally, the potential energy profiles for the H2S-ZnO(1010) interactions have been obtained. The surface adsorbrates formed through the dehydrogenation processes can further eliminate H2S, or react with oxygen anions to form H2O. According to our calculations, the H2O-forming via H2S-ZnO Interaction is the most probable reaction route both kinetically and thermodynamically. The same conclusions can be obtained when different functional levels are used.

ZnO has double roles during the desulfurization of H2S, one is as a catalyst to accelerate the dissociation of H2S, and the other is as the reactant participating in the reaction of H2S with ZnO leading to the formation of H2O. It is the first reason that the desulfurizer is different from the catalyst. The second reason is that an oxygen vacancy is generated in the surface during the formation of H2O, and S of H2S can be deposited on the surface leading to the loss of sulfurization activity of ZnO, but which can be regenerated in oxidational atmosphere to prolong the lifetime of ZnO.

In addition, sulfurization and regeneration are two important processes for the desulfurization, both of which determine the desulfurization efficiency and lifetime of ZnO. The regeneration mechanisms of the sulfurized and oxygen-decorated ZnO(1010) surfaces in the presence of O2 will be investigated in subsequent studies.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.fuproc.2012.08.001.

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