Theoretical exploration of the interaction between hydrogen and pyrite-type FeS\textsubscript{2} surfaces

Jinjia Liua,b,c, Tao Yangd, Qing Penge,⁎, Yong Yanga,b, Yong-Wang Lia,b,d, Xiao-Dong Wena,b,d,⁎

a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China
b National Energy Center for Coal to Clean Fuels, Synfuels China Co., Ltd, Huairou District, Beijing 101400, PR China
c University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing 100049, PR China
d Beijing Advanced Innovation Center for Materials Genome Engineering, Industry-University Cooperation Base between Beijing Information S&T University and Synfuels China Technology Co. Ltd, Beijing, PR China
e Physics Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

ARTICLE INFO
Keywords:
Pyrite FeS\textsubscript{2} Hydrogen adsorption Bonding analysis High coverage Surface reduction

ABSTRACT
Elucidating the interactions between hydrogen and catalysts under complex realistic conditions is of great importance in rationally modulating the catalytic performance of hydrogenation processes. Herein, we have investigated the interaction between hydrogen and four typical surfaces, (100), (210), (211), and (311) of pyrite FeS\textsubscript{2} through density functional theory calculations. On (210) surface, the hydrogen dissociative adsorption on unsaturated-coordination sulfur atoms is favorable both in thermodynamics and kinetics. The hydrogen activation barrier is 0.83 eV with slight exothermic of 0.12 eV on (311). While on (100) and (211) surface, the hydrogen dissociation is unfavorable due to the high activation barriers and remarkable positive reaction energies. For high adsorption coverage, the pure molecule adsorption mode is favorable on (100) facet, opposed to the other surfaces which have temperature and pressure dependence. The saturated coverage sequence is (100) > (210) > (211) > (311) for a wide range of temperature and pressure. The remove of sulfur atoms most likely occurs on (210) surface. Our atomistic insights might be useful in engineering hydrogen-involved processes catalyzed by iron sulfide.

1. Introduction
Due to the abundant reserves on the Earth, pyrite FeS\textsubscript{2} has been widely used in biogeochemistry, material science and chemical industry areas. It could be served as magnetic materials [1,2], photovoltaic components [3,4], and anode materials of battery [5–7]. In heterogeneous catalysis field, pyrite FeS\textsubscript{2} has been extensively employed in numerous catalytic processes, including hydrogenation [8,9], hydrodesulfurization [10], hydrodeoxygenation [11], hydrogenitrogenation [12], and electrochemical water splitting reactions, etc. [13,14]. Among these reactions, it is inevitable to involve the hydrogen adsorption, activation, re-combination, and H\textsubscript{2}S desorption on catalyst surfaces, these steps play important roles in the catalytic circles.

It has been demonstrated that when noble transition metal (TM) sulfides (TMS), such as MoS\textsubscript{2} or RuS\textsubscript{2}, are exposed to hydrogen atmosphere, the hydrogen molecule is preferred to bond with surface metal atoms. Then, the heterolytic dissociation could conduct and form TM-H and S-H moieties [15–17]. Jalowiecki et al. demonstrated that the adsorption coverage of hydrogen is dependent on the ratio of surface metal and sulfur atoms [18]. To the best of our knowledge, there are some investigations on the interaction between hydrogen and FeS\textsubscript{2} surfaces by experimental or theoretical approaches. Liu and co-workers investigated the NH\textsubscript{3} synthesis on well-ordered FeS\textsubscript{2}(100) surface under low temperature, and the hydrogen molecule is not witnessed on (100) surface by experimental characterizations at the temperature of 170 K. After hydrogen molecule dissociation on hot filament, the atomic hydrogen could bond to pyrite surface. Besides, the recombination of atomic hydrogen and desorption of H\textsubscript{2} could conduct at 225 K, suggesting the interaction between atomic hydrogen and (100) substrate is rather weak [19]. Meanwhile, they reported in later work that the H\textsubscript{2}S desorption could be detected at 260 K by Temperature Programmed Desorption (TPD) spectra, indicating that the migration of atomic hydrogen on hot filament, the atomic hydrogen could bond to pyrite surface. Besides, the recombination of atomic hydrogen and desorption of H\textsubscript{2} could conduct at 225 K, suggesting the interaction between atomic hydrogen and (100) substrate is rather weak [19]. Meanwhile, they reported in later work that the H\textsubscript{2}S desorption could be detected at 260 K by Temperature Programmed Desorption (TPD) spectra, indicating that the migration of atomic hydrogen on hot filament, the atomic hydrogen could bond to pyrite surface. Besides, the recombination of atomic hydrogen and desorption of H\textsubscript{2} could conduct at 225 K, suggesting the interaction between atomic hydrogen and (100) substrate is rather weak [19].
somewhat lower than 500 °C [21]. Poulios et al. revealed the different interaction modes between hydrogen molecule and crystal facets of FeS2. They found that the hydrogen molecule could selectively convert FeS2 surfaces other than the (100) to FeS, but the selective attack on surfaces by atomic hydrogen is not detected, indicating that the hydrogen dissociation on (100) surface is reluctant [22]. Recently, pyrite FeS2 has been extensively studied serving as an efficient catalyst for hydrogen evolution reaction with lower overpotential [23–25], suggesting the moderate adsorption energy of hydrogen atoms and feasible desorption of hydrogen molecule on FeS2 surfaces. Ran et al. used theoretical method and demonstrated that the hydrogen evolution reaction on FeS2(210) surface is exothermic with released energy of 0.55 eV, and (210) surface presents superior catalytic activity compared to (100) surface [26].

These previous studies indeed enrich the understanding of interaction between hydrogen and pyrite surfaces. However, the interaction from a microcosmic or even atomic perspective is still unclear, especially for high miler-index facets and high adsorption coverage. Density functional theory (DFT) provides a powerful characterization approach to reveal the adsorbate behavior on solid surfaces in heterogeneous catalysis processes. Therefore, in the current work, we employed DFT approach combined with ab initio atomistic thermodynamics to investigate the hydrogen adsorption on FeS2 surfaces under different coverage and dynamic external conditions. The electronic interaction between hydrogen and substrate was studied from a chemical bonding insight. At last, the equilibrium phase diagram between hydrogen adsorption and surface reduction was explored at various temperatures and gaseous pressures.

2. Calculation models and methods

2.1. Calculation models

The most exposed surfaces of micro-crystal morphology of FeS2 are (100), (210), (211), and (311) [27]. These four surfaces were selected to explore the interaction with hydrogen, and the surface structures were presented in Fig. 1. A (2 × 2) supercell slab model with 12 atomic layers of ~9.36 Å thickness was used for (100), a (2 × 1) supercell slab model with 15 atomic layers of ~7.96 Å thickness was used for (210), and (1 × 1) supercells with 15 atomic layers of ~7.78 Å and 17 atomic layers of ~7.66 Å were used for (211) and (311), respectively. Note that in (210), (211), and (311) surface models, the distance between some adjacent layers was very close, so we considered them as the same layer if the distance is smaller than 0.2 Å. By comparing with previous studies [25,28] and according to our convergence test (Table S1), the atomic layers were thick enough to eliminate their influence on calculation results. In (100) model, there are 32 Fe and 64 S atoms, where the bottom two S-Fe-S layers were fixed (~3.97 Å), and the other layers were allowed to relax to their equilibrium positions. For (210) surface model, it contains 28 Fe and 64 S atoms, where 16 Fe and 32 S were relaxed, and others (~3.06 Å) were kept in their positions as in the bulk phase. The (211) model contains 14 Fe and 32 S atoms, where 8 Fe and 16 S atoms were relaxed and the others (~3.37 Å) were fixed. The (311) surface model contains 16 Fe and 38 S atoms, 12 Fe and 27 S atoms were relaxed, and the others (~1.63 Å) were frozen. According to our test (Table S2), the value of fixed layers used here has little influence on calculation results.

2.2. Computation details

All spin-polarized calculations were performed with VASP code [29]. The interaction between electron and ion was described by the projector augmented wave pseudopotential (PAW) [30]. The electron exchange and correlation energy was treated by generalized gradient approximation with Perdew–Burke–Ernzerhof formalism (GGA-PBE) [31,32]. The van der Waals correction (D3 with Becke–Jonson damping) was also considered [33,34]. The Γ-point-centered Monkhorst-Pack k points was used to sample the Brillouin zone. Based on convergence test (Table S3), 2 × 2 × 1 was used for (100) and (210) surface, 3 × 3 × 1 for (211) and 2 × 3 × 1 for (311) planes. The plane cutoff of energy of 400 eV was used to describe the electronic wave function. The criterion for self-consistent iterations is that the change in energy between successive steps is converged to 1.0 × 10−4 eV/atom, and the forces on each atom are converged to 0.03 eV/Å. In all slab models, the vacuum was set to 15 Å. Compared to the previous used ones in iron sulfide [25,35] and according to our convergence test (Table S4), the vacuum layer of 15 Å is thick enough to neglect the slab slab interaction.

We used adsorption energy (E_{ads}) and stepwise adsorption energy (ΔE_{ads}) to evaluate the interaction between hydrogen species and surface without considering the effect of temperature and pressure. The adsorption energy was calculated based on Eq. (1), where \(E_{H2/slab}\) and \(E_{H/slab}\) is the total energy of the slab with hydrogen adsorbed, \(E_{slab}\) is the energy of bare surface, and \(E_{H}\) is the energy of gaseous hydrogen molecule. Therefore, the more negative \(E_{ads}\) corresponds to more stable interaction.

\[
E_{ads} = E_{H2/slab} - E_{slab} - E_{H} \quad \text{or} \quad E_{ads} = E_{H/slab} - E_{slab} - 1/2E_{H2} \quad (1)
\]

The reaction energy (\(E_r\)) was calculated by Eq. (2), where \(E_{final}\) and \(E_{initial}\) indicates the total energy of final and initial state, respectively.

\[
E_r = E_{final} - E_{initial} \quad (2)
\]

We defined the stepwise adsorption energy (ΔE_{ads}) in Eq. (3), where \(n\) is the number of hydrogen molecules or atoms, so a positive ΔE_{ads} suggests the saturated adsorption coverage with \(n\) adsorbed hydrogen.
molecules/atoms. The zero-point energy correction (ZPE) was considered in all calculations.

\[
\Delta E_{\text{ads}} = E_{(0)\text{slab}+1/2\text{H}} - E_{(0)\text{slab}} - E_{\text{H}} \quad \text{or} \quad \Delta E_{\text{ads}} = E_{(n)\text{slab}+1/2\text{H}} - E_{(n)\text{slab}} - 1/2E_{\text{H}} \tag{3}
\]

When considering the temperature and gaseous pressure, the Gibbs free energy (G) of free gas is calculated by Eq. (4), where \(E_{\text{GFT}}\) is the calculated electronic energy, \(\beta(T, P)\) is the change of hydrogen chemical potential under different temperatures and standard pressure, which could be obtained from the NIST thermodynamic table [36].

\[
G_{\text{ads}} = G_{(n)\text{slab}} - G_{\text{slab}} - nG_{\text{H}} \quad \text{or} \quad G_{\text{ads}} = G_{(n)\text{slab}} - G_{\text{slab}} - n/2G_{\text{H}} \tag{5}
\]

The equilibrium phase diagram between hydrogen adsorption and surface reduction is calculated by Eq. (6), where \(E_{\text{H}/\text{FeS}_2}\) is the perfect surface with n adsorbed hydrogen, \(H_{(n-2)/\text{FeS}_{2-n}}\) represents the surface with (n-2)H adsorption and one sulfur vacancy, and \(H_2S\) is the free gas.

\[
\Delta G = G_{(n-2)/\text{FeS}_{2-n}} + G_{H_2S} - G_{(n)/\text{FeS}_{2-n}} \tag{6}
\]

Climbing image nudged elastic band method (CI-NEB) was used to search the transition states [37]. To confirm the searched transition state, the stretching frequencies analyzed was performed since a transition state has only one imaginary frequency.

3. Results and discussion

3.1. Hydrogen adsorption at the lowest coverage

We firstly calculated the single hydrogen molecule adsorption on (100), (210), (211), and (311) surface, the adsorption configurations and adsorption energies were presented in Fig. 2. On (100) surface, the hydrogen molecule is bonded to iron atom with the adsorption energy of −0.29 eV, this adsorption mode has also been reported for hydrogen binding on top of iron atoms (−0.37 eV vs −0.20 eV). After the fully optimization of geometry structure, the H-H bond elongated from 0.75 Å in free molecule to 2.02 Å as showed in Fig. 2b, indicating that the dissociation of hydrogen on (210) surface is a spontaneous process. On (211) and (311) surface, the hydrogen molecule is preferred to be adsorbed on top of iron atoms with the adsorption energy of −0.26 eV and −0.08 eV, respectively, suggesting that their binding strength with surface is even weaker than that on (100) surface. Based on the H-H bond length analysis, the adsorbed hydrogen molecule on (100), (211), and (311) surfaces was slightly activated since the H-H bond length after adsorption is somewhat longer than the H-H bond length of free gas. According to the Fe-H bond length (Table S1 to S3), the adsorption configurations were very similar on (100), (211), and (311) surfaces, which could be used to explain their almost similar adsorption energies. On (210) surface, the hydrogen dissociation adsorption is spontaneous on SFe-Fe site. On (211) and (311) surfaces, there exist SFe-S atoms which the S atom connects one iron and one sulfur. From the coordination environment view, the SFe-S might be caused by their different electronic structures.

In order to reveal the electronic interaction between adsorbed hydrogen and FeS\(_2\) facets, the charge density difference calculation was carried out and the isosurface contour was presented in Fig. 2. The charge density difference is calculated as \(\Delta \rho = \rho_{\text{ads}} - \rho_{\text{slab}}\), where \(\rho_{\text{x}}\) is the total charge density of slab with adsorbate x, \(\rho_{\text{slab}}\) is the total charge density of pure slab, and \(\rho_{\text{ads}}\) is the charge densities of pure slab and adsorbate, respectively. From Fig. 2, one can distinguish that the adsorbed hydrogen molecule gains electrons from the 3d orbital of surface Fe atoms (the violet region) on (100), (211), and (311) surfaces, which would benefit for hydrogen activation, this is consistent with the results of H-H bond length analysis. Meanwhile, the shared electrons between H and Fe atoms benefit to the formation of Fe-H bonds. On FeS\(_2\)(311) surface (Fig. 2d), the electron transfer between hydrogen and substrate is somewhat less than it on (100) and (211) surfaces, which is in accordance with the slightly weaker hydrogen adsorption energy on (311) than it on (100) and (211) surfaces. Noting that on (210) surface (Fig. 2b), the hydrogen is dissociative adsorption on bridge SFe-Fe atom, and the electrons are delocalized due to the formation of covalent bonds between hydrogen and sulfur atoms.

![Fig. 2. The configuration and charge density difference of H\(_2\) adsorption on FeS\(_2\) surfaces, a (100), b (210), c (211), and d (311) surfaces.](image)

The inset values represent the adsorption energy (\(E_{\text{ads}}, \text{eV}\)) and the H-H bond length (Å). For charge density difference, the violet and turquoise regions represent electron aggregation and deficiency, respectively. The blue, yellow, and white sphere represents iron, sulfur, and hydrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
To further elucidate the bonding interaction of adsorbed hydrogen molecules, the projected electron density of states (PDOS) and Crystal Orbital Hamilton Population (COHP) of adsorbed hydrogen were presented in Fig. 3. From the calculated PDOS, one can find that the occupied states of adsorbed hydrogen broaden and distribute from $-8$ eV to the Fermi level, while the mainly DOS distribution of free hydrogen molecule locates at $-6 \sim -4$ eV [39], the broaden peaks would hybrid with the $3d/2p$ orbitals of Fe/S to form bonding interactions. On (100), (211), and (311) surfaces, the overlapping between H 1$s$ and Fe 3$d$ states is very similar, also indicating the close bonding strength between hydrogen molecule and the substrates. While on (210) surface, there is a large overlapping between H 1$s$ and S 2$p$ states, corresponding to the strong hydrogen adsorption strength. Meanwhile, the strength of H-H bonds is evaluated by COHP calculation. The COHP methodology is comparable to the Crystal Orbital Overlap Population (COOP) which is developed by Roald Hoffmann in the basis of extended Hückel calculations [40,41]. From COHP (COOP) analysis, the chemical bonding information could be extracted based on standard DFT calculations. For consistent with the expression of COOP, the -COHP was used here, where the positive and negative values correspond to bonding and anti-bonding chemical interactions, respectively. Therefore, the zero-value COOP or -COHP indicates a non-bonding interaction. The integrated -COHP/COOP (-ICOHP/ICOOP) up to the Fermi level could indicate the strength of chemical bonding, the larger -ICOHP/ICOOP correlates to the more stable interaction.

As shown in Fig. 3, there is a negative-value peak below the Fermi level in COHP analysis for hydrogen adsorbed on (100), (211), and (311) surfaces, indicating that the anti-bonding orbital of hydrogen molecule (1$s^*$) is partially occupied, resulting in the activation of hydrogen molecule. This is different from the free hydrogen molecule where the bonding orbital (1$s$) is fully occupied and anti-bonding orbital (1$s^*$) is empty. It is worth mentioning that on (210) surface, the peaks intensity of COHP is negligible compared to it on other three surfaces, indicating the non-bonding interaction due to the large distance between two hydrogen atoms. In other words, the interaction between two hydrogen atoms is rather weak. According to calculated -ICOHP up to the Fermi level (Figure S1), the value is 4.41, 4.71, and 4.81 eV on (100), (211), and (311), respectively, suggesting that the activation degree of H-H bond on (100) surface is slightly higher than it on other two facets, which is consistent with the results of charge difference analysis. Meanwhile, the -ICOHP is only $-0.03$ eV for (210) surface, also indicates the weak strength of H-H interaction.

It is desirable to establish the correlation between the catalytic activity and surface structure for rational design of catalysts. Therefore, we investigated the hydrogen molecule dissociation on different surfaces. The energy profile of H$_2$ adsorption and dissociation was plotted in Fig. 4a, and the adsorption configurations of intermediates were provided in Figure S2. We found that the heterolytic dissociation mechanism is preferred on (100), (211), and (311) surfaces. The same mechanism has also been reported on other transition metal sulfides [15,16,42]. The dissociation of H$_2$ are endothermic processes with the reaction energies of 0.79 eV and 0.56 eV on (100) and (211) surface, respectively. The activation barrier is 1.65 eV on (100) and 1.21 eV on (211) surface, indicating that the hydrogen dissociation is reluctant both in thermodynamic and kinetics on these two surfaces. Our result is in accordance with previous work that the hydrogen desorption is preferred than dissociation on well-ordered FeS$_2$(100) [19].

On (311) surface, the heterolytic dissociation is followed by the hydrogen atom migration from iron to sulfur site, and the activation barrier of hydrogen dissociation is moderate of 0.83 eV. As presented in Fig. 4a, the interaction strength between hydrogen and (311) surface is weak with the hydrogen adsorption energy of $-0.08$ eV, but the hydrogen dissociation on this facet is thermodynamically favorable with the exothermal energy of 0.12 eV. As we mentioned above, the dissociation of H$_2$ on (210) surface is spontaneous with the exothermal energy of 0.37 eV, suggesting that the activation of H$_2$ and atomic hydrogen recombination is favorable. Ran and co-workers demonstrated that the mesoporous FeS$_2$ without the aid of hard template present remarkable electronic HER catalytic performance in alkaline conditions [26], and they elucidated the main contribution is derived from (210) facet. Their theoretical calculations also indicated that the catalytic performance of (210) facet is much superior than (100) surface, which is agree well with our calculation results.

In Fig. 4b, the activation barriers ($E_a$) presents a good linear
correlation with the reaction energies ($E_r$). In other words, the interaction strength between adsorbate and catalyst substrate determines the hydrogen activation behavior. A strong adsorption would induce the high activation barrier, but if the adsorption is too weak, the desorption of adsorbates would be feasible, no reactions would happen. The adsorption strength is closely related to the surface structures including the ratio of surface metal and non-metal atoms, ions vacancy, and defects. Therefore, our efforts uncover the significance of interaction strength between hydrogen and pyrite surfaces for hydrogen activation.

### 3.2. Hydrogen adsorption at high coverage

According to calculations at low coverage, the molecule adsorption is preferred on (100) and (211) surfaces, while atomic adsorption is desirable on (210) and (311) facets. In this section, we investigated the hydrogen adsorption at high coverage. The stepwise adsorption energy ($\Delta E_{\text{ads}}$) was calculated by Eq. (3) and the results were presented in Table 1, the corresponding adsorption configurations were provided in Figure S3-S6. On (100) surface, the adsorption of hydrogen molecule on iron site is more stable than other adsorption modes. There are eight surface iron atoms in our slab model, the stepwise adsorption energy of 0.90 eV per hydrogen atom, and the final calculated saturated coverage is 12.3H/nm$^2$ on (210) facet.

In heterogenous catalysis, the surface adsorption coverage has a significant effect on catalytic activity and selectivity [43–45]. The essence of saturated adsorption coverage is the equilibrium of chemical potential ($\mu$) between gaseous phase and adsorbed state on surface, and the chemical potential is determined by external experimental conditions, i.e. temperature and gaseous pressure. Therefore, in this section, we have combined DFT with ab initio atomistic thermodynamics to explore the change of hydrogen chemical potential ($\mu_{H_2}$) with respect to the temperatures and pressures, and we have further investigated the hydrogen adsorption on pyrite surfaces under dynamic $\mu_{H_2}$. Our goal is to explore the change of hydrogen chemical potential ($\mu_{H_2}$) with respect to the temperatures and pressures, and to investigate the hydrogen adsorption on pyrite surfaces under dynamic $\mu_{H_2}$.

![Fig. 4.](image-url) The energy profile of $H_2$ dissociation on FeS$_2$(100), (210), (211), and (311) surfaces. The adsorption configurations of intermediates were provided in Supplementary Information. $b$ the relationship between hydrogen activation barriers ($E_a$, eV) and reaction energies ($E_r$, eV), also named the Bronsted-Evans-Polanyi (BEP) relationship.

<table>
<thead>
<tr>
<th>$E_{\text{ads}}$, eV</th>
<th>$E_{\text{ads}}$, eV</th>
<th>$E_{\text{ads}}$, eV</th>
<th>$E_{\text{ads}}$, eV</th>
<th>$E_{\text{ads}}$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{H_2}$</td>
<td>$\mu_{H_2}$</td>
<td>$\mu_{H_2}$</td>
<td>$\mu_{H_2}$</td>
<td>$\mu_{H_2}$</td>
</tr>
<tr>
<td>1H$_2$</td>
<td>1.7</td>
<td>2H</td>
<td>2H</td>
<td>2H</td>
</tr>
<tr>
<td>2H$_2$</td>
<td>3.4</td>
<td>4H</td>
<td>4H</td>
<td>4H</td>
</tr>
<tr>
<td>3H$_2$</td>
<td>5.1</td>
<td>6H</td>
<td>6H</td>
<td>6H</td>
</tr>
<tr>
<td>4H$_2$</td>
<td>6.9</td>
<td>8H</td>
<td>8H</td>
<td>8H</td>
</tr>
<tr>
<td>5H$_2$</td>
<td>8.6</td>
<td>8H + 1H</td>
<td>1H</td>
<td>1H</td>
</tr>
<tr>
<td>6H$_2$</td>
<td>10.3</td>
<td>8H + 2H</td>
<td>2H</td>
<td>2H</td>
</tr>
<tr>
<td>7H$_2$</td>
<td>12.0</td>
<td>8H + 3H</td>
<td>3H</td>
<td>3H</td>
</tr>
<tr>
<td>8H$_2$</td>
<td>13.7</td>
<td>8H + 4H</td>
<td>4H</td>
<td>4H</td>
</tr>
</tbody>
</table>

Table 1

The stepwise adsorption energy ($\Delta E_{\text{ads}}$, eV) and coverage ($\theta$, H/nm$^2$) of hydrogen on different surfaces.

<table>
<thead>
<tr>
<th>$E_{\text{ads}}$, eV</th>
<th>$E_{\text{ads}}$, eV</th>
<th>$E_{\text{ads}}$, eV</th>
<th>$E_{\text{ads}}$, eV</th>
<th>$E_{\text{ads}}$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{H_2}$</td>
<td>$\mu_{H_2}$</td>
<td>$\mu_{H_2}$</td>
<td>$\mu_{H_2}$</td>
<td>$\mu_{H_2}$</td>
</tr>
<tr>
<td>1H$_2$</td>
<td>0.37</td>
<td>1.5</td>
<td>2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>2H$_2$</td>
<td>0.40</td>
<td>3.0</td>
<td>5.6</td>
<td>0.8</td>
</tr>
<tr>
<td>3H$_2$</td>
<td>0.46</td>
<td>4.6</td>
<td>0.09</td>
<td>7.0</td>
</tr>
<tr>
<td>4H$_2$</td>
<td>0.25</td>
<td>6.1</td>
<td>0.09</td>
<td>8.4</td>
</tr>
<tr>
<td>5H$_2$</td>
<td>0.19</td>
<td>7.6</td>
<td>0.19</td>
<td>9.8</td>
</tr>
<tr>
<td>6H$_2$</td>
<td>0.19</td>
<td>11.2</td>
<td>0.19</td>
<td>11.2</td>
</tr>
<tr>
<td>7H$_2$</td>
<td>0.19</td>
<td>13.7</td>
<td>0.19</td>
<td>12.3</td>
</tr>
<tr>
<td>8H$_2$</td>
<td>0.20</td>
<td>12.0</td>
<td>0.19</td>
<td>13.0</td>
</tr>
</tbody>
</table>
to obtain the change of adsorption performance under varying experimental conditions, and provide a guiding reference for adsorption coverage modulation in experiment.

Based on Eq. (4), the contour of $\mu_{H_2}$ versus temperature and pressure was plotted in Figure S7. One can distinguish that the high temperature and low hydrogen pressure would induce a lower chemical potential. Among the region we considered, where the temperature is from 0 K to 1000 K, and the hydrogen pressure ranges from ultra-high vacuum to ultra-high ($10^{-12}$ atm to $10^4$ atm), the calculated hydrogen chemical potential is varying from $-10.3$ eV to $-6.5$ eV, which provides a critical condition for further investigation and discussions.

The hydrogen adsorption free energy ($G_{ads}$) under different adsorption coverage versus $\mu_{H_2}$ was calculated by Eq. (5) and presented in Figure S8. With the increasing of hydrogen chemical potential (lower temperature and higher gaseous pressure), the $G_{ads}$ is down hilling, indicating that the higher environmental chemical potential could facilitate the hydrogen adsorption on solid substrates. On these four surfaces, the $G_{ads}$ becomes negative until $\theta_{H_2}$ is beyond $-6.9$ to $-6.7$ eV, this is consistent with the weak interactions between hydrogen and FeS$_2$ surfaces.

On (100) surface, the adsorption of eight hydrogen molecules ($\theta = 13.7$ H/nm$^2$) is always preferred in energetics than other coverage within the $\mu_{H_2}$ boundary conditions we considered (Figure S8a). Therefore, in thermodynamic equilibrium phase diagram (Fig. 5a), there are only two regions, either $\theta = 0$ or $\theta = 13.7$H/nm$^2$. In experiment, Tao and co-authors have demonstrated that there is no evidence of interaction between hydrogen and well-ordered FeS$_2$(100) surface at 170 K and $P = 1$ bar. [19] But from our predicted phase diagram, the hydrogen adsorption is possible under this condition. This discrepancy might be partially attribute to the limitation of our computational method and model. Theoretical equilibrium adsorption phase diagram is only based on thermodynamics, but the kinetic aspects were not considered, such as the gas diffusion and adsorption energy barrier. On the other hand, in experiment, the error induced by resolution of characterization is also non-negligible.

For (210) surface, when $-6.9 < \mu_{H_2} < -6.7$ eV, the dissociation adsorption of hydrogen is preferred with $\theta = 6.1$ H/nm$^2$. When the $\mu_{H_2}$ is beyond $-6.7$ eV, the molecule adsorption becomes feasible, as presented in Figure S8b and Fig. 5b. On (211) surface (Figure S8c and Fig. 5c), the pure molecule adsorption mode could exist in a narrowed region (the red region). Under high hydrogen chemical potential ($\mu_{H_2} > -6.75$ eV), the co-adsorption of hydrogen molecule and atom is favorable, and the final saturated coverage is 11.2H/nm$^2$.

As for (311) surface, when $\mu_{H_2} > -6.75$ eV, the co-adsorption of hydrogen molecules and atoms is preferred in thermodynamics, and the saturated coverage reaches 10.3 H/nm$^2$ under low temperature and high pressure (Figure S8d and Fig. Sd). Our theoretical predictions might provide a valuable reference to adjust the hydrogen adsorption coverage on pyrite surfaces under realistic conditions.

3.3. Adsorption or surface reduction

The formation of surface anion vacancy is inevitable for transition metal sulfides when exposed to hydrogen atmosphere. Many works have demonstrated that the anion vacancy of sulfides has a momentous effect on catalytic performance [10,46,47]. Based on the predicted hydrogen coverage mentioned above, we have investigated the sulfur vacancy formation on different FeS$_2$ facets in this section. Under typical conditions, the saturated hydrogen coverage is 13.7, 12.3, 11.2, and 10.3H/nm$^2$ for (100), (210), (211), and (311) surface, respectively.

Fig. 5. The equilibrium phase diagrams of hydrogen adsorption on FeS$_2$ surfaces, a (100), b (210), c (211), and d (311) surface. The corresponding adsorption coverage ($\theta$) is marked in brackets. The adsorption configurations under different coverage were also inserted. The blue, yellow, and white sphere represents iron, sulfur, and hydrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
At saturated coverage, the equilibrium phase diagram between hydrogen adsorption and surface reduction is plotted based on Eq. (6). From the equilibrium thermodynamic phase diagram (Fig. 6), one can distinguish that the high temperature and low H2S pressure is beneficial for surface reduction. Increasing hydrogen pressure is desired for surface sulfur vacancy formation. The sulfur vacancy formation on (210) surface is feasible even at T < 400 K (Fig. 6b), which is easier than other surfaces. This indicates that the bridging sulfur atom (S_{Fe-Fe}) on (210) which has high activity for hydrogen dissociation is also easily be removed by hydrogen, and results in the decreased activity. To keep the hydrogen dissociation activity, the gaseous pressure of hydrogen should be moderate.

For (311) surface, the sulfur vacancy formation is also favorable in thermodynamics (Fig. 6d). As for (100) and (211) surfaces, only when the temperature is above 600 K and 700 K can surface sulfur atoms be removed (Fig. 6a and c). Temprano et al. have demonstrated that in the presence of an incandescent Ta filament, the desorption of H2S could occur at 260 K [20], much lower than the temperature we predicted. This means that once the atomic hydrogen bond with sulfur atoms, the H2S desorption is facile. In other words, the hydrogen dissociation is the rate-determining step for (100) surface reduction.

**4. Conclusions**

We have explored the interaction between hydrogen and mainly exposed surface, (100), (210), (211), and (311) of FeS2 at different adsorption coverage by employing DFT calculations combined with ab initio atomistic thermodynamics.

At low coverage, the adsorption of hydrogen molecule is weak on (100), (211), and (311) surfaces with the adsorption energy of −0.29, −0.26, and −0.08 eV, respectively. The high activation barrier (1.68 and 1.21 eV) and remarkable endothermal energy (0.79 and 0.56 eV) hinders the hydrogen dissociation on (100) and (211) facets. On (311) surface, even the adsorption is weak, the dissociation is possible due to the moderate activation barrier of 0.83 eV and slightly exothermal energy of 0.12 eV. While on (210) surface, the exposed bridging sulfur atoms (S_{Fe-Fe}) have high activity for hydrogen activation, resulting in the spontaneous dissociation adsorption with the exothermal energy of 0.37 eV. The electronic calculations and bonding analysis manifest that on (100), (211), and (311) surfaces, the electrons donated from 3d orbital of exposed iron atoms to antibonding orbital of hydrogen molecule (1σ*) leads to the H-H bond activation. On (210) surface, after the dissociation adsorption, the electron density is delocalized to form covalent bond of S-H.

At high coverage, the pure molecule adsorption configuration is preferred on (100) surface. But on (210), (211), and (311) surface,
the adsorption mode is determined by temperature and gaseous pressure. Within the boundary condition (T: 0–1000 K and P\textsubscript{H2}: 10\textsuperscript{-12}–10\textsuperscript{4} atm), the saturated coverage sequence is (100) > (210) > (211) > (311). According to thermodynamic phase diagram between hydrogen adsorption and surface reduction, the exposed surface sulfur atom (S\textsubscript{LPS}) of (210) is easier to be removed than the sulfur atoms of other surfaces. The hydrogen coverage and sulfur vacancy formation are closely dependent on temperature and gaseous pressure. This work enriches the understanding of the interaction between hydrogen and pyrite substrates, and provides a useful theoretical reference for modulating the hydrogen adsorption coverage and surface structures in relevant processes catalyzed by iron sulfide.

CRediT authorship contribution statement

Jinjia Liu: Data curation, Formal analysis, Writing - original draft. Tao Yang: Formal analysis, Validation, Writing - review & editing. Qing Peng: Supervision, Validation, Writing - review & editing. Yong-Wang Li: Supervision. Xiao-Dong Wen: Conceptualization, Methodology, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors are grateful for the financial support from the National Natural Science Foundation of China (No. 21473229, No. 91545121), Key R&D plan of Beijing Municipal Science and Technology Commission (Z181100005118014), funding support from Synfuels (KFUPM) for funding this work through project No. SR191013. The authors acknowledge the support provided by the Deanship of Scientific Research (DSR) at King Fahd University of Petroleum & Minerals (KFUPM) for funding this work through project No. SR191013.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apusc.2020.147900.

References

study, Catalysts 8 (2018) 450.


