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A DFT study on benzene adsorption over a corner site of tungsten sulfides

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Abstract

Benzene adsorption on a model for a corner site of a WS_2 slab is considered by periodic DFT calculations. Under typical hydrotreating reaction conditions a fourfold coordination of the corner W atom is thought to be more favorable for benzene adsorption than five- or sixfold coordinated W atoms in conventional edge surfaces. Although no benzene adsorption site was identified on such a corner site, replacement of the W atom adjacent to the W corner site by Ni creates a potential adsorption site around the W corner site. Benzene was found to adsorb with $\Delta E = -0.19$ eV on this Ni-substituted model for the corner site of a WS_2 slab.

Keywords: Benzene; Adsorption; Tungsten sulfides (WS_2); Hydrogenation (HYD); Density-functional theory (DFT); Pseudo-corner site; Fourfold coordinated tungsten

1. Introduction

Due to the importance of MoS_2-based catalysts in the clean up of oil feedstock, their morphology and surface structure has been the subject of intense study [1]. Recently, computational methodologies at the DFT level have allowed improved insight into the local coordination of the metal sulfide surface under reaction conditions [2–8], adsorption of hydrogen and organo-sulfur compounds [3,7,9–11] and the elementary reaction steps underlying desulfurization of simple organo-sulfur compounds over such surfaces [12–14]. Relatively few such studies [15] have been carried out for tungsten-based hydrotreating catalysts because they are applied too a much lesser extent. Nevertheless, especially Ni-promoted WS_2 is an important hydrogenation ingredient of hydrocracking catalysts [16]. Sun et al. have studied the stable configuration of WS_2, Ni–WS_2 and Co–WS_2 surfaces [17]. We have recently studied the adsorption of benzene on a WS_2 slab [18]. Benzene only adsorbed to a bare W edge, whereas no benzene adsorption sites were identified on sulfur-containing tungsten and sulfur edges of WS_2 representative for typical hydrotreating reaction conditions.

In the present study, we will focus on a corner structure of WS_2. The most probably structure of WS_2 like MoS_2 is one of the ^{2}H–MeS_2 (Me = Mo and W) type from which various types of surfaces can be formed. Of special interest for hydrogenation have been regarded the corner sites [1]. Previous DFT studies have mainly focused on (infinite) edge structures, but little attention was paid to a corner structure of MoS_2 [19]. In an attempt to elucidate whether benzene adsorption may be more favorable over a corner site of WS_2, we have modeled a pseudo-corner structure in a periodic fashion and studied the interaction with benzene.

2. Computational methods and model

DFT calculations were performed with the VASP code [20] employing the projected augmented wave (PAW) method [21] and the generalized gradient approximation [22]. We used a rhombic supercell (12.511 Å × 16.477 Å × 28.000 Å) containing three unit cells in the *b*-direction, two slabs in the *a*-

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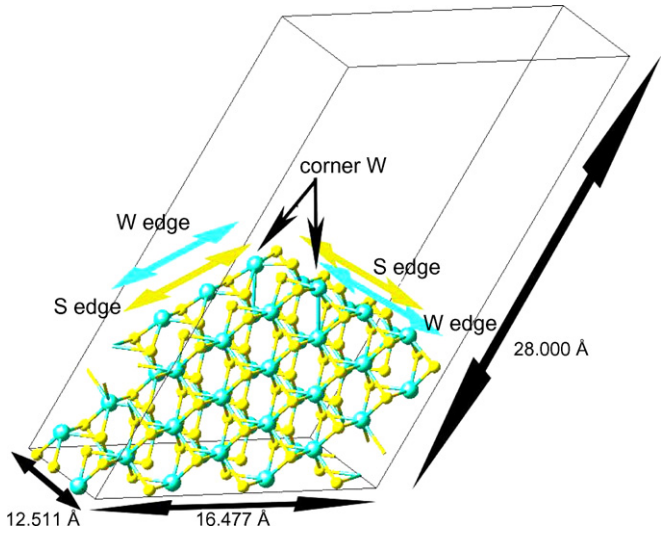

Fig. 1. Idealized WS_2 (0 1 0) surface model, blue: W atom; yellow: S atom. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

direction, and a vacuum space of 11 Å along the *c*-direction (Fig. 1). This structure has three potential W adsorption sites at each edge. The two top layers from the surface were allowed to relax, whereas the other layers were kept fixed at their optimized bulk positions to simulate bulk constraints. Full geometry optimization was allowed for the adsorbing molecule. All geometries and energies of the models were computed at Γ-point with a cutoff energy of 360 eV. The convergence criterion for the self-consistency cycle and the maximum force were set at 10^{-4} eV and 0.02 eV/Å, respectively. Spin polarization was applied to all calculations for the systems containing nickel atoms.

3. Results and discussion

The supercell of the pseudo-corner WS_2 (0 1 0) surface is presented in Fig. 1. At the corner sites, the W edge with unsaturated W atoms coordinated by four sulfur atoms meets the S edge where each tungsten atom is saturated by six sulfur atoms. In the as-cut surface the corner W atoms are fourfold coordinated by sulfur. Logadóttir et al. established that benzene adsorption may take place on a fivefold coordinated Mo atom in the Mo edge of MoS_2 [11]. We have also reported benzene adsorption over the defective W edge with benzene adsorbed to the bridging site between two 5-fold coordinated W atoms [18]. Similarly, Cristol et al. described thiophene derivatives adsorbed on the defective bridging site between two 5-fold coordinated Mo atoms in Mo edge of MoS_2 [10]. Therefore, a lower sulfur coordination number of the corner sites of the WS_2 slab than that of the saturated one are expected to favor adsorption of nucleophilic organic molecules such as benzene, thiophene and pyridine.

Under typical industrial conditions that entail the presence of a relatively small amount of H_2S in excess H_2 (typically, $H_2S/H_2 = 0.01$) in the gas and/or liquid phase, the surface coverages with sulfur deviate from this idealized surface (IS).

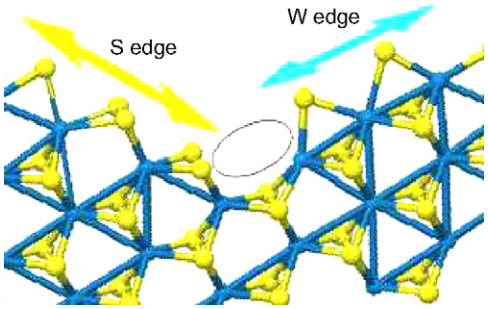

Fig. 2. A view of the connection of neighboring cells (2W–5S) (shown is one of the slabs of the unit cell).

The free energy changes upon adding *n* sulfur atoms in terms of the following reactions

$$\text{W edge}: \quad \text{IS} + n\text{H}_2\text{S} \leftrightarrows \text{IS-}n\text{S} + n\text{H}_2 \tag{1}$$

$$\text{S edge}: \quad \text{IS-}n\text{S} + n\text{H}_2 \leftrightarrows \text{IS} + n\text{H}_2\text{S} \tag{2}$$

can be calculated from

$$\Delta G = \Delta E - n\Delta\mu \tag{3}$$

where ΔG, ΔE and $\Delta\mu$ are the Gibbs free energy, the electronic energy of the considered surfaces computed with VASP and the chemical potential difference between H_2 and H_2S, respectively. To avoid unrealistic repulsions of the sulfur atoms at the S edge and the neighboring W edge, the sulfur atom at the W edge furthest away from the corner site was left vacant (Fig. 2). Table 1 summarizes the relative energies of optimized structures as a function of the sulfur coverage on the WS_2 (0 1 0) corner site model of the W and S edge. The resulting optimized geometries of the WS_2 structures are similar to those calculated before for MoS_2 [2,3,9,10] and WS_2 [17]. The most stable surface is the one where two and five S atoms are adsorbed on the W and S edge, respectively (2W–5S). This corresponds to sulfur coverage of 50% at the W edge and 83% at the S edge. This result is very similar to our previous work on the W and S edges in WS_2 (1 0 0), which resulted in sulfur coverages of 50% at the W edge and 87.5% at the S edge [18]. We conclude that surface stability of the normal edge plane for alternating W and S edge in the WS_2 slab is maintained even around the corner of the hexagonal structure between W and S edge.

Table 1
Relative Gibbs free energies (eV) of WS_2 (0 1 0) with varying amounts of sulfur atoms at W and S edges ($\Delta\mu = -4.96$ eV, $T = 623$ K, $H_2S/H_2 = 0.01$ mol/mol)[a]

S edge							
Number of S atom	0	1	2	3	4	5	6
W edge							
0	–	–	–	–	–	–	1.23
1	–	–	–	–	–	−2.08	−0.77
2	1.87	–	−1.06	–	−2.65	−3.92	−2.39
3	–	–	–	–	–	−3.01	−1.16
4	–	–	–	–	–	–	0.00

[a] The reference energy is that of the fully sulfided surface (4W–6S), including the energy of hydrogen molecules in the supercell.

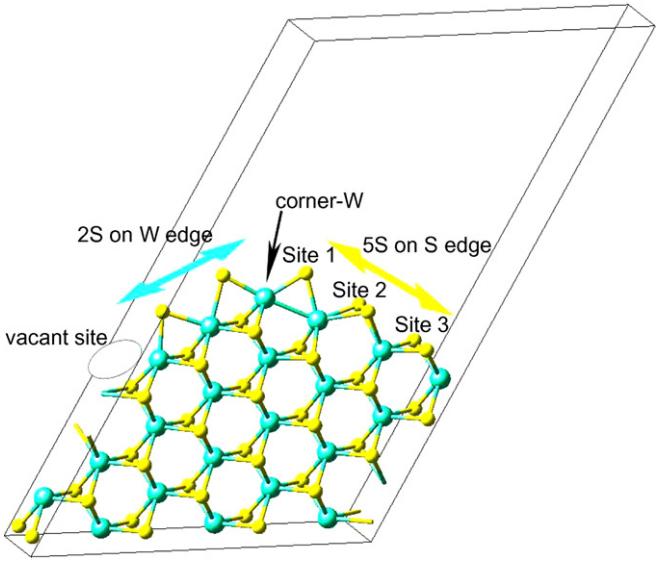

Fig. 3. The most stable WS_2 (0 1 0) under the typical hydrotreating reaction conditions (2W–5S) (shown is one of the slabs of the unit cell).

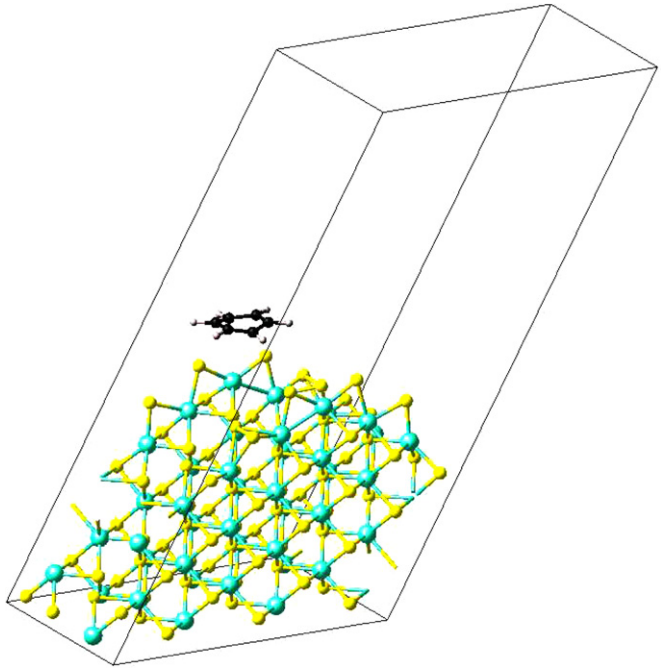

Fig. 4. Benzene configuration over 2W–5S.

The 2W–5S configuration has one sulfur atom less compared to the fully saturated state in S edge. We investigated the effect of the location of the defective site in the S edge of the corner model. Three possible defective sites indicated by sites 1–3 are shown in Fig. 3. The corresponding free energies of the resulting 2W–5S configurations are summarized in Table 2. Removal of a sulfur atom from site 1 is more favorable than removal from the other two sites. The remaining sulfur atom at site 1 was found to be located in a bridging position on the sulfur edge. In this most stable configuration of 2W–5S (Fig. 3), the corner W atom binds bridging S atoms at W and S edge. Therefore, tungsten at this corner site is fourfold coordinated. This coordination number is lower than that of W atom in the W and S edges under the typical reaction conditions. By the atomic arrangement at the corner site, a larger space around the corner site is available than over the normal W and S edges, which could favor benzene adsorption. Schweiger et al. found a fourfold coordinated corner Mo atom in the MoS_2 cluster model [19]. In a similar fashion, they found that such structures exhibit decreased sulfur coordination of the corner Mo atoms.

In our previous work, we only identified an adsorption site for a fourfold coordinated W atom on the cleaved W edge with ample room for benzene coordination to W. On the more realistic surface representative for reaction conditions containing two 5-fold coordinated W atoms a stable configuration was identified although this did not lead to adsorption. This unfavorable interaction energy was related to the large energy required with the reorganization of sulfur atoms to accommodate benzene close to the catalytic surface [18]. To investigate benzene adsorption on the corner site, we studied the interaction of benzene with the most stable 2W–5S configuration with adsorption modes planar and perpendicular to the catalytic surface. However, no favorable interaction was found for these cases (Fig. 4) and we could not identify an adsorption site for benzene over this corner site. This result indicates that adsorption of an aromatic molecule cannot be made only by the electrophilicity of W atom represented by the coordination number. We suggest that repulsion by the S atoms influences the stabilization of the adsorbing complex negatively. Creating a vacant space for adsorption of benzene could be more important than the electrophilicity of the metal ion.

Table 2
Relative Gibbs free energies (eV) of WS_2 (0 1 0) with a defective sulfur site at the S edge ($\Delta\mu = -4.96$ eV, $T = 623$ K, $H_2S/H_2 = 0.01$ mol/mol)[a]

Configuration	Defective sulfur	ΔG
2W–6S	–	−2.39
2W–5S	Site 1	−3.92
2W–5S	Site 2	−3.50
2W–5S	Site 3	−3.51

[a] The reference energy is that of the fully sulfided surface (4W–6S), including the energy of hydrogen molecules in the supercell.

Taking into account the importance of spatial requirements around the adsorbing W atom, we introduced a Ni atom into the W edge of WS_2 (0 1 0) next to the corner W atom. Nakamura [23] and Sun et al. [17] reported that on a Ni-promoted W edge the sulfur atoms bind directly atop to the tungsten atoms. This result is different from the one found for CoMo sulfide surfaces and can be understood in terms of a lower Ni–S bond strength compared to Co–S. Introduction of the Ni atom in the W edge of our pseudo-corner site model leads to a decreased sulfur coverage at the corner site. In simple terms, one can view the introduction of Ni as the replacement of one W^{4+} to S^{2-} unit by a Ni^{2+}. Several configurations of Ni-promoted W edge structures were considered by an investigation of the infinite edge surface (Table 3). We found that substituting a W atom for a Ni atom in the W edge leads to a stable configuration with two bridging S atoms in the present model (configuration 1–2B). This result shows that introduction of a nickel atom into W edge

Table 3
Relative Gibbs free energies (eV) of a Ni-substituted WS_2 (1 0 0) with varying number of sulfur atoms in the W edge in the four-unit cell model like Ref. [17] ($\Delta\mu = -4.96$ eV, $T = 623$ K, $H_2S/H_2 = 0.01$ mol/mol)[a], blue: W; yellow: S; green: Ni.

Configuration	Number of atoms in W edge		ΔG	Outermost layer
	Ni	S		
1–2A	1	2	2.33	
1–2B	1	2	−0.10	
1–3	1	3	0.00	
1–4	1	4	0.75	

[a] The reference energy is that of the configuration as the replacement of one W^{4+} to S^{2-} unit by a Ni^{2+}., including the energy of hydrogen molecules in the supercell.

creates a large space over the introduced nickel atom, which may be beneficial for benzene adsorption. We applied this result to the corner model and introduced a Ni atom next to the corner W atom in the W edge. The most stable configuration of this Ni-promoted WS_2 slab is shown in Fig. 5. The most stable configuration on the S edge has a sulfur vacancy at site 2, resulting in a fourfold coordinated W atom adjacent to the Ni atom in the W edge. Different from previous results [17,23], a sulfur atom on the W edge remains slightly bended towards the Ni atom although no covalent Ni–S bonding was found. This may be due to repulsion of sulfur atoms at the S edge of a neighboring supercell. In the situation of a more extended W edge representative of the edge surface of the WS_2 slab, this sulfur atom is expected to bind directly atop the W atom. This new corner site configuration with Ni replacement creates a large vacant space over the corner W site.

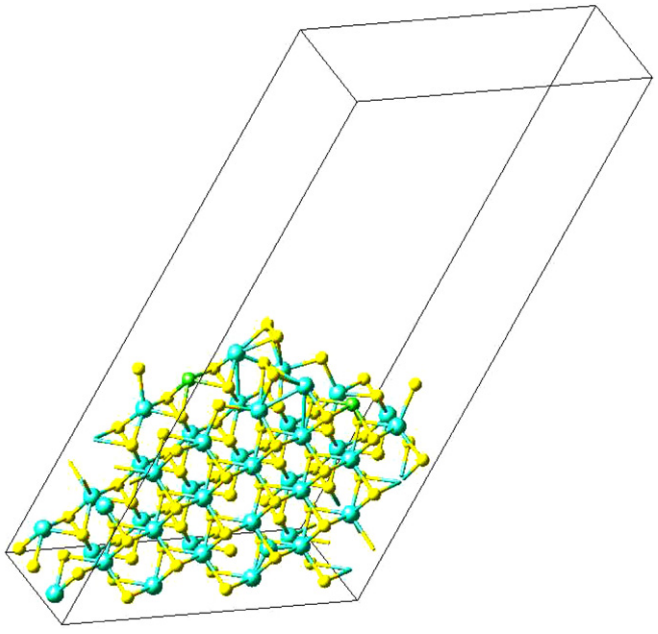

Fig. 5. The most stable Ni-promoted WS_2 (0 1 0), blue: W; yellow: S; green: Ni. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

To investigate benzene adsorption on the corner site of the Ni-promoted WS_2, we studied the interaction of benzene with the stable configuration of Ni-promoted WS_2 slab as shown in Fig. 5. A stable coordination was identified where benzene coordinates η^2 to the corner W atom (Fig. 6). The adsorption energy was found to be −0.19 eV. While this adsorption energy represents a rather weak adsorption of benzene to the surface compared to those of thiophene derivatives (from −0.4 to −0.7 eV) to the defective edge site of MoS_2 [10], it is comparable to that of benzene adsorption energies (from −0.14 to −0.17 eV) on the Mo edge in MoS_2 [11]. Briefly, this difference should be related to the larger nucleophilicity of the thiophenic ring due to the presence of sulfur than of the aromatic ring.

The bond length of the corner W atom and the bridging S atom on the S edge was increased upon benzene adsorption from 2.52 Å to 2.60 Å. In addition, the sulfur atom bonding atop to the remained W atom on the W edge slight moved away from adsorbed aromatic. These small reconstructions do not imply large energy changes such as in the situation where the W–S bonds are broken. This is due to the weak steric hindrance of the leaning adsorption mode as η^2 coordination to the corner

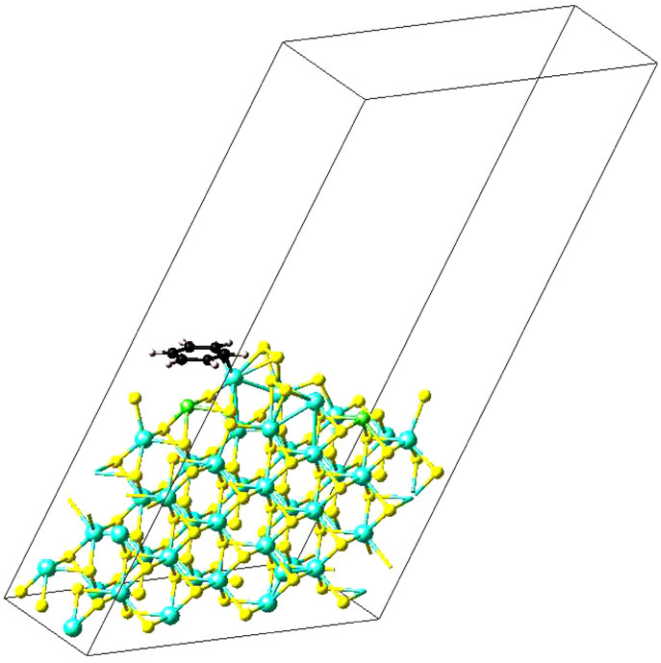

Fig. 6. Benzene configuration on the Ni-promoted WS_2 (0 1 0), blue: W; yellow: S; green: Ni. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

W atom. A longer W edge model can accommodate S atom atop to the next W atom to Ni on W edge. This may change the adsorption energy of benzene, but it should be limited for the leaning adsorption mode.

It is well known that promotion of WS_2 by Ni enhances the hydrogenation activity considerably [24]. Clearly, introduction of Ni to the WS_2 slab leads to a favorable yet weak adsorption mode for benzene. This result indicates that the decreased sulfur coverage through replacement of W by Ni facilitates adsorption of aromatics. Here, we considered the introduction of Ni next to the W corner site in the sulfur edge. Introduction of additional Ni atoms to the model, for instance adjacent to the W corner site in the W edge, is expected to further decrease the sulfur coverage and relieve steric constraints for benzene adsorption. An important implication of our work is that benzene can only adsorb on corner sites with decreased sulfur coverage induced by the presence of Ni. Of future interest is also the replacement of the corner W atom by Ni, as well as placement of Ni promoter ion in the S edge.

4. Conclusion

A pseudo-corner site of WS_2 (0 1 0) surface was constructed and used to carry out periodic DFT calculations. A stable configuration of the corner site was a fourfold coordinated W corner atom under typical hydrotreating conditions, which should be more favorable for benzene adsorption than a five- or sixfold coordinated W atom on the infinite edge surface. Nonetheless, this did not lead to favorable benzene adsorption. Introduction of Ni adjacent to the corner site decreased the sulfur coordination and led to favorable benzene adsorption. Our work points to the importance of corner sites and the presence of promoter ions for the hydrogenation of aromatics.

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