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DFT study of thiophene adsorption on molybdenum sulfide

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Abstract

Density functional theory calculations of thiophene adsorption on the different surfaces of MoS_2 show, unlike previous theoretical works, that the most probable adsorption mode is η^1 through the sulfur atom of the molecule on the sulfur edge of the catalyst particles. The adsorption proceeds on the stable surface, and there is no need to remove a sulfur atom from the surface before the adsorption. The calculated vibrational wavenumbers of the adsorbed molecules allowed us to confirm previously published experimental spectral assignments. This work demonstrates the importance of an accurate description of the surface taking into account the nature of the surrounding atmosphere.

Keywords: Density functional theory; Hydrodesulfurization; MoS_2; Thiophene adsorption

1. Introduction

The treatments of petroleum feedstocks with hydrogen at high temperature (i.e., hydrotreatment) is a key process in petroleum refining [1], performed mainly to decrease the sulfur content in fuels (naphtha and gasoil). Increasing interest in these reactions has been sparked by new, more stringent environmental legislations in most developed nations (e.g., <10 ppm of sulfur in diesel fuel before 2009 in Europe [2]). One way to achieve these objectives is to improve catalyst performance toward the refractory sulfur-containing compounds that are aromatic or polyaromatic rings, such as dibenzothiophene (DBT) and its substituted derivatives. The active phases of these hydrodesulfurization (HDS) catalysts consist of MoS_2 nanocrystallites well dispersed on high-specific surface alumina and usually promoted by cobalt or nickel atoms. It is now well accepted that the HDS active sites are located on the edges of these nanocrystallites that correspond to the (100) edge plane of the layered MoS_2 structure [3]. This (100) plane exhibits, in its perfect crystallographic stoichiometry, alternative rows of sulfur-terminated layers (hereafter called S, or sulfur edge) and molybdenum-terminated layers (hereafter called Mo, or molybdenum edge) [4,5].

Thiophene, the simplest homologue of the family of sulfur-containing molecules that are refractory to classical HDS, is often used to perform a rapid evaluation of the catalytic performance of a new catalytic formulation, although the validity of such a screening is under debate [6]. Even for this simple molecule, the reaction mechanism remains unclear. The reaction products of thiophene desulfurization are butane and different isomers of butene, but the primary products (hydrogenated intermediates like dihydrothiophene or tetrahydrothiophene vs. butadiene) are still a matter of controversy; numerous mechanisms have been proposed in the literature [7].

Density functional theory (DFT) calculations may provide insight into the thiophene HDS mechanism and first require a detailed study of the adsorption of this molecule on the active MoS_2 phase. Different ab initio calculations of thiophene adsorption have been reported [8–14]; however, all of these studies but one [8] considered adsorption only on the molybdenum edge of perfect crystallographic surface, even though previous studies [15–20] demonstrated that this surface is not stable under catalytic conditions. From an experimental standpoint, the adsorption of thiophene on supported MoS_2 has been characterized only by vibrational spectroscopy. Tarbuck et al. and Mills et al. [21–23] reported FTIR experiments, whereas Mitchell et al. [24] dealt with INS characterizations; each group proposed different geometries of adsorption. Based on compar-

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ison with organometallic complexes, Mitchell et al. proposed a flat adsorption of the thiophene molecule, whereas Mills et al. were in favor of a η^1 adsorption through the sulfur atom. These proposals were deduced from the interpretation of vibrational features observed in quite different spectral ranges: the out-of-plane C–H deformation in the low-wavenumber region for the INS study and the C=C stretching mode in the high-wavenumber range for the IR study.

A systematic study of thiophene adsorption on the stable MoS_2 surfaces is clearly needed. In the present study, we used periodic DFT calculations to explore the different adsorption geometries of thiophene on the various $MoS_2(100)$ surface. We first report the adsorption on the perfect surface to compare our results with available calculations and address the few discrepancies between the previously published data. We then study the adsorption on the surfaces that are stable under catalytic conditions. Finally, we use the comparison between the calculated frequencies of the stretching modes of the adsorbed thiophene molecule with the data given in the aforementioned experimental works to discuss the assignment of the vibrational spectra.

2. Computational details

Ab initio calculations were performed with the Vienna Ab initio Simulation Package (VASP) [25,26] based on Mermin's finite-temperature local DFT [27]. The calculations use a plane wave basis set, and the electron–ion interactions are described through the optimized projector augmented plane wave (PAW) method [28,29]. Resolution of the Kohn–Sham equations is performed using an efficient matrix diagonalization routine based on a sequential band-by-band residual minimization method for the one-electron energies. An improved Pulay mixing method is used to update the charge density. The optimization of the atomic positions is performed via a conjugate gradient minimization of the total energy using the Hellmann–Feynman forces on the atoms. This work used the large super cell ($12.641 \times 12.294 \times 20.000$ Å^3) shown in Fig. 1, which contains four elementary MoS_2 asymmetric units in the x direction, four in the z direction, and two layers along the y-axis (Fig. 1). Previous studies [5,15,17] showed that this model is suitable for predicting the electronic and structural properties of the MoS_2 surface. The two upper rows were allowed to relax while the two lower were kept fixed at the bulk geometry to simulate bulk constraints. The calculations were performed at the Γ point with a cut-off energy of 300 eV and a Methfessel–Paxton [30] smearing with $\sigma = 0.1$ eV. The exchange correlation functional of Perdew and Zunger [31] was used with the generalized gradient corrections proposed by Perdew et al. [32]. Frequency calculations were performed through numerical differentiation of the force matrix, including all degrees of freedom of the molecule and of the neighboring atoms (i.e., the first and second neighbors).

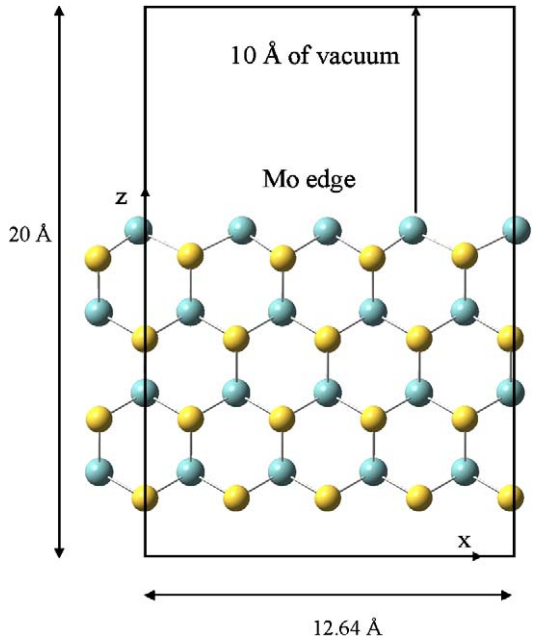

Fig. 1. Unit cell used all through this work. Molybdenum atoms are in blue, sulfur atoms are in yellow.

3. Results and discussion

3.1. Thiophene adsorption

The study of thiophene adsorption has been divided in four parts. The first part deals with the adsorption on the metallic edge of the perfect surface, the second part concerns the sulfur edge of the perfect surface, the third part is devoted to the adsorption on the stable edges under different reaction conditions, and the fourth part studies the adsorption on defects (coordinatively unsaturated sites [CUSs]) created by reaction with hydrogen under reductive conditions. Finally, comparison between these various adsorption modes allows us to discuss which one can be involved in the HDS process. All through this work, a positive adsorption energy corresponds to an exothermic process.

3.1.1. Adsorption on the perfect molybdenum edge

We studied the adsorption of thiophene on the molybdenum edge of the perfect (100) plane to compare the results obtained in this study with previous calculations performed using a cluster [13] or a periodic model [12]. These various modes of adsorption are presented in Fig. 2. On this edge, the most stable adsorption mode for thiophene was reported by Orita et al. to be parallel to the surface, with the thiophene molecule interacting with two metallic atoms (Fig. 2A). One of the molybdenum atoms interacts with both the sulfur atom and one of the α carbon atoms, and the other molybdenum atom interacts with two of the other carbon atoms. Thus, Orita et al. labeled this adsorption mode "η^2-S,C and η^2-C"; we denote it by "adsorption A" in what follows. As can be inferred from the number of interactions and the strong unsaturation of the surface, the adsorption energy is substantial (2.72 eV).

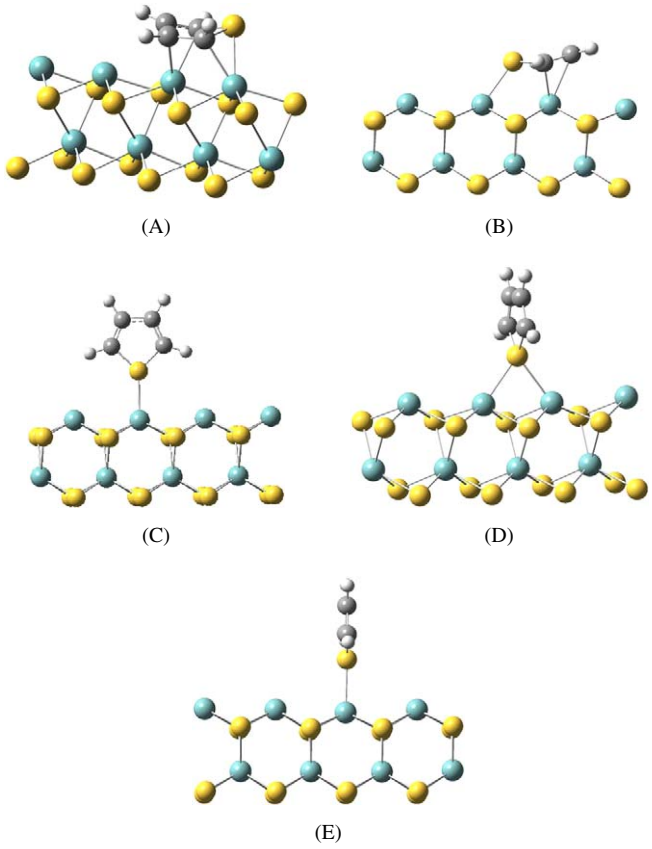

Fig. 2. Different geometries investigated for the adsorption on the perfect metallic edge.

The other adsorption modes discussed in the two aforementioned works can be grouped into two main types, "flat" adsorption and "vertical" adsorption. Flat adsorption is confusing. Indeed, Raybaud et al. proposed that the most stable adsorption mode (except for mode A, which is not reported) is "bridging η^5" (adsorption B in Fig. 2B), in which the sulfur atom is in a bridging position between two molybdenum atoms while the whole π system of the molecule is in interaction with one molybdenum atom. The computed adsorption energy is quite large (2.0 eV). In contrast, Orita et al. reported a slightly different interaction energy (1.81 eV) for this mode (labeled "η^4,S-μ^2"), although they claimed that this is not a real minimum, because this configuration presents two imaginary frequencies. Both groups reported other flat adsorption modes but with lower adsorption energies, and we do not consider these here.

When vertical "η^1" adsorptions are considered, several geometries can be envisioned. First, the plane of the thiophene ring can coincide with the plane of the molybdenum atoms of MoS_2; we denote this configuration by C (Fig. 2C). Raybaud et al. reported an adsorption energy of 1.08 eV, in agreement with that of Orita et al. (1.11 eV). Alternatively, the plane of the thiophene ring can be orthogonal to the plane of the molybdenum atoms. In this case, the sulfur atom can lie between two molybdenum atoms (bridge; Fig. 2D) or above a single molybdenum atom (top; Fig. 2E). Raybaud et al. reported that the bridge configuration is more stable than the top configuration

Table 1
Thiophene adsorption energies for different adsorption modes on the perfect molybdenum edge of MoS_2

Configuration	A	B	C	D	E
E_{ads} [a] (eV)	2.72	1.81	1.11	n.r.	n.r.
E_{ads} [b] (eV)	n.r.	2.00	1.08	1.27	0.94
E_{ads} [c] (eV)	2.84	1.77	1.11	1.32	0.89

n.r.: Not reported.
[a] From Ref. [13].
[b] From Ref. [12].
[c] This work.

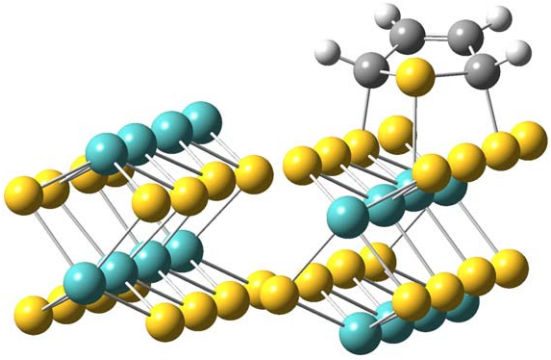

Fig. 3. Thiophene adsorbed on the perfect S-edge.

(1.27 vs. 0.94 eV). We call these configurations (not reported by Orita et al.) D (bridge) and E (top). Because each group used quite different approaches (a cluster model with an atomic orbital basis set by Orital et al. [13], vs. a periodic model with a plane wave basis set by Raybaud et al. [12]), one may wonder whether the discrepancies between the results stem from the computational methods. Consequently, we optimized the geometries of adsorptions starting from the configurations A–E proposed by those two groups. The results, along with the aforementioned literature data, are summarized in Table 1.

First, comparing the adsorption energies obtained by Raybaud et al. and those obtained in the present work for adsorptions C, D, and E reveals that going from ultrasoft pseudopotentials with an energy cutoff of 200 eV to PAW with a cutoff of 300 eV has only a marginal effect on adsorption energy. Moreover, the table also shows that for adsorptions A, C, D, and E, the different computational approaches produce different adsorption energies, all of which are no greater than 0.1 eV. For configuration B, our results are closer to the results obtained by Orita et al. than to those obtained by Raybaud et al. We confirm that a tight optimization starting from geometry B, which presents an imaginary frequency, leads to geometry A without any activation barrier. This comparison allows us to consider our approach reliable, because we can reproduce with a good accuracy the results obtained by different groups with different computational approaches.

3.1.2. Adsorption on the perfect sulfur edge

We also considered the thiophene adsorption on the perfect sulfur edge. Surprisingly, the flat adsorption on such a saturated edge (Fig. 3) is exothermic ($E_{ads} = 0.4$ eV); however, this ad-

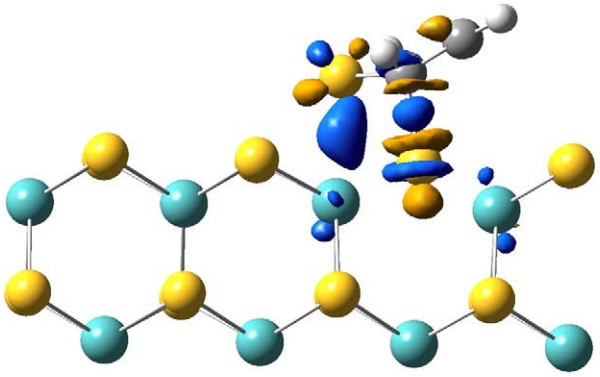

Fig. 4. Electron density transfer occurring upon adsorption on the perfect S-edge. Electron density increase in blue, electron density decrease in yellow (i.e., electron density goes from the yellow to the blue region upon adsorption).

sorption mode is less favorable than the adsorption on the perfect molybdenum edge. The interaction energy can be decomposed in three terms: deformation of the molecule (−1.83 eV), deformation of the surface (−0.52 eV), and interaction energy between the deformed molecule and the deformed surface (2.74 eV). This decomposition demonstrates that the interaction between the molecule and the surface is rather strong even if the adsorption energy is not high. Fig. 4 shows the electronic density transfers between the molecule and the surface. The formation of bonds between the carbon atom of the molecule and the sulfur atoms of the surface results from an interaction between the unoccupied π^* orbitals of the molecule and the 3p orbitals of the surface sulfur atoms, which play important roles in the highest occupied band of the bare surface [5,33]. In addition, the formation of a bond between the thiophene sulfur atom and the molybdenum atom of the surface is evidenced by the increase in the electron density between the two atoms. This bond results from the donation of the sulfur lone pair into the low-energy empty bands that make important contributions on the edge molybdenum atoms. The result of this important electronic transfer between the surface and the molecules is an increase in the C–S bond lengths (1.84 vs. 1.73 Å) with an important reduction in the aromatic character of the molecule, as evidenced by the distortion of the molecule, which is no longer planar.

From this preliminary study, it can be concluded that the most favorable adsorption mode on the perfect edges is configuration A (i.e., flat adsorption on the molybdenum edge), as proposed by Orita et al. [13]. But we previously showed that this perfect surface is not present under the HDS conditions; thus adsorptions on surfaces that are stable within the pressure and temperature conditions relevant to the HDS operating conditions must be considered.

3.1.3. Adsorption on the stable surfaces

It is now well established that the sulfur stœchiometries of the different MoS_2 edges are strongly dependent on the H_2/H_2S partial pressure ratio. Therefore, we consider successively different conditions: large excess of H_2 and 10% H_2S in H_2.

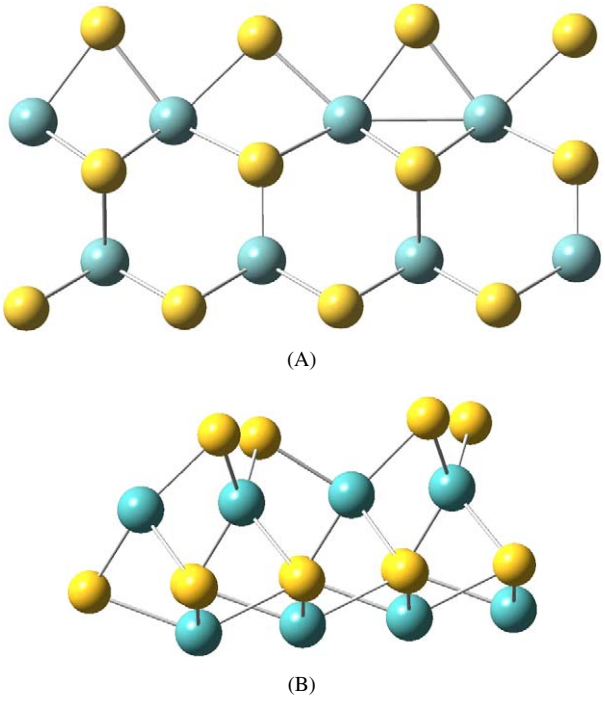

Fig. 5. (A) Stable M-edge under sulfo-reductive conditions showing the different Mo–Mo distances (see text for details). (B) Stable S-edge under the same conditions.

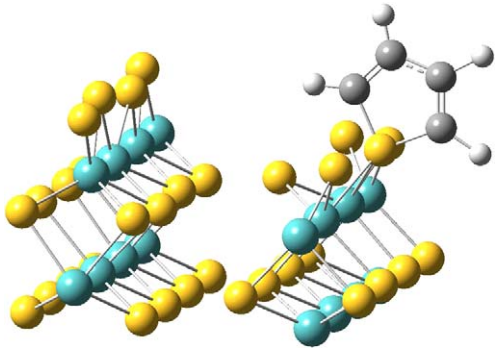

Fig. 6. Thiophene adsorbed on the S-edge stable under reductive conditions.

3.1.3.1. Large excess of H_2 Under catalytic conditions ($H_2/H_2S \sim 100$), the molybdenum edge represented in Fig. 5A is covered with sulfur atoms, yielding sixfold-coordinated Mo edge atoms (Mo_{6c}) [16,17,19]. This induces an important reconstruction of the surface with the formation of short (2.81 Å) and long (3.50 Å) Mo–Mo distances, the formation of this Mo–Mo bond inducing a weakening of the Mo–S bond between the Mo atoms that are 3.50 Å apart. Whatever the starting geometry on this metallic edge, the thiophene molecule does not adsorb. Only a weak physisorbed adsorption mode was found that should not be relevant for thiophene hydrodesulfurization, because the reaction is performed at high temperature. We thus assume that the stable metallic edge is not involved in the HDS reaction.

Within the same partial pressure range, the sulfur edge is reduced; that is, one of every two sulfur atoms is removed

from the surface [16,17,19]. As shown in Fig. 5B, this leads to surface molybdenum atoms that are only fourfold coordinated (Mo_{4c}). We found only one stable adsorption mode on this sulfur edge, the sulfur atom of the thiophene molecule being located in a bridging position between two Mo atoms in a position similar to that of a sulfur atom in the perfect crystallographic MoS_2 surface. The adsorption geometry is shown in Fig. 6. This adsorption is endothermic ($E_{ads} = -0.21$ eV), reflecting the stability of the Mo_{4c} atoms, but it corresponds to a real minimum on the potential energy surface. The Mo–S distances are quite large (2.65 and 2.73 Å vs. 2.41 for a Mo–S distance in MoS_2), and the S–C distances are only slightly enlarged (0.03 Å). Although endothermic, this adsorption mode may play a role in thiophene HDS; because all of the Mo atoms of the sulfur edge can be involved in the catalytic cycle and there is no need for extra vacancy, this is always an endothermic and strongly activated step [34].

3.1.3.2. 10% H_2S in H_2 Typically, a catalyst is sulfided in an atmosphere containing 10% H_2S in H_2, and it is assumed that under the reaction conditions considered above, the H_2/H_2S ratio is on the order of 100. Under the sulfiding conditions, the stable surface exhibits a saturated molybdenum edge similar to that computed under reductive conditions. However, the sulfur edge is strongly influenced by the H_2/H_2S ratio. Formally, a new S edge is created by dissociative addition of H_2 on the perfect sulfur edge of the surface, leading to the formation of SH groups. The surface sulfur stoichiometry is similar to that of the perfect sulfur edge, although four SH groups along with four S atoms, not eight S atoms, are present on the perfect surface. The limit between reductive and sulfiding conditions is rather difficult to define from a theoretical standpoint, however. The interchange between the two surfaces was previously computed for a H_2/H_2S ratio equal to 20 for atmospheric pressure and found to be even larger when total pressure effects were taken into account [16].

Considering the approximations made for the computation of these stability domains, it is rather difficult to rule out the presence of a hydrogen-covered saturated sulfur edge during the reaction. Therefore, we also considered thiophene adsorption on such a saturated sulfur edge. The geometry of the adsorbed thiophene on the fully hydrogenated edge is represented in Fig. 7A. This geometry is very similar to the adsorption geometry on the nonhydrogenated edge. Despite the presence of the hydrogen atoms that saturate the sulfur atoms, adsorption is still possible, but it is now strongly endothermic. For the adsorption on the fully hydrogenated edge, the adsorption energy is −2.04 eV. The deformation energy of the molecule and surface are −1.70 and −0.76 eV, respectively. The interaction energy is then 0.42 eV, which is 2.3 eV lower than the interaction between the deformed molecule and the perfect surface. This decreased interaction energy is due to a modification of the low-energy surface states induced by hydrogen dissociation. Indeed, the occupied states located on the sulfur atoms are now engaged to form bonds with the protons. Furthermore, the reduction of the surface fills the states located on the molybdenum atom and then reduces the acceptor properties of the metal and

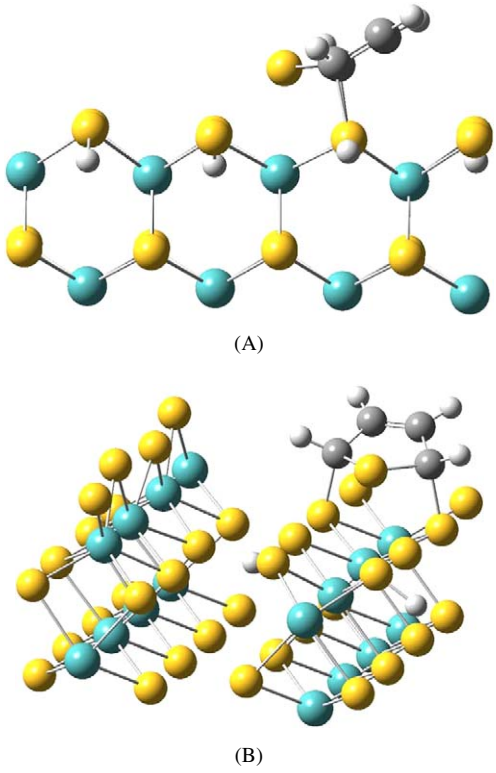

Fig. 7. (A) Thiophene adsorbed on the fully hydrogenated S-edge (B) on the partially hydrogenated S-edge.

its interaction with the thiophene sulfur lone pair. The value of the adsorption energy is influenced by the respective positions of the thiophene molecule and hydrogen atoms on the edges. When only two hydrogen atoms are added to the perfect surface (one on each side of the sulfur edge), the adsorption energies range from −1.96 eV when the hydrogen atoms are located below the thiophene ring to −0.52 eV when they are located on the remaining sulfur atoms (Fig. 7B). Whatever the surface considered, the interaction between the molecule and the surface is still important, but it cannot compensate for the energy loss due to deformation of the molecule. Indeed, the Mo–S (thiophene) distances are 2.54 Å for the perfect surface and 2.54 and 2.61 for the adsorption on the surface with two and four hydrogen atoms, respectively. The evolution of the C–S (surface) bond distances is very limited (from 1.88 Å without hydrogen to 1.93 Å when the surface sulfur atoms are already bonded to one hydrogen).

In summary, adsorption on stable sulfur edges is possible in both conditions; however, the adsorption on an edge that is stable in a large excess of hydrogen is far less endothermic.

3.1.4. Adsorption on coordinately unsaturated sites

It is generally assumed that the HDS proceeds on the CUSs of the MoS_2 edges. Therefore, we also considered the adsorption on vacancies generated by removing one sulfur atom from the edge stable under reducing conditions, even if the vacancy formation is an endothermic reaction. On the metallic edge, because of the surface reconstruction, two type of vacancies can be created, yielding two fivefold-coordinated Mo atoms

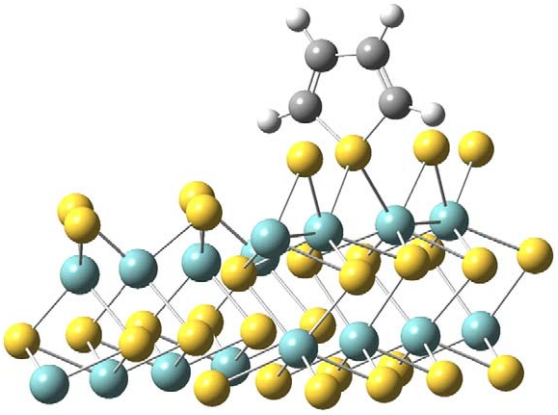

Fig. 8. Thiophene adsorbed (η^1) on a CUS located on the M-edge.

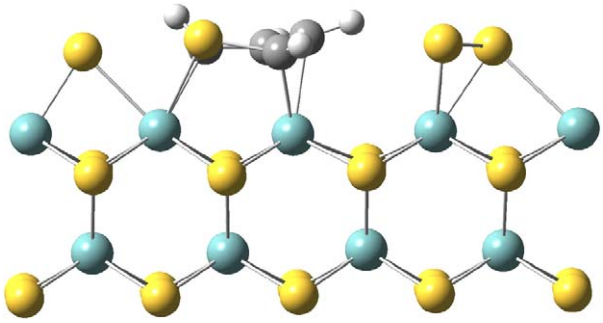

Fig. 9. Thiophene adsorbed (η^5) on a CUS located on the M-edge.

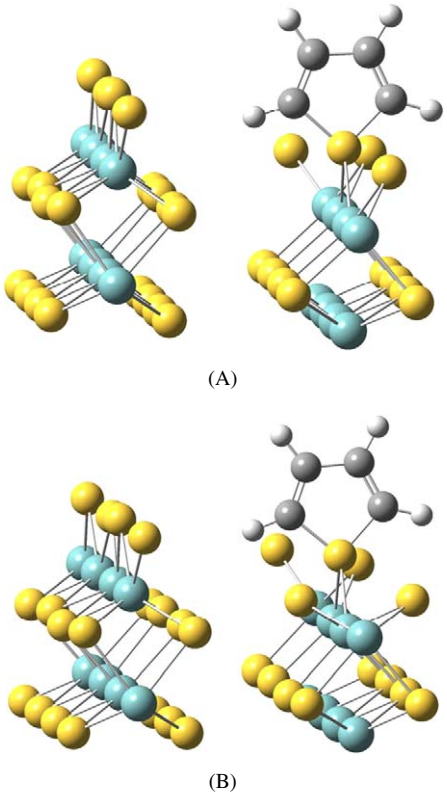

Fig. 10. Thiophene adsorbed on a CUS located on the S-edge. (A) CUS created by sulfur removal. (B) CUS created by sulfur displacement.

(Mo_{5c}). The most stable defective surface exhibits a "long" vacancy (denoted by L hereinafter) created by removing a sulfur atom originally above the long Mo–Mo distance, initially 3.50 Å ($\Delta rE = 0.56$ eV). The formation of a "short" vacancy (denoted by S hereinafter) between the two closer Mo atoms (initially $d_{Mo-Mo} = 2.80$ Å) is 0.30 eV more endothermic ($\Delta rE = 0.86$ eV). η^1 adsorption is possible on both vacancies (Fig. 8), because the sulfur atom of the molecule is located in a bridging position between the two Mo_{5c} atoms, with the adsorption energy depending on the type of vacancy. This energy is 0.20 eV for the L vacancy and −0.05 eV for the S vacancy.

These adsorption energies are rather low compared with those computed on the Mo edge of the perfect surface. To check the affinity of the Mo_{5c} for a sulfur atom that is already involved in two bonds, we computed the H_2S adsorption energies on these two vacancies. The values are of the same order of magnitude (0.27 eV for the L vacancy and 0.07 eV for the S vacancy), suggesting that the adsorptions of thiophene and H_2S on the vacancy will be competitive. It can also be concluded that the strength of the Mo–S_{4c} bond (between a Mo atom and a fourfold-coordinated S atom; see Fig. 8) is weak and that a tetrahedral sulfur atom will not be able to displace a S^{2-} anion located on the surface. Adsorption on the L vacancy does not induce any major modifications of the surface structure, whereas adsorption on the S vacancy leads to an important surface reconstruction that corresponds formally to the substitution of two strong Mo–$S_{(2c)}$ bonds by two weaker Mo–S_{4c} bonds. An increase in the distance between the two Mo atoms on which the thiophene is adsorbed (initially "short") induces an increase in the strength of the remaining Mo–$S_{(2c)}$ bonds followed by a reduction in the other Mo–Mo distances (initially "long").

Finally, adsorption of the molecule by only one lone pair (on top of one Mo atom) was also tested and found to be impossible because of the steric repulsion of the remaining sulfur atoms. All geometry optimizations starting from such geometries led to the bridging position without any activation barrier. A flat adsorption on the metallic edge with one vacancy is possible (see Fig. 9) with a geometry similar to that on the perfect surface. The adsorption is now endothermic ($E_{ads} = -0.15$ eV), however, and the surface reconstruction is important; one S atom is displaced and located on top of one Mo atom, forming one S–S bond with its neighbor. The adsorption energy can be decomposed in two terms: −1.90 eV for the surface reconstruction and +1.75 eV for the thiophene adsorption on this unstable surface. The interaction energy, similar to that obtained on the naked surface, is not sufficiently large to balance the important energetic cost of the surface reconstruction.

The vacancy formation by removal of one S atom is even more endothermic ($\Delta rE = 1.98$ eV) on the sulfur edge than on the molybdenum edge. This value is so high that the creation of such CUSs should not occur during the catalytic reaction. Nevertheless, adsorption on this type of site has been tested to draw a global picture of the molecule interaction with the catalyst. On this vacancy, created by the removal of one sulfur atom, the adsorption energy is 0.95 eV, reflecting the high unsaturation of the Mo_{3c} atoms (Fig. 10A). A second type of vacancy can be created on the sulfur edge through isomerization of the

S edge by the displacement of one sulfur atom [35], which requires a reasonable amount of energy ($\Delta rE = 1.38$ eV). Taking into account the activation energy required for vacancy creation [34], this type of vacancy can be considered the activation energy for the HDS reaction estimated at 0.5–1.0 eV [3,36,37]. The adsorption of thiophene on this vacancy created by the isomerization is also exothermic ($E_{ads} = 1.29$ eV) (Fig. 10B).

3.1.5. Comparison of the different adsorption modes

To compare the adsorption on the defective and stable surfaces, the whole process must be considered. The adsorption on defective surfaces must take into account the whole process, including vacancy formation: the energy required for the creation of the vacancy plus the energy released by the adsorption according to reaction (2) below. Reaction (1) describes the adsorption of thiophene on the stable surfaces or on the isomerized one, and reaction (2) describes the adsorption on defective surfaces:

$$\text{Stable surface} + C_4H_4S(g) = \text{Surface–}SC_4H_4, \quad (1)$$

$$\text{Surface–S} + H_2(g) + SC_4H_4(g) = \text{Surface–}SC_4H_4 + H_2S(g). \quad (2)$$

For adsorption proceeding on the defective sulfur edge, the calculation of these reaction energies shows that the adsorption on the isomerized surface is by far less endothermic (0.11 eV) than that on the vacancy created by sulfur removal (1.03 eV). The energies of the various reactions involved in the adsorption on the two types of surfaces in the HDS reaction conditions (i.e., in the reductive conditions) are given in Table 2.

This table also shows that, under reductive conditions corresponding to the reaction conditions, the most probable adsorption modes are η^1 on the nondefective sulfur edge or η^1 on the isomerized sulfur edge. Kinetic considerations support the former, however, because the activation energy of creation of this vacancy was found around 1 eV [34]. Hence, adsorption on the nondefective sulfur edge that does not require such an activated step will be strongly favored. This result, in opposition to that obtained for the adsorption on the perfect surface that favors a flat adsorption, supports the importance of taking into account the environment for the description of the surface on which the adsorption will proceed. These calculations also demonstrate that CUSs are not required for thiophene adsorption on the sulfur edges of the MoS_2 nanoparticles.

Table 2
Computed reaction energies for thiophene adsorption starting form the stable surfaces under reductive conditions. When several geometries are possible, only the most stable is considered

Surface/edge	Reaction	Adsorption mode	Reaction energy (eV)
Stable surface/Mo	1	No adsorption	
Stable surface/S	1	η^1	0.21
Defective surface/Mo	2	η^1	0.36
Defective surface/Mo	2	η^5	0.71
Defective surface/S	2	η^1	0.11

3.2. Vibrational spectra of adsorbed molecules

To compare our results with the experimental vibrational data cited in Section 1, and also to propose an assignment for the observed features of adsorbed thiophene, we computed the wavenumbers of the normal modes for the different adsorption geometries. The results, along with the experimental and calculated values of the free molecule, are presented in Table 3. We restrict our analysis to wavenumbers above 1000 cm^{-1}, because below this value an important mixing of the various normal modes occurs when thiophene is adsorbed, hindering a comparison of free and adsorbed molecules.

For the free molecule, the agreement between the experimental data [13,38] and the calculated ones is very good. This agreement, obtained without using a scaling factor (which is generally needed in such calculations), is close to previously published data obtained with scaled frequencies and standard molecular orbital calculations [39].

The infrared spectra [21–23] exhibit important differences between adsorbed- and the gas-phase thiophene molecules in the region of the C=C stretching modes (i.e., around 1400 cm^{-1}). The spectra of adsorbed thiophene exhibit a band characteristic of the free molecule at 1405–1410 cm^{-1} with

Table 3
Vibrational frequencies (cm^{-1}) for free and adsorbed thiophene. In parentheses are reported the relative shifts with respect to the calculated frequencies for the free molecule

Assignment	Experimental (free molecule)	Calculated					
		Free molecule	η^1 adsorption on the S-edge	η^1 adsorption on a CUS on the S-edge	η^1 adsorption on a CUS on the Mo-edge	η^5 adsorption on a CUS on the Mo-edge	η^5 adsorption on the saturated S-edge
ν(C–H)	3126	3115	3131 (+16)	3113 (−2)	3127 (+12)	3070 (−45)	3072 (−43)
ν(C–H)	3125	3115	3124 (+9)	3108 (−7)	3120 (−5)	3120 (−62)	3040 (−75)
ν(C–H)	3098	3072	3069 (−3)	3069 (−3)	3074 (+2)	3074 (−44)	2961 (−111)
ν(C–H)	3098	3056	3053 (−3)	3057 (+1)	3063 (−7)	3063 (−128)	2957 (−99)
νC=C as	1507	1489	1534 (+45)	1538 (+49)	1525 (+36)	1402 (−87)	1566 (+77)
νC=C sym	1409	1411	1443 (+32)	1439 (+28)	1434 (+23)	1324 (−87)	1320 (−91)
ν ring	1360	1351	1319 (−32)	1320 (−31)	1328 (−23)	1218 (−133)	1210 (−141)
δ(C–H)	1256	1233	1215 (−18)	1221 (−12)	1227 (−6)	1181 (−52)	1196 (−37)
δ(C–H)	1085	1071	1071 (0)	1071 (0)	1078 (+7)	1073 (+2)	1125 (+54)
δ(C–H)	1083	1065	1062 (−3)	1067 (+2)	1074 (+9)	1029 (−36)	1104 (+39)
ν ring	1036	1049	1018 (−31)	1003 (−46)	1016 (−33)	993 (−56)	1094 (+45)

a shoulder at 1431 cm^{-1} assigned to the stretching mode of the molecule adsorbed on MoS_2. Another shoulder observed at 1400 cm^{-1} was assigned to adsorption on the alumina. Table 3 shows that a flat adsorption induces a decrease in the C=C stretching wavenumbers computed at 1409 cm^{-1} for the gas-phase molecule. Indeed, the computed values are 1402 cm^{-1} for the flat adsorption on the defective metallic edge and 1320 cm^{-1} for the adsorption on the stable sulfur edge under sulfiding conditions. This decreased stretching frequency can be attributed to the donation of the electrons of the π system of the molecule to the bonds formed between the carbon atoms and the sulfur atoms of the surface. In contrast, a vertical adsorption induces an increase in wavenumber (1434 and 1439 cm^{-1} for adsorption on the defective metallic and sulfur edge, respectively, and 1443 cm^{-1} for adsorption on the stable reduced S edge). Moreover, this adsorption mode induces activation of the molecule with a decrease in C–S bond strength, because the sulfur atom is now fourfold coordinated, implying an increase of the C=C bond order, in agreement with the bond order conservation principle. In this spectral range, our results are in good agreement with the data of Mills et al. [22], suggesting a vertical adsorption. The flat adsorption proposed by Mitchell et al. [24] would induce very important modifications of the spectrum, which are not observed here.

In the C–H stretching spectral range, no significant differences are observed between thiophene adsorbed on Al_2O_3 and thiophene adsorbed on a Mo/Al_2O_3 catalyst. Both spectra exhibit frequencies at 3104, 3088, and 3074 cm^{-1}, shifted slightly with respect to the gas-phase frequencies (3125 and 3098 cm^{-1}). The aforementioned values are closed to the values obtained in the liquid phase, suggesting some physisorption. These results are also compatible with a η^1 adsorption (Table 3) but, once again, not with a flat one as proposed by Mitchell et al. [24], because the C–H stretching modes should have shifted downward by at least 50 cm^{-1}. This discrepancy may originate from the fact that the INS attribution is based on analysis of the low-frequency modes. As explained above, this spectral range is difficult to analyze because of the mixing of the various normal modes.

Orita et al. [13] reached the same conclusion, even though they computed frequencies for thiophene adsorbed on perfect surfaces. Taking into account the effect of the surrounding atmosphere on the computation of thiophene adsorption and vibrational frequencies on realistic surfaces explains why η^1 adsorption is observed rather than η^5 adsorption, which is more stable on perfect surfaces.

4. Conclusion

In this work we first showed that periodic PAW calculations accurately reproduce both cluster calculation and periodic USPP calculations. We also showed that thiophene adsorption on MoS_2 surfaces that are stable under reductive conditions is always endothermic. However, it has been experimentally shown that desorption does not occur at low temperature, indicating that this process is also activated [22]. Thus, such endothermic adsorption modes in the reaction path cannot be ruled out.

On defective surfaces, the adsorption is exothermic, but vacancy creation (the limiting step of the process) is strongly endothermic and activated. Therefore, the number of vacancies created would be very small [34] and certainly not compatible with the amount of adsorbed thiophene molecule as estimated by IR measurements [22]. The DFT calculations allowed us to consider that the reported IR features should be considered not characteristic of adsorption on a CUS, but rather representative of η^1 adsorption on the stable sulfur edge in reductive conditions corresponding to the HDS reaction conditions. Furthermore, the adsorption of large molecules, such as DBT and DMDBT, is not possible on such sites [35], and extension of thiophene desulfurization activity to deep desulfurization should be performed with caution.

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