Adsorption of Thiophene on the Catalytically Active Surface of MoS₂: An *Ab Initio* Local-Density-Functional Study

P. Raybaud,^{1,2} J. Hafner,¹ G. Kresse,¹ and H. Toulhoat²

¹Institut für Theoretische Physik and Center for Computational Material Science, TU Wien,

Wiedner Hauptstraße 8-10, A-1040 Wien, Austria

²Institut Français du Pétrole, Groupe de Modélisation Moléculaire, B.P. 311, F-92852 Rueil-Malmaison, France

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The adsorption of thiophene on the catalytically active $MoS_2(010)$ surfaces has been studied using *ab initio* local-density-functional molecular dynamics. It is shown that thiophene adsorbs in an η^5 configuration with the molecular ring parallel to the surface, centered above a coordinatively unsaturated Mo atom, and with the sulfur atom in a binding position between two Mo surface atoms. This configuration provides not only the highest adsorption energy, but activates in addition the thiophene molecule with respect to both C-S bond cleavage (and hence desulfurization) and hydrogenation. Hence it represents a realistic scenario for the first step in catalytic hydrodesulfurization. [S0031-9007(98)05327-7]

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Catalytic hydrodesulfurization (HDS) is a vital step in the processing of crude oil into many useful hydrocarbon products. Natural petroleum contains different organosulfur compounds. The HDS process consists in the reaction of the sulfur-containing compound with hydrogen to form hydrocarbons and H_2S [1-3]. Among the various organosulfur compounds the aromatic species like thiophene are the least reactive. The most widely used catalysts for HDS are based on layered transition-metal disulfides—usually a combination of Mo and W sulfides with Co and Ni [4]. The two basic steps in the HDS process are desulfurization and hydrogenation. Much of the theoretical and experimental work on HDS catalysis has concentrated on the breaking of the C-S bond in thiophene (SC₄H₄) on MoS₂. However, many fundamental factors such as the initial adsorption geometry, the nature of the active site, and a model for the bond-breaking processes remain unclear. For thiophene on MoS_2 the most extended theoretical studies have been performed by Zonnevylle, Hoffmann, and Harris [5] using the extended-Hückel tight-binding method and Diez and Jubert [6] using molecular-orbital techniques. Still, a clear picture of a possible mechanism for the HDS process seems to be remote: the sites identified as active in modifying the C-S bond are found to be unfavorable for adsorption and vice versa.

A major handicap of the semiempirical techniques applied so far to the theoretical investigation of the HDS process consists in their lack of electronic self-consistency and their inability to proceed to a full optimization of the geometry of the adsorbate/substrate complex. Very recently, it has been shown that *ab initio* local-density-functional (LDF) techniques can contribute to a significantly improved understanding of certain elementary steps in catalytic processes [7,8]. In the present work we demonstrate that the accuracy and efficiency of plane-wave based *ab initio* LDF techniques have been developed sufficiently far to allow for a detailed study of the adsorption of thiophene on the catalytically active surfaces of MoS₂.

Our investigation has been performed in two steps: In the first we show that the bulk-terminated MoS_2 (010) surface exposing in alternating S-Mo-S sandwiches rows of unsaturated S and Mo atoms remains stable at temperatures corresponding to the conditions in HDS reactors. In the second step we examine a number of possible adsorption geometries, and we demonstrate that the highest adsorption energy is realized in an η^5 -bound geometry (in the terminology of organometallic chemistry) in which the thiophene ring lies parallel to the surface, with its center approximately above an unsaturated Mo atom. At the same time this geometry is also shown to be most effective in weakening the C-S bond and in reducing the aromatic character of the molecular bond. Hence the adsorption activates the thiophene molecule both with respect to hydrogenation and C-S bond breaking.

Our calculations have been performed using the Vienna *ab initio* simulation program VASP [9,10]. VASP performs an iterative solution of the generalized Kohn-Sham equations of LDF theory via an unconstrained band-by-band minimization of the norm of the residual vector to each eigenstate. VASP also allows a dynamical or static optimization of the atomic geometry using the exact Hellmann-Feynman forces. The calculations are performed in a plane-wave basis with a cutoff energy of 200 eV. The electron-ion interactions being described by fully nonlocal ultrasoft pseudopotentials [11,12]. We used the local exchange-correlation functional proposed by Perdew and Zunger [13], adding the generalized-gradient corrections (GGC's) proposed by Perdew et al. [14]. Extensive investigations of the structural, cohesive, and electronic properties of a large number of transition-metal sulfides have been published recently [15]; we refer to this paper concerning details of the ultrasoft pseudopotentials.

In hexagonal MoS₂ the atoms form close-packed triangular layers stacked in the (001) direction. Mo layers at z = 1/4 and z = 3/4 are surrounded on either side by S layers such that the Mo atoms center trigonal prisms formed by the S atoms. The stacking sequence is $B\underline{C}BC\underline{B}C$ (Mo layers underlined). S-Mo-S trilayers are separated by van der Waals contacts between S atoms. MoS_2 crystals are easily cleaved along basal planes. These surfaces are catalytically inactive because the atoms exposed at the surface are chemically saturated. Cleavage parallel to the (100) or (010) planes exposes in neighboring S-Mo-S trilayers alternatingly rows of coordinatively unsaturated Mo atoms and double rows of unsaturated S atoms (see Fig. 1). There is a general agreement that this is the catalytically active surface.

Our model for the MoS₂ (010) surface is shown in Fig. 1. It consists of two S-Mo-S sandwiches stacked in the *z* direction; each slab consists of three rows of trigonal prisms stacked in the *y* direction (plus rows of terminating Mo atoms on one side) and four rows of trigonal prisms in the *x* direction. This 72-atom unit (composition Mo₂₄S₄₈) is periodically repeated in the *x* and *z* directions, in the *y* direction neighboring slabs are separated by a vacuum layer of 12.8 Å. All calculations have been performed at the equilibrium lattice parameters of a = 3.170 (3.160) Å and c = 12.584 (12.294) Å calculated in the LDF + GGC (experimental values in parentheses). The upper half of the slab was allowed to relax, while the lower half was held at a fixed geometry. A static conjugate-gradient relaxation shows that the unsaturated

Mo atoms relax inwards by $\Delta y = -0.04$ Å, while the underlying S atoms relax outwards by $\Delta y = 0.05$ Å and by $\Delta x = \pm 0.05$ Å (shortening the S-S distance across the trilayer), the Mo atoms below relax outwards by $\Delta y = 0.04$ Å. The surface energy is 0.675 eV/atom, the energy gain by relaxation is 21 meV/atom. To make sure that the relaxed structure remains stable under the usual conditions of a HDS reaction, the entire system was gradually heated in 2.5 ps to 700 K, using Nosé dynamics to control the temperature. No indication for a reconstruction of the surface was found even at the highest temperature reached in the molecular dynamic simulation. Bulk MoS₂ is a semiconductor with an indirect gap of 0.89 eV. The MoS₂ (010) surface is metallic, with a high density of states in the bulk gap located mainly at the coordinatively unsaturated Mo and S surface sites (details of the electronic surface states will be reported elsewhere).

The molecular structure of free thiophene calculated using VASP is in good agreement with experiment [16] (see Table I): C-C and C-S bond lengths are accurate within 0.01 Å, C-H bond lengths within 0.02 Å.

The adsorption of thiophene on MoS₂ (010) was studied starting from different configurations: (a) with the molecular ring perpendicular to the surface [the coordination is η^1 , i.e., the molecule bonds to the substrate via only one atom (the S atom) in the ring. The ring is parallel to the



FIG. 1. Graphical representation of the adsorbate/substrate complex used to study the adsorption of thiophene on MoS₂ (010). Large circles, sulfur; small circles, molybdenum. Sites 1 to 3 are the unsaturated, 4 to 6 the saturated Mo atoms at the surface. Sites 7 to 9 [and the corresponding sites mirrored at the (x, y) plane] represent the saturated, sites 10 to 12 the unsaturated S-surface atoms. The thiophene atom is depicted in the energetically most favorable 1-bridge- η^5 coordination (cf. text), Δx , Δy stand for the surface relaxations (in Å) induced by the adsorption. The labeling of the atoms in the thiophene molecule is explained in the inset.

TABLE I. Bond lengths [in Å and bond angles (in degrees)] calculated for the free thiophene molecule (compared with experiment) and for thiophene absorbed in different coordinations on MoS_2 (010). The last line gives the adsorption energies (in eV, layer 1 only). The atoms in the molecule are labeled as shown in Fig. 1.

			Тор	Тор	Тор	Bridge	Bridge
	Exp. ^a	Theory	$\eta^{\hat{1}}$	$\eta^{\hat{1\prime}}$	$\eta^{\hat{5}}$	η^{1}	η^{5}
SC ₂	1.714	1.722	1.727	1.734	1.745	1.768	1.815
C_2C_3	1.378	1.389	1.391	1.382	1.416	1.367	1.428
C_3C_4	1.427	1.434	1.435	1.432	1.444	1.451	1.428
C_2H_6	1.069	1.089	1.093	1.098	1.093	1.086	1.093
C_3H_7	1.081	1.094	1.091	1.091	1.095	1.098	1.093
$\widehat{C_5SC_2}$	92.57	92.26	94.53	92.74	91.12	92.06	84.51
$S\widehat{C_2H_6}$	120.25	120.25	120.43	121.10	118.95	119.51	119.61
$C_3 \widehat{C_4} H_7$	124.07	120.18	124.03	123.34	125.79	122.71	125.97
α	180.00	180.00	180.00	180.00	172.72	180.00	152.30
SMo			2.48	2.45	2.58	2.61	2.72
							2.98
$\operatorname{Mo-}G^{b}$					2.41		2.05
Ead			0.94	1.08	1.44	1.27	2.00

^aFree molecule, experimental data after Ref. [16].

 ${}^{b}G$ —center of the thiophene ring.

yz (η^1) or to the yx ($\eta^{1'}$) plane] or with the ring parallel to the surface in the xz plane (the coordination is η^5); (b) with the S atom on top of an Mo atom or in a bridge position between two Mo atoms; and (c) on the sandwich exposing the unsaturated Mo atoms (layer 1) or on the sandwich exposing the unsaturated S atoms (layer 2). In each case this defines only the starting configuration, the coordinates of all atoms in the molecule and in the top S-Mo-S layers of the substrate are allowed to relax to their energetically most favorable positions.

We find that η^5 coordination is always energetically more favorable than η^1 or $\eta^{1'}$ coordination, bridge bonding more than on-top bonding; see Table I. Positive adsorption energies are obtained only on the S-Mo-S sandwiches exposing the unsaturated Mo atoms, adsorption on the S-terminated slabs is always endothermic. The most stable adsorption site is bridge η^5 on layer 1. This is also confirmed by molecular-dynamics simulation at 300 K starting with a molecule in an η^1 configuration. In a very short time the molecule rotates to a position parallel to the surface close the bridge- η^5 geometry. The predicted energetic preference for η^5 over η^1 and for bridge over top is in direct contradiction to the extended Hückel results of Zonnevylle et al. [5]. The calculated equilibrium geometries of the adsorbed thiophene (Table I) give important information on the adsorption-induced modifications of the molecular bond: (a) Whereas in η^1 and $\eta^{1'}$ coordinations the molecule remains planar, in η^5 coordination it is tilted about the C_2 - C_5 axis. (b) The C-S bond length is increased, with the largest increase (0.09 Å) predicted for the bridge- η^5 configuration. (c) In the η^5 configurations the difference in the lengths of the double C_2 - C_3 and single C_3 - C_4 bonds is reduced, in the bridge- η^5 configuration on layer 1 the difference is zero. This indicates that in this configuration the aromatic character of the thiophene ring has been destroyed by the adsorption. (d) In this configuration the C-S-C bond angle is also reduced. (e) In the most stable 1-bridge- η^5 configuration the shortest distances between Mo and the S atom in the thiophene are 2.72 and 2.98 Å (to be compared to Mo-S distances of 2.35 and 2.98 Å in MoS₂). This means that the energetically most favorable adsorption geometry is also the one that is most effective in weakening the C-S bond and in reducing the aromatic character of the thiophene ring, i.e., in activating the molecule both for desulfurization and hydrogenation. All the features predicted for the stable η^5 adsorption geometry are also characteristic for η^5 thiophene organometallic complexes [17].

The mechanism causing the activation of the thiophene molecule may be studied by examining the spectral properties of the free and adsorbed molecules and the charge flow due to adsorption. Figure 2 shows the density of states of the free molecule and the local DOS of the bridge- η^5 adsorbed molecule. The highest occupied molecular orbitals (labeled 10 to 13) represent bonding C-C and S-C π states (symmetry 1b₁), the S lone pair (8a₁), bonding C-C and S-C π states (2*b*₁), and bonding C-C π states (1*a*₂), the lowest unoccupied orbital antibonding C-S π orbitals $(3b_1)$, in good agreement with the experimental spectrum [18]. On adsorption in an η^5 configuration, bands 10 to 14 interact strongly with the Mo- $d-\bar{S}-P$ band complex of the substrate. In particular, the bonding C-C and C-S π bands are broadened so that they overlap with the Fermi level. In addition, the S-lone-pair state and the antibonding C-S π state are involved in the reaction. In contrast, adsorption in an η^1 configuration leads only to a modest change of the molecular spectrum.

The charge redistribution induced by the adsorption is illustrated in Fig. 3 in the form of difference electrondensity plots (adsorbed molecule plus substrate minus



FIG. 2. Local electronic density of states for a free thiophene molecule (dashed lines) and for thiophene adsorbed on MoS_2 (010) (full lines); cf. text.

clean substrate minus free, but deformed molecule). Charge flows into the nonbonding Mo- d_{yz} surface orbitals (and to a smaller degree into the $d_{x^2-y^2}$ surface states), illustrating the donor properties of thiophene, and into the antibonding C-S- π states (backdonation); see Fig. 3(a). The charge density is reduced in bands 12 and 13, i.e., in the bonding C-C- π states, in the lone-pair band, and in the d_{xy} and d_{z^2} surface orbitals; see Fig. 3(b). The depletion



FIG. 3. Isosurfaces of the difference electron density of adsorbed thiophene plus substrate minus clean substrate minus free, deformed thiophene. (a) Positive isosurface indicates charge accumulation, and (b) negative isosurfaces indicate charge depletion; cf. text.

of the bonding C-C- π states causes the destruction of the aromatic character of the ring and hence facilitates hydrogenation, the incipient population of the antibonding S-C- π states the weakening of the C-S bond.

In summary, our ab initio studies yield new and to some extent unexpected insight of the electronic factors governing HDS of thiophene on MoS₂. We have demonstrated that the bridge- η^5 coordination on the unsaturated Mo atoms of the MoS_2 (010) surface is not only the most effective in activating thiophene for both C-S bond breaking and hydrogenation (as already suggested by extended Hückel studies [5] in contradiction to MO calculations [6]), but that it represents also the energetically most favorable adsorption geometry. It is also important that we have been able to show that the bulk-terminated MoS_2 (010) surface which exposes unsaturated Mo atoms in alternating S-Mo-S sandwiches remains at least metastable at high temperatures. Hence our investigations suggest a particularly attractive scenario for the first elementary step towards HDS of thiophene.

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