

FULL PAPER

## Cluster Approach of Active Sites in an MoS<sub>2</sub> Catalyst

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**Abstract** The present paper reports a Density Functional Theory (DFT) study of a Mo<sub>12</sub>S<sub>24</sub> cluster as a model of the active phase in hydrodesulphurisation (HDS). Different types of sulphur vacancies are considered and compared. The interaction of a thiophene molecule with a double vacancy is simulated leading to the determination of a stable configuration which corresponds to a flat adsorption on the edge of the MoS<sub>2</sub> sheets. The dissociative adsorption of molecular hydrogen on a double vacancy is also considered.

**Keywords** Density functional, Hydrotreatment, Molybdenum disulphide, Catalytic sites

### Introduction

The increasing demand to convert sulphur-rich petroleum feed stocks as well as the need to produce clean fuel based on the pressing environmental requirement to reduce the emission of sulphur compounds necessitates an improvement of the hydrodesulphurisation (HDS) catalysts. The use of CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts is well known for the hydrotreatment of petroleum fractions. The active phase consists of molybdenum disulfide nanocrystallites well dispersed on a  $\gamma$ -alumina support and it is usually assumed that the sulphur vacancies at the edge of the MoS<sub>2</sub> slabs are the active sites [1,2]. However, no experimental data are available for the precise description of the nature of these sites, nor of the mechanism of HDS.

Computational approaches can be used to give some insight into the microscopic processes responsible for the HDS. In previous studies, the structure of an Mo<sub>12</sub>S<sub>24</sub> cluster was optimised with the Density Functional Theory (DFT) method; its interaction with the alumina support [3] as well as its stability upon the exchange of some Mo atoms by Co atoms [4] were analysed. This cluster approach with the DFT method was chosen to avoid the possible artefacts caused by the periodicity of defects in a periodic approach. The mean length of the disulfide crystallite determined by high resolution electron microscopy (HREM) [5,6] is always about 3 nm. A corresponding MoS<sub>2</sub> cluster would have the formula Mo<sub>27</sub>S<sub>54</sub>, but it is unfortunately too large for a treatment with reasonable bases. The neutral Mo<sub>12</sub>S<sub>24</sub> cluster is a good compromise permitting a quantum treatment on a model representing the real active phase [3].

In the present work the same Mo<sub>12</sub>S<sub>24</sub> cluster has been used to study the influence of the creation of sulphur vacan-

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**Table 1** Description of the basis of atomic orbitals used in ADF [7]

	Frozen core	STO-DZ exponents	Polarisation exponents
Hydrogen		1s: 0.76; 1.28	2p: 1.25
Carbon	1s	2s: 1.24; 1.98 2p: 0.96; 2.20	3d: 2.20
Sulphur	1s-2p	3s: 1.60; 2.60 3p: 1.15; 2.15	3d: 1.50
Molybdenum	1s-3d	4s: 3.25; 4.85 4p: 2.65; 4.35 4d: 1.30; 3.05 5s: 1.00; 1.80	5p: 1.36

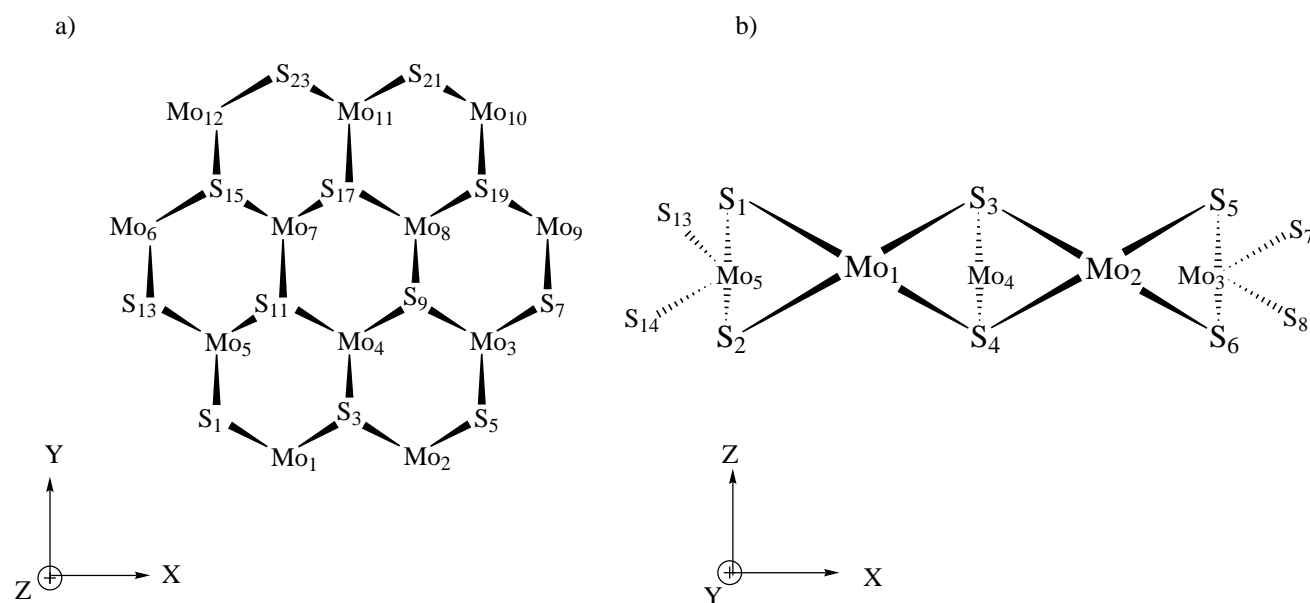
cies on its structure and electronic properties as well as its reactivity toward thiophene and hydrogen.

### Computational technique and models

The DFT calculations were performed with the package Amsterdam Density Functional, ADF, version 2.0.1 [7] on SGI workstations with R4400 and R10000 processors. The local density approximation (LDA) to the exchange-correlation functionals is parametrised according to Vosko et al.[8]. The non-local gradient corrections were used as post-SCF treatment according to Becke [9] for exchange and to Perdew [10] for correlation. Thus all reported geometries correspond to optimisations performed at the LDA level. All atoms were described by Slater-type orbital (STO) basis sets implemented in ADF and the frozen-core approximation defined in Table 1. All the calculations reported in this paper were performed

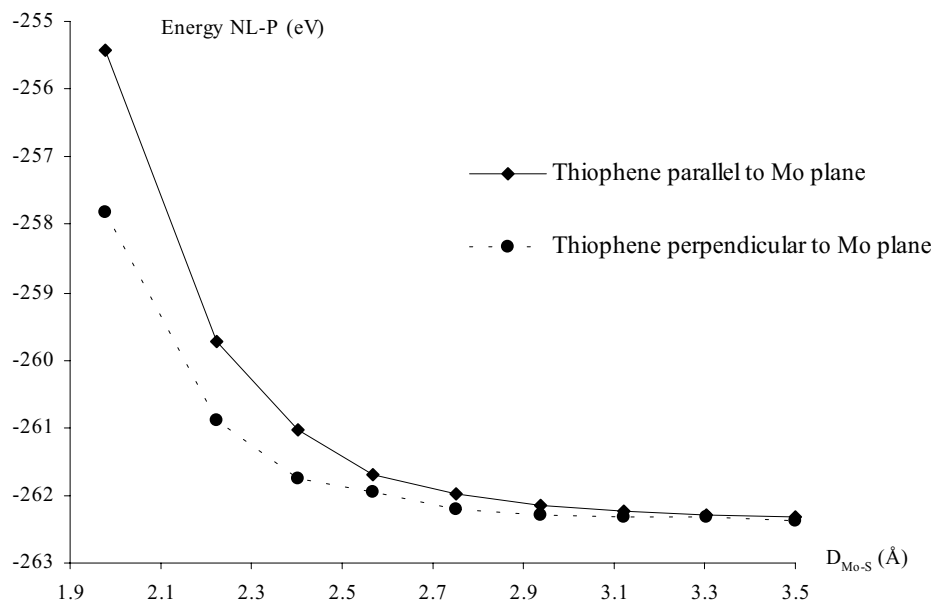
with the double zeta plus polarisation (DZP) basis set, except Mo, which was treated with DZ. The default convergence criteria of ADF were used for the SCF process as well as for the geometry optimisation. Symmetry conditions were applied when possible in order to reduce the computing time. The charges reported are taken from the standard Mulliken[11] analysis. Other descriptions of the charge distribution like the Hirshfeld scheme[12] calculated in ADF were also considered. Although the absolute values are different, they lead to the same conclusions and will not be reported here.

As far as the energy is considered, the fact that ADF yields a bonding energy which is related to the fragments building the molecules has to be taken into account. The fragments are the atoms but they are considered as spherical spin-restricted atoms (equal up and down spin densities), while real atoms correspond to a spin-unrestricted, usually not spherically-symmetric, situation [13]. This difference is important when clusters with different numbers of atoms are



**Figure 1** Schematic representation of the  $Mo_{12}S_{24}$  Model cluster. a) Projection on the  $xOy$  plane. b) Partial projection in the  $xOz$  plane

**Figure 2** Non-local post-SCF bonding energy of the  $\eta_1$  thiophene on the  $\text{Mo}_{12}\text{S}_{22}$  cluster as a function of the Mo-S<sub>T</sub> distance

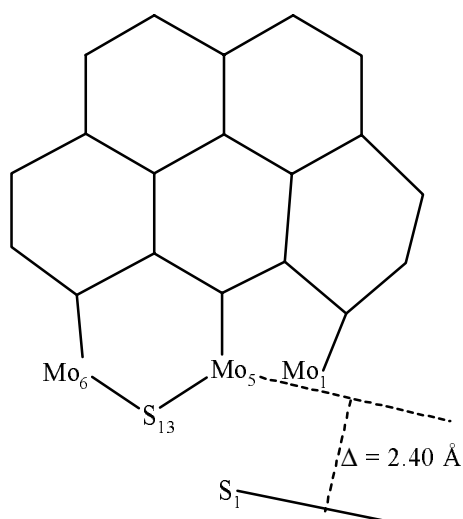


compared or when a real bond energy is discussed or compared with experimental values. The correction of  $-0.84$  eV for Becke-Perdew was already calculated and published for sulphur [13] and we performed the corresponding calculation of the correction for Mo. It turns out that for a triple-zeta basis set with the frozen core up to and including the 3d shell this correction is  $-4.52$  eV, a reasonable value when compared with Cr ( $-5.53$  eV) in the preceding row of the periodic table [13]. In the following we will use the term bonding energy for the non-corrected output of the ADF program and bond energy for the corrected energies. For simplicity in Figures 2 and 4, where only relative energies are considered

as the number of atoms is constant, these corrections were not applied.

Models with sulphur vacancies have already been studied by molecular mechanics on a  $\text{Mo}_{27}\text{S}_{54}$  cluster [14] and by DFT on  $\text{H}_6\text{Mo}_3\text{S}_9$  [15]. The first species is presently not tractable with quantum techniques but the second one is so small that it can be expected that the molybdenum atoms are different from those present in the active disulfide nanocrystals. It has been shown that  $\text{Mo}_{12}\text{S}_{24}$  is a good compromise permitting a quantum treatment on a model representing the real active phase [3] because the core atoms of the cluster were shown to have structural properties identical to those of the bulk compound and the interactions of the cluster with alumina turned out to be of local nature. Therefore it is reasonable to assume that a cluster of this size is a good representation of the active catalytic compound and that this model can lead to at least qualitative hints about the microscopic processes. This cluster is represented in Figure 1, according to two projections with the numbering of the atoms used hereafter. In part (a) only the upper layer of sulphur atoms corresponding to the odd atoms is represented; the parent sulphur atoms with even numbers have been omitted.

In this model three types of molybdenum atoms exist: i) internal hexa-coordinated atoms noted  $\text{Mo}_{(6)\text{int}}$  (Mo atoms 4, 7 and 8), ii) external hexa-coordinated atoms noted  $\text{Mo}_{(6)\text{ext}}$  (Mo atoms 3, 5 and 11) and iii) tetra-coordinated atoms noted  $\text{Mo}_{(4)}$  (Mo atoms 1, 2, 6, 9, 10, 12). Similarly three types of sulphur can be identified: i)  $\text{S}_{(3)\text{int}}$  (S atoms 9, 10, 11, 12, 17, 18), ii)  $\text{S}_{(3)\text{ext}}$  (S atoms 3, 4, 15, 16, 19, 20) and iii)  $\text{S}_{(2)}$  (S atoms 1, 2, 5, 6, 7, 8, 13, 14, 21, 22, 23, 24). Upon reduction non-bridging sulphur atoms are easily eliminated. Therefore, they are not considered in the present model, which contains Mo atoms with unsaturated coordination; they can be considered as potential active sites in the catalytic process. Bridging S atoms are eliminated at higher temperature and coordi-



**Figure 3**  $\eta_5$  interaction of thiophene with  $\text{Mo}_1$

**Table 2** Comparison of the uncorrected bonding energies (non-local post-SCF: NL-P) and corrected bond energies in eV of the clusters as a function of the vacancies (See text)

Model	Vacancies	Bonding energy NL-P	Bond energy	Mean bond energy
Mo <sub>12</sub> S <sub>24</sub>	–	-219.719	-145.32	-2.42
Mo <sub>12</sub> S <sub>23</sub>	S <sub>1</sub>	-215.502	-141.94	-2.45
Mo <sub>12</sub> S <sub>23</sub>	S <sub>3</sub>	-214.297	-140.74	-2.43
Mo <sub>12</sub> S <sub>23</sub>	S <sub>11</sub>	-214.011	-140.45	-2.42
Mo <sub>12</sub> S <sub>22</sub>	S <sub>1</sub> , S <sub>2</sub>	-209.835	-137.11	-2.45
H <sub>2</sub>	–	- 6.728	-4.828	–
H <sub>2</sub> S	–	-10.814	-8.084	–

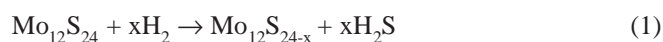
native unsaturated sites (CUS) are created. Because of the symmetry only three sulphur vacancies may be created on this Mo<sub>12</sub>S<sub>24</sub> cluster; they correspond to the elimination of sulphur atoms in the positions 1, 3 and 11 leading to a cluster Mo<sub>12</sub>S<sub>23</sub>.

## Results and discussion

### Sulphur vacancies

Table 2 presents the energies of the different Mo<sub>12</sub>S<sub>23</sub> clusters. It turns out that the creation of a vacancy in position S<sub>1</sub> (S<sub>(2)</sub> elimination) leads to a configuration with larger bonding and bond energies; it will be more stable than the two other lacunary structures. This stability is mainly due to the fact that only two MoS bonds have to be broken to create an S<sub>1</sub> vacancy while three are necessary for the creation of S<sub>3</sub> or S<sub>11</sub> defects. The mean bond energy is slightly higher for clusters with S<sub>3</sub> or S<sub>11</sub> vacancies (-2.43 eV or -234 kJ/mol) than with S<sub>1</sub> (-2.45 eV or -236 kJ/mol). We come to the conclusion that the creation of a vacancy at the edge of the model is

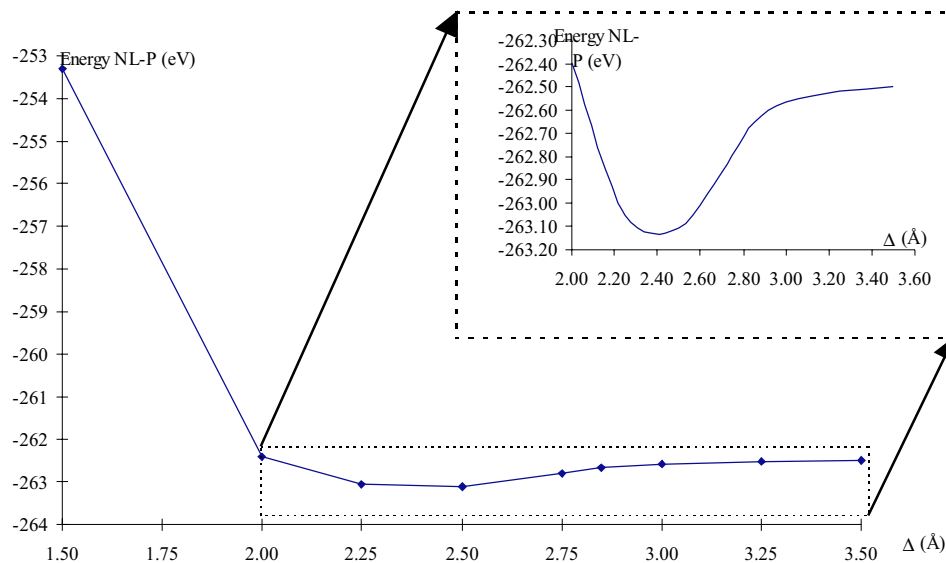
the most favourable possibility. This vacancy leads to a system in which the MoS mean bonding energy is larger than in the original Mo<sub>12</sub>S<sub>24</sub> model or in models with a vacancy in the bulk. It is also possible to analyse the data of Table 2 according to the reaction



which yields the energy necessary for the creation of a vacancy during the treatment under hydrogen. Considering the energies of formation of H<sub>2</sub> (- 4.83 eV) and H<sub>2</sub>S (- 8.08 eV), obtained with a DZP basis and corrected by the atomic terms -0.95 eV for H and -0.84 eV for S [13], the energy of formation of a single vacancy in position S<sub>1</sub> is 0.12 eV; this value is reasonable if one considers that the activation treatment occurs at high temperature under hydrogen atmosphere.

The molecular structure is hardly modified upon creation of S<sub>3</sub> or S<sub>11</sub> vacancies, as indicated in Table 3, which reports the mean values of the different types of MoS bonds in the clusters. The decrease of the coordination of an Mo atom leads to a mean decrease of the corresponding bond length of about 0.04 Å, but the elimination of one sulphur atom on a side of the slab does not significantly modify the structure

**Figure 4** Non-local post-SCF bonding energy of the  $\eta_5$  interaction of thiophene with the Mo<sub>12</sub>S<sub>22</sub> cluster as a function of the distance between (Mo<sub>1</sub>Mo<sub>3</sub>) and the aromatic ring of thiophene



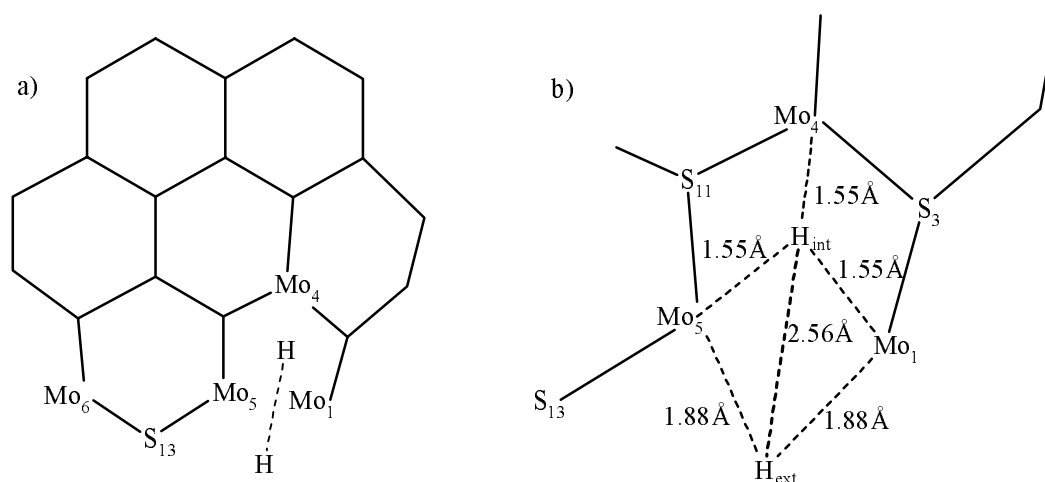
**Table 3** Mean bond lengths of the MoS bonds (in Å)

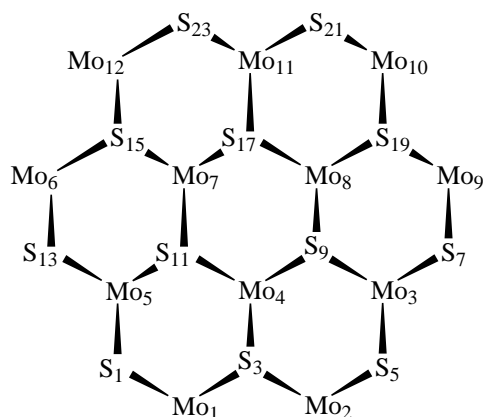
Bonds	Mo <sub>12</sub> S <sub>24</sub>	Mo <sub>12</sub> S <sub>23</sub> Vacancy S <sub>(3)int</sub>	Mo <sub>12</sub> S <sub>23</sub> Vacancy S <sub>(3)ext</sub>	Mo <sub>12</sub> S <sub>23</sub> Vacancy S <sub>(2)</sub>
Mo <sub>(6)int</sub> - S <sub>(3)int</sub>	2.392	2.405	2.398	2.398
Mo <sub>(6)int</sub> - S <sub>(3)ext</sub>	2.414	2.415	2.405	2.417
Mo <sub>(6)ext</sub> - S <sub>(3)int</sub>	2.414	2.431	2.427	2.448
Mo <sub>(6)ext</sub> - S <sub>(2)</sub>	2.380	2.390	2.403	2.381
Mo <sub>(5)int</sub> - S <sub>(3)int</sub>	***	2.375	2.362	***
Mo <sub>(5)int</sub> - S <sub>(3)ext</sub>	***	2.395	2.371	***
Mo <sub>(5)ext</sub> - S <sub>(3)int</sub>	***	2.415	***	2.383
Mo <sub>(5)ext</sub> - S <sub>(2)</sub>	***	2.370	***	2.368
Mo <sub>(4)</sub> - S <sub>(3)ext</sub>	2.350	2.353	2.350	2.350
Mo <sub>(4)</sub> - S <sub>(2)</sub>	2.315	2.319	2.315	2.312
Mo <sub>(3)</sub> - S <sub>(3)ext</sub>	***	***	2.305	2.271
Mo <sub>(3)</sub> - S <sub>(2)</sub>	***	***	2.268	2.292

around the sulphur atom on the other side of the layer. The situation is completely different when the vacancy is created in an S<sub>1</sub> position. Indeed, the parent sulphur atom (S<sub>2</sub>) relaxes. This leads to an equilibrium position in the mean plane defined by the Mo atoms and with longer MoS bonds (Table 3). The effect of the creation of such a vacancy on the modification of the electronic distribution has been studied through the Mulliken distribution reported in Table 4. It shows that significant variations are only localised on the three first spheres of coordination around the vacancy. The largest variations reach 23 (Mo<sub>8</sub>), 32 (Mo<sub>4</sub>) and 57 % (Mo<sub>4</sub>) for the Mo atoms, but only 17 (S<sub>9</sub> or S<sub>17</sub>), 18 (S<sub>11</sub>) and 23 % (S<sub>2</sub>) for the S<sub>11</sub>, S<sub>3</sub> and S<sub>1</sub> vacancies, respectively. The creation of an S<sub>1</sub> vacancy induces the strongest variation with an increase of the positive charge of the Mo atoms situated on the edge of the model (atoms Mo<sub>1</sub>, Mo<sub>2</sub> and Mo<sub>6</sub>). Thus, the Mo atoms on the edges of the model acquire an electrophilic character. Such a vacancy in an S<sub>1</sub> position could be a suitable site for catalytic processes, but the relaxation of the parent sulphur

atom (S<sub>2</sub>) into the central plane may limit the accessibility of the potentially active Mo atoms.

It was therefore useful to study a double sulphur vacancy obtained by elimination of two parent S<sub>(2)</sub> atoms (S<sub>1</sub> and S<sub>2</sub>). The corresponding energy of this Mo<sub>12</sub>S<sub>22</sub> model is reported in Table 2. While the creation of a single S<sub>1</sub> vacancy corresponds to an energy difference of 3.38 eV (or 326 kJ/mol) between the clusters, the following elimination of S<sub>2</sub> necessitates 4.83 eV (or 466 kJ/mole). Thus, the creation of two separated single vacancies (E = 2\*3.38 eV) would be easier than the creation of a double vacancy S<sub>1</sub>-S<sub>2</sub>. The energy of formation of a second defect according to reaction (1) is 1.58 eV, i.e. a total energy of formation for the double vacancy of 1.70 eV. The geometry of the cluster is strongly but only locally modified upon creation of this double vacancy. The distance Mo<sub>5</sub>-Mo<sub>1</sub> of the Mo atoms which was 3.05 Å in Mo<sub>12</sub>S<sub>24</sub> decreases to 2.87 Å in Mo<sub>12</sub>S<sub>23</sub> but to 2.32 Å in Mo<sub>12</sub>S<sub>22</sub> upon creation of the S<sub>1</sub> and S<sub>1</sub> - S<sub>2</sub> vacancy, respectively. This result is in agreement with the EXAFS data of

**Figure 5** Optimised configuration of a hydrogen molecule dissociatively adsorbed on a sulphur vacancy of Mo<sub>12</sub>S<sub>22</sub>; b) zoom on the active site



Agostini et al. [16] who found that the MoS bond length decreases with the size of the clusters, i.e. when the number of unsaturated Mo atoms increases. Thus, it can be considered that the creation of a double lacunary defect induces a metallic interaction between the surrounding Mo atoms. The Mo-Mo distance is similar to that observed in the  $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$  compound (2.72 Å) [17]. The Mulliken charges reported in Table 4 reveal a decrease of the overall positive charge carried by the molybdenum atoms and indicate that this decrease occurs mainly on the three atoms surrounding the vacancy ( $\text{Mo}_1$ ,  $\text{Mo}_4$  and  $\text{Mo}_5$ ), the atoms located at the other side of the cluster remaining nearly unchanged ( $\text{Mo}_8$ – $\text{Mo}_{12}$ ). The atom  $\text{Mo}_5$  has the highest positive charge which is compensated by a decrease of the charge of  $\text{Mo}_1$  and  $\text{Mo}_4$ ; it is therefore the most electrophilic atom of the cluster. In a disulfide crystallite both edge and corner sulphur atoms are present [18], but the simulation of edge sites implies a larger cluster, at least  $\text{Mo}_{27}\text{S}_{54}$ . The present double vacancy corresponds to a corner site that is the only one tractable with the cluster model without periodic conditions; it gives some interesting hints about the appearance of a metallic interaction by creation of double sulphur vacancies. It represents corner sites which are not very numerous on the real active phase; their easy accessibility can compensate the low number of such sites and allow a high turnover, particularly for large aromatic molecules. This is the reason why we will now focus on the interaction of sulphur-containing molecules with such vacancies, considering this interaction as being the first step of the HDS process. Thiophene was chosen as it is the simplest molecule occurring in the petroleum feed stocks and generally used as test molecule.

#### Interaction with thiophene

Two extreme configurations were considered: (i) thiophene lying flat with its ring parallel to the edge surface of the

**Table 4** Mulliken charges of the molybdenum atoms in three clusters ( in electronic charges)

	$\text{Mo}_{12}\text{S}_{24}$ No vacancy	$\text{Mo}_{12}\text{S}_{23}$ Vacancy $\text{S}_1$	$\text{Mo}_{12}\text{S}_{22}$ Vacancies $\text{S}_1$ and $\text{S}_2$
$\text{Mo}_1$	0.603	0.609	0.395
$\text{Mo}_2$	0.605	0.604	0.633
$\text{Mo}_3$	0.530	0.476	0.474
$\text{Mo}_4$	0.586	0.253	0.338
$\text{Mo}_5$	0.532	0.682	0.653
$\text{Mo}_6$	0.606	0.633	0.609
$\text{Mo}_7$	0.593	0.522	0.531
$\text{Mo}_8$	0.591	0.599	0.595
$\text{Mo}_9$	0.608	0.591	0.609
$\text{Mo}_{10}$	0.605	0.582	0.607
$\text{Mo}_{11}$	0.534	0.513	0.507
$\text{Mo}_{12}$	0.607	0.620	0.597

disulfide cluster, (ii) thiophene perpendicular to this surface, binding to the active CUS through the sulphur atom. These two modes, respectively named  $\eta_1$  and  $\eta_5$  according to the organometallic chemistry nomenclature are the most plausible configurations proposed by Angellicci [19] through a comparative study with organometallic complexes. In order to reduce the calculation time the Cs symmetry of the cluster interacting with the thiophene was preserved.

For the  $\eta_1$  configuration two orientations of the thiophene molecule were studied with respect to the molecular plane of the adsorbate (i) perpendicular and (ii) parallel to the plane of the Mo atoms of the cluster. The S atom of thiophene ( $\text{S}_T$ ) was set at the position of the  $\text{S}_2$  atom in the  $\text{Mo}_{12}\text{S}_{23}$  cluster, i.e. in the plane of the molybdenum atoms and the  $\text{C}_2$  axis of thiophene was set perpendicular to the  $\text{Mo}_5$ - $\text{Mo}_1$  direction. All trials to relax the internal coordinates of thiophene and the intermolecular distances between the cluster and the thiophene molecule for both configurations led to a separation of the thiophene molecule from the  $\text{Mo}_{12}\text{S}_{22}$  cluster without any significant modification of its molecular structure. The evaluation of the total energy by stepwise varying the intermolecular distance with fixed internal coordinates led to Figure 2 which obviously indicates the repulsive interaction between the molecule and the cluster, whatever the orientation of the thiophene molecule. This conclusion cannot be inverted by the Basis Set Superposition Error (BSSE) which was estimated at 0.107 eV. It is interesting to note that the interaction of thiophene with the cluster was also studied in the absence of vacancies and that these calculations qualitatively led to the same result, whatever the starting configuration.

As mentioned above, the  $\text{Mo}_{12}\text{S}_{24}$  cluster could also be considered as a lacunary structure by the absence of the monocoordinated terminal sulphur atoms ( $\text{S}_{(1)}$ ) on the edge leading to Mo atoms which are only tetracoordinated. The thiophene molecule could interact with such unsaturated Mo atoms through its  $\text{S}_T$  atom. Starting with configurations hav-



**Table 5** Mulliken charges of the three models for the interaction of thiophene with  $Mo_{12}S_{22}$  (in columns 2 and 3 these digits correspond to a distance of 2.40 Å)

	$Mo_{12}S_{22}$ thiophene isolated	$Mo_{12}S_{22}$ thiophene Perpendicular	$Mo_{12}S_{22}$ thiophene Parallel	$Mo_{12}S_{22}$ thiophene $\pi$ electrons interaction
<b>Catalyst</b>				
Mo <sub>1</sub>	0.395	0.396	0.410	0.632
Mo <sub>2</sub>	0.633	0.621	0.615	0.610
Mo <sub>3</sub>	0.474	0.465	0.472	0.471
Mo <sub>4</sub>	0.338	0.380	0.378	0.344
Mo <sub>5</sub>	0.653	0.543	0.562	0.543
Mo <sub>6</sub>	0.609	0.598	0.620	0.609
Mo <sub>7</sub>	0.531	0.515	0.518	0.534
Mo <sub>8</sub>	0.595	0.592	0.591	0.595
Mo <sub>9</sub>	0.609	0.604	0.601	0.599
Mo <sub>10</sub>	0.607	0.604	0.601	0.598
Mo <sub>11</sub>	0.507	0.506	0.511	0.510
Mo <sub>12</sub>	0.597	0.596	0.592	0.590
S <sub>13</sub>	-0.385	-0.381	-0.387	-0.419
S <sub>3</sub>	-0.348	-0.346	-0.346	-0.357
S <sub>11</sub>	-0.222	-0.220	-0.221	-0.220
<b>Thiophene</b>				
S	-0.116	0.052	0.022	-0.010
C <sub>a</sub>	-0.015	-0.090	-0.086	-0.087
C <sub>b</sub>	0.016	-0.039	-0.024	-0.072
H <sub>a</sub>	0.059	0.098	0.089	0.114
H <sub>b</sub>	0.001	0.052	0.058	0.072

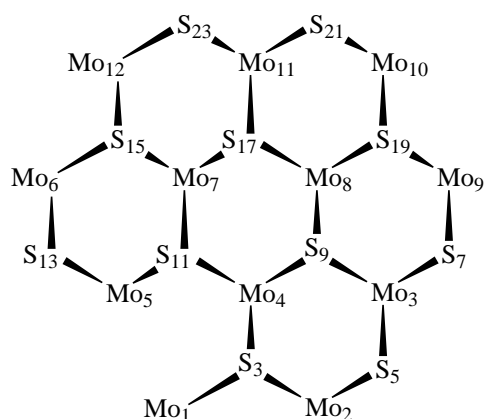
ing the S<sub>T</sub> atom in the plane of the Mo atoms of the cluster in front of the Mo atoms a similar repulsion was observed.

In a next step we tried to determine a possible interaction of the  $\pi$  electrons of the adsorbate with the Mo<sub>1</sub> atom of the  $Mo_{12}S_{22}$  cluster which presents an electrophilic character. For this purpose a thiophene molecule with fixed geometry and with its molecular plane perpendicular to the plane of the Mo atoms and parallel to the Mo<sub>5</sub>-Mo<sub>1</sub> was located with its sulphur atom S<sub>T</sub> at the same distance of the Mo<sub>5</sub> and Mo<sub>1</sub> atoms and with Mo<sub>1</sub> pointing in the direction of the aromatic

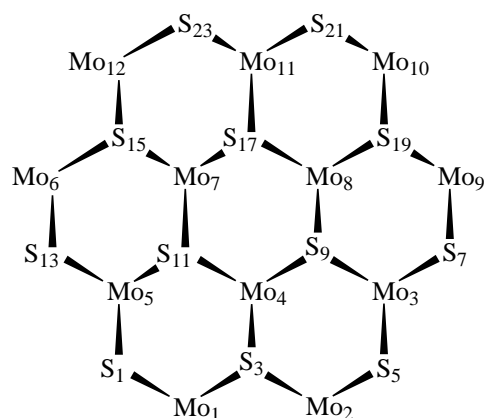
ring (Figure 3). The energy was determined step by step by varying the distance between Mo<sub>1</sub> and the plane of the thiophene molecule from 1.50 to 3.50 Å. Figure 4 shows the plot of the energy versus this distance. An energy minimum is observed for a distance of 2.40 Å, corresponding to Mo<sub>1</sub>S<sub>T</sub>=Mo<sub>5</sub>S<sub>T</sub> bond distances of 2.66 Å. In this geometry the energy is stabilised by 0.745 eV (or 71.8 kJ/mol) in comparison with the energy of the separated components obtained for distances above 3 Å. This value corresponds to usual adsorption energy of molecules on supports [20,21].

It is also useful to compare the Mulliken charges for the three models of the interaction of  $Mo_{12}S_{23}$  with thiophene in order to identify eventual charge transfers. The corresponding values are gathered in Table 5. Whatever the configuration, the intermolecular transfer can be neglected because the charge remains near zero for each interacting component. But the distribution inside each component of the models does really vary, particularly in the case of a flat adsorption. At the minimum of energy the polarity of the Mo<sub>1</sub>-Mo<sub>5</sub> interaction is inverted by the adsorption, while the polarity of the molecule remains similar. In the two  $\eta_1$  configurations which do not correspond to an adsorption, the polarity of the molecule is inverted and yields a positive sulphur atom.

This series of calculation on the adsorption of thiophene on a possible active site leads to the conclusion that the probability to have an interaction of the thiophene with its sulphur atoms inserted in a vacancy of MoS<sub>2</sub> is low. The most stable configuration is found to be the flat h<sub>3</sub> adsorption of



**Scheme 1** Atomic positions corresponding to table 5



**Scheme 2** Atomic positions corresponding to table 6

thiophene through an interaction of the p electrons with the Mo<sub>1</sub> atom at the corner of the Mo<sub>12</sub>S<sub>22</sub> cluster. This interaction induces a strong variation of the charge distribution in the vacancy. Similarly, a flat adsorption is observed when a thiophene molecule is approached to the Mo<sub>12</sub>S<sub>24</sub> cluster (results not reported here) in agreement with *ab initio* periodic calculations performed by Raybaud et al.[22].

#### Interaction with hydrogen

There is a general agreement in the literature to associate the active sites with the CUS located at the edges of the MoS<sub>2</sub> phase, but a complete description of the HDS process should take the presence of hydrogen species[23] into account and that point is presently far from being completely understood. The chemical state of the involved hydrogen is still not clear and the nature of the adsorption of hydrogen on the transition metal sulfides is still open. Does it participate through a non-dissociative or a dissociative adsorption of the hydrogen molecules? Is it an homolytic or an heterolytic adsorption? It was therefore interesting to test the behaviour of hydrogen molecules on the vacancies of the Mo<sub>12</sub>S<sub>22</sub> cluster.

Similarly to the calculations performed for thiophene, we defined several configurations preserving the C<sub>s</sub> symmetry. The hydrogen molecule was therefore constrained to remain in the plane of the Mo atoms. Two initial geometries were defined:

i) H<sub>2</sub> perpendicular to the Mo<sub>5</sub>-Mo<sub>1</sub> direction, both MoH distances being 1.89 Å.

ii) H<sub>2</sub> parallel to the Mo<sub>5</sub>-Mo<sub>1</sub> direction with a distance of 1.51 Å between each hydrogen atom and the nearest Mo atom.

In both cases the structure was relaxed, supposing that the Mo<sub>12</sub>S<sub>22</sub> cluster was rigid and that only the H-H distance, the mutual orientation and the distances between the cluster and the hydrogen atoms could vary. Whatever the starting position of the H<sub>2</sub> molecule, the final geometries after relaxation were identical. The H-H bond length increases from 0.767 Å for the isolated molecule to 0.911 Å after the adsorption on the Mo<sub>1</sub> site and the MoH distances are 1.89 Å. This geom-

**Table 6** Mulliken charges of H<sub>2</sub> and Mo<sub>12</sub>S<sub>22</sub> in the different configurations discussed in the text

	Mo <sub>12</sub> S <sub>22</sub> + H <sub>2</sub> isolated	Mo <sub>12</sub> S <sub>22</sub> + H <sub>2</sub> adsorbed	Mo <sub>12</sub> S <sub>22</sub> + H <sub>2</sub> dissociated
<b>Catalyst</b>			
Mo <sub>1</sub>	0.395	0.485	0.642
Mo <sub>2</sub>	0.633	0.620	0.622
Mo <sub>3</sub>	0.474	0.471	0.468
Mo <sub>4</sub>	0.338	0.383	0.628
Mo <sub>5</sub>	0.653	0.556	0.848
Mo <sub>6</sub>	0.609	0.612	0.600
Mo <sub>7</sub>	0.531	0.504	0.529
Mo <sub>8</sub>	0.595	0.589	0.589
Mo <sub>9</sub>	0.609	0.608	0.603
Mo <sub>10</sub>	0.607	0.608	0.600
Mo <sub>11</sub>	0.507	0.504	0.510
Mo <sub>12</sub>	0.597	0.601	0.598
S <sub>13</sub>	-0.385	-0.419	-0.354
S <sub>3</sub>	-0.348	-0.358	-0.340
S <sub>11</sub>	-0.222	-0.220	-0.210
<b>Hydrogen</b>			
H <sub>int</sub>	0	0.016	-0.609
H <sub>ext</sub>	0	-0.076	-0.214

etry can be compared with the results of Martinez et al.[24] on the interaction of H<sub>2</sub> with a single molybdenum atom. They observed an homolytic dissociation with formation of two MoH bonds (1.73 Å) and a distance of 2.73 Å between the H atoms. Obviously, the hydrogen molecule interacts differently with the Mo atom of a vacancy and with metallic molybdenum.

The energy of the relaxed system corresponds to a stabilization by 0.53 eV (or 51 kJ/mol) in comparison with the isolated components, whereby the BSSE correction is only 0.049 eV. This adsorption energy is smaller than the value obtained by Fréchard et al. for the adsorption of hydrogen molecules on RuS<sub>2</sub> with periodic *ab initio* calculations [20] (129.6 kJ/mol), but is of the same order of magnitude as the aforementioned adsorption energy of thiophene on MoS<sub>2</sub>. Finally, it is interesting to note that from both initial configurations an interaction between one hydrogen atom and the nearest sulphur atom S<sub>13</sub> was not observed during the relaxation. Such an interaction could have led to the dissociation of the molecule. The whole space could not be explored systematically, but this preliminary attempt leads to the conclusion that the adsorption on Mo<sub>1</sub> is a stable configuration to be reached from several different initial conditions.

Another configuration was discovered during the exploration of the space, which is energetically not optimal but which could be interesting for the role of the hydrogen in the HDS process. The initial geometry was defined by setting the H<sub>2</sub> molecule in the plane of the Mo atoms with one hydrogen atom in the middle of the Mo<sub>1</sub>-Mo<sub>5</sub> line (H<sub>int</sub>) and the second one (H<sub>ext</sub>) at a distance of 0.77 Å outside the va-



cancy. The optimised geometry is given in Figure 5. We can consider that the hydrogen molecule is dissociated as the H-H distance reaches 2.56 Å; the MoH<sub>int</sub> distances are 1.55 Å from all the Mo atoms of the vacancy (Mo<sub>1</sub>, Mo<sub>4</sub> and Mo<sub>5</sub>) whereas the MoH<sub>ext</sub> ones are 1.88 Å. The mean value of these MoH distances (1.71 Å) is similar to the bond length obtained by Martinez et al. for MoH<sub>2</sub>, while the HH distance is somewhat shorter (2.73 Å in MoH<sub>2</sub>) [24]. The total bonding energy calculated for this system (-214.186 eV) is higher than for the adsorbed molecules discussed above and for the isolated components by 2.913 eV (280.8 kJ/mol) and 2.377 eV (229.1 kJ/mol), respectively. Such a structure cannot be a stable configuration of the system, but it could be an interesting transient state representing a model for the heterolytic dissociation of H<sub>2</sub> (Table 6). Both hydrogen atoms have a large negative charge, particularly inside the vacancy, and get an hydride character as proposed in ref. [25]. Finally, as already observed for the adsorption of thiophene, the major charge variations are observed on the Mo atoms surrounding the vacancy Mo<sub>1</sub>, Mo<sub>4</sub> and Mo<sub>5</sub>.

## Conclusions

This DFT study of a cluster Mo<sub>12</sub>S<sub>24</sub> considered as a model of a MoS<sub>2</sub>-based HDS catalyst leads to the conclusion that the model has the suitable size to analyse potential catalytic sites, because all perturbations only affect the model locally so that no frontier effect has to be expected. Several models of sulphur vacancies have been tested leading to the conclusion that edge double sulphur vacancies are potentially active catalytic sites. The interaction of the sulphur atom of thiophene molecules with sulphur vacancy ( $\eta_1$  configuration) is not the energetically most favourable state. The  $\eta_5$  mode of adsorption, in which the thiophene interacts through its  $\pi$  system with one of the Mo atom near the vacancy appears to be a more stable configuration. Hydrogen adsorption on this Mo atom is also suggested whereas a dissociation could occur as a transient state through a direct interaction with the double vacancy.

This work shows the power of the DFT techniques to study reaction processes and reveals the fact that in the cluster approach Mo<sub>12</sub>S<sub>24</sub> is a good model for the HDS study, permitting a realistic description of the microscopic behaviour with a reasonable computing time. Preliminary results on cobalt-promoted clusters show a strong influence of the doping on the electronic distribution and work on the creation of vacancies on such promoted clusters is under progress.

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**Supplementary material available** The ADF optimised structure of Mo<sub>12</sub>S<sub>24</sub> is available in PDB format.

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