

Role of hydrogen in HDS/HYD catalysis over MoS_2 : an ab initio investigation

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Abstract

The structures of MoS_2 crystallites present in industrial HDS/HYD catalysts in the reaction conditions are mimicked by using tiny single layer clusters (slabs) consisting of seven Mo atoms. These are the smallest clusters possessing the main structural features of the MoS_2 slabs. The structures of the various clusters are optimized and examined by using ab initio MO approaches, in order to obtain the total energies at their stationary points. On the basis of the information obtained from the ab initio calculations, the different S atoms in the MoS_2 structures are identified. As the real industrial catalysts work in a reducing atmosphere, the effect of removing S atoms from edges is discussed, providing information for a better understanding of the activation mechanisms of HDS/HYD catalysts.

The cluster terminated by S atoms in all directions (i.e. with 24 S atoms) gains stability when containing two additional electrons. The charged and not charged clusters can readily form –SH (sulfhydryl) groups from terminal S atoms. Two-fold unsaturated coordination of Mo (2-CUS) is readily obtained by removal of these –SH groups; 3-CUS and 4-CUS Mo are formed by breaking one S–Mo bond of bridging S atoms or further removing all bridged S atoms. This needs a form of hydrogen more reactive than molecular hydrogen, e.g. a hydrogen atom, together with hydrogen molecules. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Much effort has been devoted to the understanding of the MoS_2 sites active for hydrodesulfurization (HDS) and hydrogenation (HYD) during the last decades [1–5]. It has been experimentally proven that

properly reduced MoS_2 edges could provide unique activities for hydrodesulfurization and hydrogenation. However, the mechanism of formation of the active sites and the exact structural configuration of the atoms constituting these sites still remain unclear and continue to be the object of investigations in many respects [2,3].

Molecular modeling has provided one route for a deeper insight into the structural features of MoS_2 slabs (single layer clusters) as catalysts. Drew et al. investigated MoS_2 slabs of various sizes by using the molecular mechanics approach [6]. Starting from the assumption that terminal sulfur atoms (S(T))

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are present on the edge of MoS₂ slabs in the form of S(T)–H groups, they found that these S(T)–H groups are unstable and ready to be removed, which is consistent with experimental data. From the viewpoint of energy minimization, the results confirm the expected conclusion that the larger the slabs are, the more stable the MoS₂ structure is. The authors possibly mentioned this fact because they believed this tendency was exceptionally high. This tendency was observed experimentally in the laboratory as well as in industry [7,8]. Recently, Ma and Schobert investigated the HDS of thiophenic compounds over MoS₂ model clusters by using the semi-empirical quantum chemistry approaches of the ZINDO package [9]. However, they based their model of the active site on the old picture identifying active sites with sulfur vacancies. This led them to make their calculations with two-fold coordinatively unsaturated sites (or two-fold CUS in short). Experiments actually attribute catalytic activity to highly reduced three-fold CUS's [10,11]. Recent rapid progress by using density functional theory (DFT) approaches to calculate the electronic properties of the MoS₂ catalysts has focused on the interpretations of HDS/HYD catalysis based on band structures of model atomic arrangements [12–19]. However, the models used in these analyses did not represent all the structural features of the MoS₂ crystallites present in a real HDS/HYD catalyst, especially the geometry of the different sites (atoms) present on the surface of these “clusters”.

It is known experimentally that the active MoS₂ crystallites are extremely small, sometimes consisting of a single sheet of the MoS₂ structure, with lateral dimensions of just a few nanometers, even in catalysts having worked for some time in industrial conditions [20]. One could therefore hope to approach the real situation by using tiny clusters. At least it is reasonable to expect that tendencies deduced from computation on such clusters would reflect those exhibited by real catalysts.

However, in order to provide valuable information, computation should correspond to sufficiently representative situations. The MoS₂ clusters should possess sites in a coordination environment representative of some of the sites situated on the edges of the nanometer size crystallites observed experimentally. The occurrence of sulfur vacancies in such atomic arrangements should be considered. The real

catalysts work in a highly reducing atmosphere. This should be taken into account, by considering clusters in equilibrium with such atmospheres, and by examining the possibility of a reaction of hydrogen with the cluster. One of the theories explaining the synergy between MoS₂ and group VIII metals rests on the capacity of an atomic form of hydrogen to control the coordination of edge Mo atoms [1]. Reactions with molecular hydrogen and an atomic form of this element therefore merit examination.

The present work proposes a detailed approach to explore the HDS and HYD reaction mechanisms by using *ab initio* MO methods. The reader will understand that the present work cannot be exhaustive. The role of the number of S atoms relative to Mo, and that of hydrogen in the reactivity of the different S atoms on the edges of MoS₂ slabs will be examined in cases selected because they are representative of the situation of MoS₂ during catalysis.

2. *Ab initio* calculations

The size selected for MoS₂ slabs typically corresponds to the formula Mo₇S_xH_y. These tiny clusters are designed to have D_{3h} symmetry. This allows the computational expenses to be reduced and nevertheless to correspond to arrangements of atoms identical to those of active sites on corners of a large MoS₂ cluster. Our cluster is obtained by cutting a small part of a large MoS₂ slab in the way shown in Fig. 1. The model cluster has basically seven Mo atoms and 24 S atoms that form S layers on both sides of a Mo plane in between. The typical features of this model cluster is that all the edge Mo atoms are environmentally identical to the Mo atoms sitting on corners of the original slab (Fig. 1). This starting structure possesses all the types of S atoms present in a real MoS₂ structure, namely the terminal S(T), the bridged S(B) and the three-fold bonded S(S) atoms. This gives the possibility to investigate the reduction mechanism of the catalyst edges by removing different S atoms. In this way, reduced Mo sites having proven to be especially active for HDS/HYD reactions can be mimicked [1–11].

All the calculations were performed on a Pentium II computer with GAMESS-US (PC version) [21,22]. Molecular images were processed by the molecular

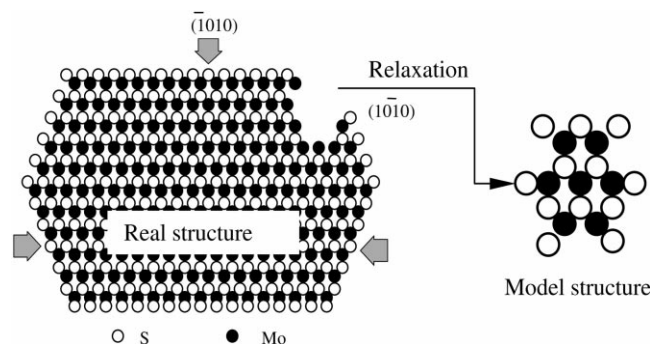


Fig. 1. Model cluster of MoS₂: large crystal (actually a “slab” about 4 nm × 6 nm in size) of MoS₂ with all the Mo atoms saturated by S atoms; the model cluster is cut from the upper right corner of this real crystal; the model cluster possesses all three types of S atoms, namely terminal S(T), bridged S(B), and basal S(S); all the Mo atoms on edge of the model cluster correspond to the Mo sites on the corner of the real crystal.

graphics program MOLDEN [23]. The geometry of model MoS₂ slabs has been optimized at the level of the unrestricted Hartree–Fock (UHF) approach with the combination of the MINI basis set with the effective core potential (ECP) due to Stevens, Basch and Krauss (SBK) [21,22]. The choice of the theoretical method with the low level basis set, MINI, ensures that useful information can be deduced from the calculations with acceptable computational difficulties. In addition, this choice of methods has shown the best convergence behavior for our case of Mo containing clusters. The calculation concerned two typical cases, fully saturated clusters, Mo₇S₂₄ and Mo₇S₂₄H₁₂, and reduced clusters with seven Mo atoms. The vibrational analysis of Mo₇S₂₄H₁₂ was performed to validate the equilibrium structure. The reduction of fully sulfided slabs, namely Mo₇S₂₄ and Mo₇S₂₄H₁₂, is analyzed on the basis of the ab initio results.

Geometry optimization of the Mo₇S_xH_y starts with an initial structure with coordinates of all atoms identical to those deduced from the lattice parameters of an infinite MoS₂ crystal as given in literature [24]. We took full advantage of the various symmetries of the finite cluster in order to facilitate the ab initio calculations. The whole optimization process sometimes showed an unstable behavior, which normally led to divergence in self-consistent field (SCF) calculations. In this case, namely when the calculation gave serious oscillation of density and energy, proper adjustments of the initial coordinates were made in order to allow optimization.

3. Results and discussion

3.1. Charges of Mo₇S₂₄

The model structure cut from the MoS₂ crystal structure (as indicated in Fig. 1) is originally not neutral. This constitutes a frequent difficulty when non-stoichiometric structures are used as models for theoretical analysis [14]. The problem here is that the terminal S atoms bonded with Mo atoms will definitely need to be saturated without too much influencing the electronic features of the original structure. One solution is to add H atoms on the unsaturated S atoms. Another solution used in many cases is to add positive or negative charges. This has been done for example for very simple models with one single Mo atom in many qualitative analyses (see [2,3] and the reference therein). If stoichiometry is maintained, a simple rule can be used: charges are balanced for obtaining positive Mo⁴⁺ and negative S²⁻. Using this rule, Mo₇S₂₄ should possess a very large number of negative charges, namely –20. This is quite unrealistic as regards both theoretical bases and experimental data. But theory can help attribute a realistic number of charges. Here, to investigate the effect of a change in the number of possible charges, systematic calculations have been conducted for a number of negative charges from 0 to 6. The corresponding total and HOMO energies are shown Fig. 2. The first two charges assigned to the cluster result in a decrease of total energy, while additional charges increase the

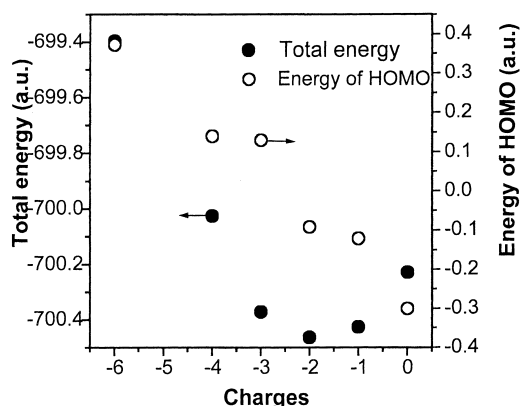


Fig. 2. Energy-charge relationships of the cluster Mo_7S_{24} : energies (in atomic units) when electrons are added to the neutral cluster.

total energy. The HOMO energy becomes positive when the assigned charges increase to 3, indicating strong electron–electron repulsion. According to this result, the theoretical maximum number of charges for this cluster is 2 instead of the value of 20 corresponding to simple valence estimation. This shows that it is very hard to predict a priori how many charges should be added to a cluster in which the S/Mo ratio is not equal to 2. Validation is needed for every case, but at the cost of much additional computational difficulty when large clusters are concerned. One should also be aware of the fact that the real environment of the cluster needs to be considered when one adds charges on the cluster. For HDS and HYD catalysis, the environment is composed of H_2 and H_2S . Hydrogen-saturated terminal S atoms are therefore a realistic choice for theoretical calculations. In our calculations, both cases were considered. The basis is therefore a “neutral cluster” (from which 20 electrons have been removed). When hydrogen is added, the corresponding electrons are introduced into the new cluster. Charged (negatively charged) clusters are obtained by adding electrons to these neutral clusters.

3.2. Implications concerning structure

The crystallographic parameters of the optimized structures are listed in Table 1. Three types of sulfur atoms, namely terminal, bridged, and basal plane sulfur atoms, were mentioned above. They correspond to S(T) (in Fig. 3a) or S(T)–H (or sulhydryl group) (in

Fig. 3b), or S(B), or S(S), respectively. The two types of molybdenum atoms correspond to Mo(E) for *edge* molybdenum atoms and Mo(B) for the non-*edge* or *basal* plane molybdenum atom. The ab initio calculations were performed in six different cases (Table 1). The first two cases correspond to Fig. 3a and concern the changes of the fully sulfided structure, namely (I), the electronically neutral Mo_7S_{24} , and (II), the negatively charged $\text{Mo}_7\text{S}_{24}^{2-}$ clusters (Fig. 3a). Case III is the electronically neutral cluster containing S(T)–H groups of Fig. 3b, and case IV, the reduced cluster of Fig. 3c. Further reduction of IV leads to V and VI as shown in Fig. 3d and e, respectively.

As expected, the results show that the electronically neutral (I) and the negatively charged (II) Mo_7S_{24} clusters have different bond parameters. The existence of negative charges leads to a stretching of the S(S)–Mo(B) bonds from 248 to 251 pm, S(B)–Mo(E) bonds from 273 to 276 pm, and S(T)–Mo(E) bonds from 218 to 220 pm, respectively, and to the shortening of S(S)–Mo(E) bonds from 269 to 261 pm. Another possible type of fully sulfided molybdenum slabs is that in which H atoms are bound to the terminal sulfur atoms (S(T)–H groups) as shown in Fig. 3b (case III). It is noted that from case I to III, the S(S)–Mo(B) and the S(S)–Mo(E) bonds change little in length while the S(B)–Mo(E) bond length is modified considerably, showing that much stronger S(B)–Mo(E) bonds are formed due to the transformation of S(T)–Mo(E) from near-double bonding to near-single bonding, creating free valence orbitals of Mo(E) to form greater overlaps with S(B) atoms. The sulhydryl S(T)–H in Fig. 3b has a length of 136 pm which is very close to the S–H bond length in H_2S . In addition, direct Mo(E)–Mo(E) bonding becomes significant in case III.

In the negatively charged cluster (II) of Fig. 3a, some extra electrons are located in the half-filled orbital of S(T) atoms, leading to the reduction of the overlap between the valence orbitals of S(T) and Mo(E), and corresponding to a stretching of the bond and a lowering of the bond order of S(T)–Mo(E). However, the S(S)–Mo(E) bond is strengthened due to the fact that more free valence orbitals are available on Mo(E). As for the S(S)–Mo(B) and S(B)–Mo(E) bonding, the strengths are reduced because of the balance of all bonding states of the cluster. No S–S bonds are found between the paired S(T) atoms bonding the

Table 1
Structural parameters (optimized at UHF/MINI/ECP-SBK level)

Case	Bonding	Length (pm)	Order	Bond angle	Degree
$E_{\text{total}} = -700.2282$ a.u.					
I Mo_7S_{24}				Mo(E)–S(S)–Mo(B)	91.96
	S(S)–Mo(B)	247.6	0.833	S(B)–Mo(E)–S(S)	130.41
	S(S)–Mo(E)	269.4	0.413	S(T)–Mo(E)–S(S)	146.10
	S(B)–Mo(E)	273.0	0.470	Mo(E)–S(S)–Mo(E)	88.53
	S(T)–Mo(E)	218.0	1.665	S(T)–Mo(E)–S(T)	104.84
				S(S)–Mo(E)–S(S)	66.94
				S(S)–Mo(B)–S(S)	73.78
$E_{\text{total}} = -700.4632$ a.u.					
II $\text{Mo}_7\text{S}_{24}^{2-}$				Mo(E)–S(S)–Mo(B)	91.43
	S(S)–Mo(B)	251.1	0.708	S(B)–Mo(E)–S(S)	131.55
	S(S)–Mo(E)	260.9	0.543	S(T)–Mo(E)–S(S)	147.96
	S(B)–Mo(E)	276.1	0.438	S(B)–Mo(E)–S(B)	75.68
	S(T)–Mo(E)	219.9	1.550	S(T)–Mo(E)–S(T)	104.10
				S(S)–Mo(E)–S(S)	69.08
				S(S)–Mo(B)–S(S)	72.15
$E_{\text{total}} = -707.3599$ a.u.					
III $\text{Mo}_7\text{S}_{24}\text{H}_{12}$	S(S)–Mo(B)	247.5	0.832	Mo(E)–S(S)–Mo(B)	88.53
	S(S)–Mo(E)	266.6	0.495	S(B)–Mo(E)–S(S)	132.35
	S(B)–Mo(E)	242.6	0.827	S(T)–Mo(E)–S(S)	132.56
	S(T)–Mo(E)	246.7	0.832	H–S(T)–Mo(E)	101.98
	Mo(E)–Mo(E)	322.2	0.231	S(T)–Mo(E)–S(T)	91.01
	S(T)–H	136.2	0.997	S(S)–Mo(E)–S(S)	67.64
				S(S)–Mo(B)–S(S)	73.70
$E_{\text{total}} = -583.0618$ a.u.					
IV Mo_7S_{12}	S(S)–Mo(B)	257.7	0.655	Mo(E)–S(S)–Mo(B)	84.65
	S(S)–Mo(E)	249.5	0.671	S(B)–Mo(E)–S(S)	135.40
	S(B)–Mo(E)	242.0	0.970	Mo(E)–S(S)–Mo(E)	89.72
	Mo(E)–Mo(E)	330.8	0.177	S(B)–Mo(E)–S(B)	78.65
				S(S)–Mo(E)–S(S)	76.40
				S(S)–Mo(B)–S(S)	73.61
$E_{\text{total}} = -553.5783$ a.u.					
V Mo_7S_9	S(S)–Mo(B)	260.0	0.659	Mo(E)–S(S)–Mo(B)	86.52
	S(S)–Mo(E)	244.1	0.756	S(B)–Mo(E)–S(S)	99.83
	S(B)–Mo(E)	235.4	1.049	Mo(E)–S(B)–Mo(E)	128.49
	Mo(E)–Mo(E)	261.0	1.096	S(B)–Mo(E)–S(B)	99.38
				S(S)–Mo(E)–S(S)	86.43
				S(S)–Mo(B)–S(S)	80.01
				Mo(E)–S(S)–Mo(E)	64.62
$E_{\text{total}} = -523.9033$ a.u.					
VI Mo_7S_6	S(S)–Mo(B)	262.5	0.537	Mo(E)–S(S)–Mo(B)	84.43
	S(S)–Mo(E)	242.7	0.814	S(S)–Mo(E)–S(S)	89.02
	Mo(E)–Mo(E)	260.6	1.268	S(S)–Mo(B)–S(S)	80.83
	Mo(E)–Mo(E)		0.177	Mo(E)–S(S)–Mo(E)	64.93

same Mo atom. This is probably due to the repulsion between the S(T)–Mo(E) bonds in the fully relaxed cluster, which may become more closely packed in real crystallites of MoS_2 . The hydrogen atom bonding

to S(T) atoms also leads to a reduction of the overlap between the valence orbitals of S(T) and Mo(E) (Fig. 3b). The repulsion between lone pairs of S(T) atoms bonding to Mo(E) atoms in case III leads the

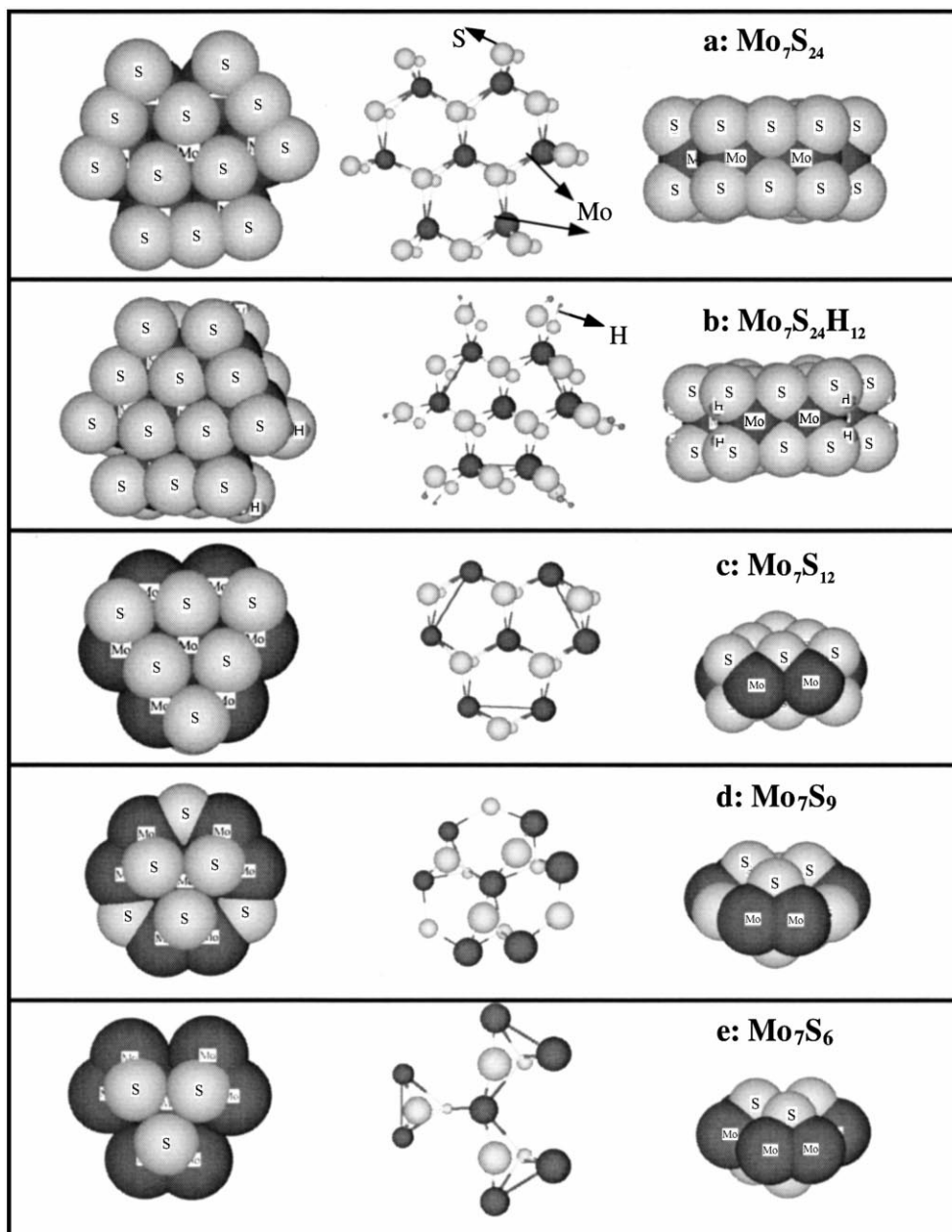


Fig. 3. Optimized molybdenum slabs with seven Mo atoms: (a) terminal S(T) atoms; (b) terminal S(T)–H groups; (c–e): reduced slabs.

hydrogen atoms connecting to the S(T) atoms to get closer to the plane consisting of all Mo atoms in the cluster, a phenomenon which cannot be attributed to any attractive interaction between the two hydrogen atoms (Fig. 4).

Reduction, more precisely removal of S atoms from the edges of fully saturated structures (cases I–III), may lead to different reduced structures, containing edge Mo sites that become exposed. Such Mo sites have been proven to be essential for the

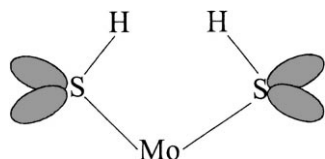


Fig. 4. Schematic picture of the geometric arrangement of terminal SH groups on one Mo site.

catalytic reactions in HDS and HYD processes. The consequence is that the reduction/activation of the catalyst in HDS/HYD is one of the most important steps in the catalyst life cycle [1–11]. Several representative reduced structures are shown in Fig. 3c–e: they are neutral clusters with different unsaturated Mo sites on edges, namely Mo_7S_{12} , Mo_7S_9 , and Mo_7S_6 , corresponding to cases IV–VI, respectively. These structures are simply assumed to be neutral, and all electrons of them are assumed to accommodate in pairs in the molecular orbitals. We underline the fact that this assumption should not lead to hasty conclusions concerning the trends related to HDS/HYD catalysis. More complicated situations may exist. The present study constitutes a first step for starting a more complete investigation.

3.3. Reactivity of edges

The ab initio calculations are aimed at evaluating the energy content of the various clusters. What we call a reduction of the edges by removing the S atoms is assumed to mimic the possible reduction paths in a real catalytic environment, namely at high hydrogen pressure. The objective is to approach the thermochemistry of the process using theoretical chemistry. The energy changes between the reactants at the ground stationary states (highly sulfided MoS_2 clusters plus H_2) and products (reduced clusters plus H_2S) are calculated on the basis of the total energies of clusters (large molecules) obtained from ab initio calculations:

$$\Delta E_j^{\text{gs}} = \sum \alpha_{i,j} E_i \quad (1)$$

where $\alpha_{i,j}$ represents the stoichiometric coefficient of component i in reaction j (for reactant, $\alpha_{i,j} < 0$, and for products $\alpha_{i,j} > 0$), E_i represents the total energy of component i , which is calculated by using the ab initio approach (see Table 1 for the $\text{Mo}_7\text{S}_x\text{H}_y$

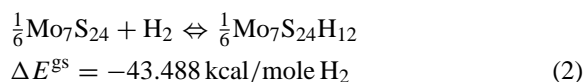
clusters). The calculated total energies for other molecules (or atomic species) needed in applying the thermo-chemistry analysis are as follows (calculated at the same level of theory):

$$E_{\text{H}_2} = -1.1193135866 \text{ a.u.},$$

$$E_{\text{H}_2\text{S}} = -10.9339150322 \text{ a.u.},$$

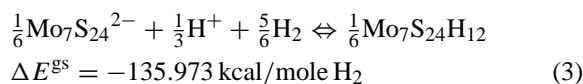
$$E_{\text{H}} = -0.4659155338 \text{ a.u.} \quad \text{and} \quad E_{\text{H}^+} = 0.0 \text{ a.u.}$$

The first case to consider is the stability of the fully sulfided structure under catalysis conditions. Starting from this situation (case I, neutral cluster), the hydrogen may interact with the edges to form terminal SH groups, namely lead to case III (Fig. 3b):



Please note that this equation as well as the following ones are written for one molecule of hydrogen, in order to obtain values directly comparable to well known energy values for reactions of hydrogen.

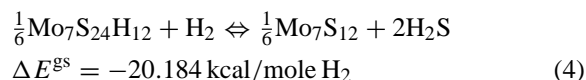
For the reasons indicated above, it was desirable to examine the possible role of single, charged or neutral, hydrogen atoms. The proton was the best choice for this exercise, because the alumina or silica-alumina supports possess Brönsted sites. A second reason was that a sulfided CoMo/silica catalyst had been proven to produce protons that created acidity on silica-aluminas [25]. It is known that hydride ions may be formed together with protons (by heterolytic dissociation of hydrogen). We did not attempt to examine their reactivity in the present work. The other typical case we examined was therefore that of $\text{Mo}_7\text{S}_{24}^{2-}$ (case II), where, in addition to molecular hydrogen, protons are necessary to balance the electronic charges in the slab, namely the electrons:



The decreases in energy for the reaction steps in Eqs. (2) and (3) indicate that hydrogen addition to the terminal S(T) atoms can significantly lower the total energy of the system, namely stabilize it. For the neutral cluster (I), the energy released from the formation of two S(T)–H bonds by reacting with molecular hydrogen is as high as 43.5 kcal/mole H_2 . This suggests

that the terminal S(T) atoms are readily transformed to SH groups in the presence of molecular hydrogen. Similarly, the negatively charged cluster (case II) is thermodynamically unstable in an environment containing hydrogen. It tends to change into the partially hydrogenated cluster (III) by reacting with protons and molecular hydrogen. With this calculation, we introduced the possibility of a mechanism involving protons. As explained above, this is speculative, but not unlikely if a heterolytic dissociation of hydrogen plays a role in HDS/HYD reactions. These results suggest that the thermodynamical stability of a fully sulfided molybdenum sulfide cluster in a real HDS/HYD catalyst is increased when in a partially hydrogenated form, namely in a form similar to that of cluster III in our model (Fig. 3b).

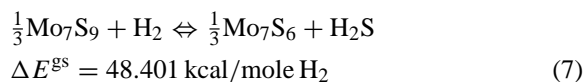
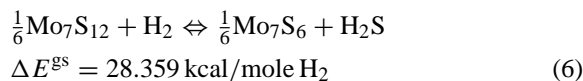
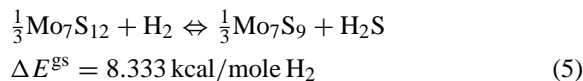
The *activation* of HDS/HYD catalysts, namely a group of reactions possibly involving the “reduction” (loss of S atoms) of the fully sulfided cluster III, is necessary to form coordinatively unsaturated (CUS) molybdenum atoms on the edges of the clusters [1–11]. One way to do that is by removal of all the terminal S(T)–H (sulfhydryl) groups. This leads to cluster IV containing two-fold CUS on Mo atoms situated on edges. This preliminary reduction of the fully sulfided cluster can be described as follows:



The energy balance of Eq. (4) shows that the fully sulfided cluster (III) actually can be reduced by molecular hydrogen, thanks to a loss of terminal S(T)–H groups. This suggests that cluster IV is more stable than the fully sulfided ones under HDS/HYD conditions (high hydrogen pressure and elevated temperature). In a previous article dealing with kinetic modeling [26], edges with structures similar to those of cluster IV were assumed to be present in the initial cluster, and the catalyst active in HDS/HYD was obtained by reduction of these initial edges. The validity of this assumption is supported by the present thermochemical results.

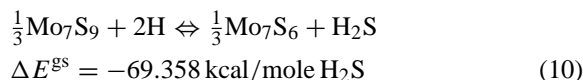
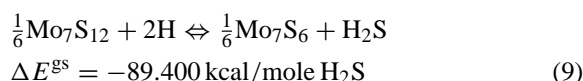
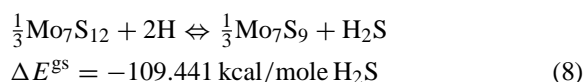
Further reduction of cluster IV by molecular hydrogen leads to more highly coordinatively unsaturated Mo sites (CUS) than those on cluster IV as shown in Fig. 3d and e. This corresponds to situations supposed to be those of sites active in HDS/HYD. Typically,

this reduction can be represented by the following reactions:



Only some combinations are presented above. More can be written. All of them can be calculated using the same method. In the above reactions, Eq. (5) represents the reduction of cluster IV with two-fold CUS, to form cluster V with three-fold CUS; Eq. (6) represents the formation of cluster VI with four-fold CUS on the edge from cluster IV, and Eq. (7) that of cluster VI from cluster V. In all these reactions, molecular hydrogen is assumed to be the reductive agent. These reactions are all endothermic, suggesting that molecular hydrogen may not be able to further reduce the MoS₂ cluster to three-fold and four-fold coordinatively unsaturated sites. This corresponds to the experimentally proven fact that molecular hydrogen cannot react directly with MoS₂ slabs under normal HYD/HDS conditions [27].

Experimentally, atomic hydrogen has been proven to be very active in the reduction of the MoS₂ structures. This corresponds to the following reactions in our case [27]:



These calculations justify the fact that the activation of the MoS₂ catalysts can be greatly facilitated by the supply of atomic hydrogen in the system. Industrial and laboratory experience shows that the addition of promoters like Co in MoS₂ catalysts increases the HDS and HYD activity, indicating that the presence

of these promoters is favorable to the creation of these highly reduced sites (3-CUS or 4-CUS, etc.). Our results make reasonable the hypothesis that the promoters act by supplying a sufficient amount of atomic hydrogen species to the MoS₂ surface. The remote control theory proposed a mechanism for this process [28,29]. The results obtained in this work also suggest that, if we accept that spillover hydrogen is necessary, it may just be a sort of atomic hydrogen, but not necessarily in the form of protons. Atomic hydrogen is sufficient to create highly reduced sites on MoS₂ edges.

Our results suggest that very small clusters containing more than the stoichiometric amount of sulfur (S/Mo > 2) may be stable. This might explain the experimental observation that HDS/HYD catalysts often contain an excess of sulfur. Retention of sulfur on the alumina support is, therefore, perhaps not the only explanation of this excess. Another remark is that the existence of this excess is not in contradiction with the existence of coordination unsaturations on the edges. It ensues that speaking of sulfur vacancies in such cases is misleading, suggesting S/Mo ratios lower than 2. Molybdenum sulfide clusters in the reaction conditions are probably over-stoichiometric in sulfur. The faculty of forming –SH groups (which contribute to this excess over stoichiometry) is corroborated by many experimental evidences of sulfhydryl groups mentioned in literature.

4. Conclusion

The smallest clusters exhibiting characteristics of the MoS₂ “slabs” active in HDS/HYD catalysis, namely those containing seven Mo atoms, are accessible to ab initio MO calculations with an acceptable amount of work. Thanks to these calculations, a consistent description of the electronic structures is obtained. The energy of the completely sulfided cluster Mo₇S₂₄ is minimum if two electrons are added to the total number of electrons normally contained in the corresponding neutral Mo and S atoms. Sulfur atoms on the edges of the fully sulfided MoS₂ cluster tend to form terminal –SH (sulfhydryl) groups in the presence of molecular hydrogen. The assistance of a proton also makes thermodynamically favorable the formation of such –SH groups in the electron-rich clusters. The removal of these terminal –SH groups by molecular

hydrogen is thermodynamically favored. This leads to the formation of two-fold coordinatively unsaturated Mo atoms (2-CUS Mo). In addition, atomic hydrogen can remove bridged S atoms, creating both 3-CUS and 4-CUS positions on the edges of the clusters.

The fact that only a limited number of situations has been examined (namely six) makes that it is not ruled out that other stable MoS_x clusters of seven Mo atoms may exhibit 3-CUS and 4-CUS positions in the presence of hydrogen in milder conditions. This work provides an insight into the genesis of the catalytic sites in HDS/HYD, believed to be (1) –SH groups; (2) 3-CUS and (3) 4-CUS Mo atoms. But this leaves the open question of whether more complex sites associating two of these sites can be formed. A cluster containing seven Mo atoms is very likely insufficient to consider this question.

The calculation made with clusters with additional electrons suggests the possibility to identify stable clusters by varying simultaneously the numbers of S atoms and electrons, and also, possibly, the number of terminal –SH groups. Clusters stable in the conditions of HDS/HYD should exhibit, in addition to –SH groups, coordinatively unsaturated Mo atoms, thus helping the identification of the active sites.

Although of limited value, due to the small size of the clusters, the results show that hypotheses concerning the role of heterolytic dissociation of hydrogen and possible remote control processes are reasonable. This is compatible with what is known of the role of promoters (Co, Ni, noble metals). The calculation code used here permits similar calculations for other combinations of number of extra electrons and removal of S atoms (“reduction”).

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