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Ab Initio Study of the Structural and Electronic Properties of a Real Size MoS_2 Slab: $Mo_{27}S_{54}$

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It is shown that ab initio MO approaches are suitable to simulate the relatively large hexagonal MoS_2 slab corresponding to the average initial size (15−20 Å) of MoS_2 on alumina-supported catalysts used in hydrodesulfurization (HDS) and hydrogenation (HYD) of petroleum fractions. By using a general ab initio MO program, GAMESS, the structure optimization of the $Mo_{27}S_{54}$ slab is possible at the UHF/MINI/ECP=SBK level of theory, providing helpful information on the structural and electronic properties of the slab. The improvement, compared to other theoretical calculations based on simplified structural models, is that the different bonding and electronic properties of the Mo and S atoms in basal plane and on different edges and corners of the slab can clearly be distinguished. The structure of the slab is relaxed toward the edges. The 2-fold coordinatively unsaturated sites (CUS) on corners have both electron-donating and -accepting properties, making them potentially active for HDS (and HYD) reactions. The 2-fold CUS's on the edges ("reduced edges") seem to permit only the HYD reaction or CO hydrogenation. The removal of the basal plane S atoms requires activated atomic hydrogen species. The unreduced ($\bar{1}010$) edges do not seem to be potentially active catalytically. This deepens the understanding of the catalytic nature of the MoS_2 structure for several reactions, especially HDS and HYD (hydrotreating reactions) and CO hydrogenation.

Introduction

Molybdenum sulfide is the essential active element in catalysts used for the most important group of processes in the petroleum industry, namely the hydrotreatments. It is usually (but not always) promoted by other elements, like cobalt or nickel. Molybdenum sulfide is also essential for the processing of coal-derived products as well as carbon monoxide hydrogenation when sulfur resistance is required. A few typical articles on the catalytic properties of molybdenum sulfide are cited at the end of this article.[1−7] Although MoS_2 and similar transition-metal sulfides have been investigated intensively during the last three decades, there is no agreement yet concerning their catalytic behavior. This is particularly the case when the active sites specific for different reactions are considered. The above remark holds for the promoted as well as unpromoted catalysts. This is the reason for the emphasis laid on pure molybdenum sulfide.

The crystal structure of MoS_2 is well-known: this corresponds to a closely packed layered sandwich with each Mo atom coordinated with six S atoms in a prismatic unit. Mo atoms are in a plane situated between two planes containing S atoms.[8] The catalytic material is thus composed of such three-layer "sandwiches", or stacked arrangements of a few such sandwiches or "slabs". Catalytic studies have demonstrated that reduced edges of small MoS_2 slabs played the essential role in at least two categories of reactions involved in hydrotreatment, namely hydrodesulfurization (HDS) and hydrogenation (HYD).[1−4] Recently, we have given a comprehensive interpretation of experimental data, including kinetics and changes of selectivity according to reaction conditions, in HDS/HYD catalysis. An exact definition of catalytic site structures was proposed.

With some simplification, we may distinguish two historical tendencies in the applications of theoretical models: (1) a molecular mechanics approach and (2) molecular orbital (MO) calculations (and more recently the density functional theory, DFT).

In the early stages, molecular mechanics calculations have been focused on the structural features of slabs with different sizes, ranging from one containing 7 to one with 61 Mo atoms. One result was that, according to energy calculations, MoS_2 slabs tend to grow infinitely[9−11] (a tendency which is confirmed by electron microscopy observations of used catalysts). By using the molecular mechanics simulation of the structure of the MoS_2 slab, in combination with experimental measurements of catalytic activity, some other stimulating conclusions have been drawn.

But a deeper analysis seems absolutely necessary. This should be based on quantum mechanics, i.e., in practice, ab initio MO calculations or band-structure calculations by DFT. The first ones were semiempirical. For the simplified MO approaches (ZINDO), the parametrization for heavy atoms such as Mo is still in question, namely the results may very much depend on how parametrization is done.[12] The Fenske−Hall MO approaches in which the electron density is assigned to each center in the multiple center system through Mulliken population analysis need no such parametrization. These last approaches thus allow the evaluation of an approximate point charge in the calculation of multiple-center Coulomb terms and exchange terms in the Hartree−Fock formalism.[13] We shall therefore use

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the ab initio approach on the basis of our former study and the corresponding identification of the various categories of catalytic sites.[14] With respect to CO hydrogenation over MoS_2 catalysts, there has been no systematical investigation yet on the details of the catalytic action. To approach reality in both cases, detailed information on the structure and electronic properties of the MoS_2 slabs representative of those present in catalysts is required. This is the other motivation of the present study.

Recent progresses in computational techniques allow the acquisition of data of a quality allowing the solution of many problems concerning MoS_2. This was done by using density functional calculations combined with molecular dynamics simulations for the relaxation of surface atoms. The other atoms in inner structures remained at positions identical to those determined from bulk crystal coordinates.[15−24] However, it can be noticed that the periodically repeated arrangement of stacked $Mo_{12}S_{24}$ units in one direction of the $x-y$ plane (basal plane) used in density functional calculations does not reflect the real geometry of MoS_2 slabs. These slabs are actually finite in size and have boundaries in all directions. All their atoms should be relaxed compared to the positions in the infinite crystal. A considerable loss of information on the electronic structure may also be caused by using oversimplified models such as the chain type ones investigated by Ryskov et al.[23,24] In addition, it should be noticed that there are two types of primary edges on a fully sulfided MoS_2 slab, namely the one with terminal S atoms called $(10\bar{1}0)$ and the other one with bridged S atoms called $(\bar{1}010)$ (see Figure 1 presented later in the section "Geometry and Bonding"). During reactions involving hydrogen, these edges may change in coordination unsaturation, due to reduction. More precisely, some of the S atoms may be removed by reacting with some form of hydrogen (atomic or protonic H atoms are more reactive than molecular hydrogen in this kind of reaction).[1−4,25−30] In most of the recent theoretical analyses, this fact has been ignored. As will be seen in this work, the two kinds of edges mentioned above are probably very different with respect to catalytic activity. This shows that there is still a lack of information concerning MoS_2 slabs similar to those observed experimentally. In summary, the analysis of the electronic and molecular orbital structures of real MoS_2 slabs by using self-consistent ab initio calculations is still incomplete. Not forgetting excellent papers as those mentioned above, neither sufficient nor adequate comparison was found for the different sites of MoS_2 on both edges and corners of slabs representative of those present in real catalysts, although these sites are essential for catalysis in hydrogen involving reactions, particularly the HDS/HYD reactions and CO hydrogenation.

Experimental investigations have proven that highly dispersed MoS_2 crystals with sizes of one to several nanometers, with boundaries in all crystallographic directions, provide the necessary active sites for HDS/HYD reactions.[4,31−34] High intrinsic activities could be obtained with even smaller clusters composed of "sandwiches" as defined above.[34] For these "single sandwich" layer slabs, it is possible to use a generalized ab initio MO method to fully explore their electronic structures at a reasonable precision level. This potentially provides the basis for increasingly more precise studies, the precision increasing when computational limitations will progressively become less stringent.

Besides this, it should be noticed that there are two main demands for theoretical chemistry approaches to be relevant to the interpretation of catalytic activity of heterogeneous catalysts. The first one is evident, but not always respected, namely that the group of atoms considered, or better, the cluster studied be similar or identical to the group of atoms detected experimentally in catalysts possessing reasonably representative activity and selectivity. The second is unfortunately almost never considered. Catalysts, as prepared, are often, or probably generally, different from the material which is formed during the reaction and on the surface of which the catalytic process takes place. The catalyst "as prepared", even after activation, is just a precursor. In metals or oxides active in selective oxidation, surface reconstruction takes place and surface composition changes upon adsorption of reactants and/or during the catalytic reaction. Highly covalent sulfides such as MoS_2 constitute a very favorable situation in this respect, because they keep the same structure (even if some crystallite growth can take place at a very slow rate). One condition relative to operation conditions must nevertheless be respected, namely that the partial surface reduction prevailing during hydrotreatment or CO hydrogenation has to be taken into account.

The work presented here takes both demands into account as starting points, namely concerning structure and size of the MoS_2 cluster and possible reduction of the surface of active faces (edges). We therefore focus on the ab initio MO calculation of a fully structured finite $Mo_{27}S_{54}$ slab, because such a slab corresponds to a size similar to the average particle size of the particles present at the beginning of their life in the industrial reactor (when activation, namely reduction-sulfidation, is conducted carefully). (Afterward, they progressively grow in size during months and years in the reactor.) Attention will be given to both $(\bar{1}010)$ and $(10\bar{1}0)$ edges, of which the former may be of essential importance for the catalytic activity.[1−4,25−34] The distinction between sites on the two edges and on corners is made without any preassumption concerning the specificity relative to activity or selectivity of these catalytic sites. Full consideration is given to the symmetry (D_{3h} group) of this cluster. The optimized structure at the UHF/MINI/ECP level permits a qualitative comparison between the electronic properties of different boundaries or edges and other different sites possibly representing those existing in real MoS_2 slabs.

Computational Methods

The optimized structure of $Mo_{27}S_{54}$ was obtained by using the geometry optimization capability of the GAMESS program (PC version '97)[35] on a PII computer (300 MHz) with 192 MB RAM. The reasons GAMESS was chosen as a tool for the present calculation, are the following. This code provides ab initio MO methods that have proven in our test cases to be more robust in structure optimization of large MoS_2 slabs than some other programs that failed. GAMESS allows ECP (effective core potential) approximation approaches with SBK potential for core orbitals. This ensures that a great reduction of computational expense can be achieved. As concerns the basis sets, the MINI sets were chosen because they have been optimized for all elements in the periodic table and proved to provide better performance than the original STO-3G basis sets (see, for example, references in ref 35), at the level of which MINI sets are constructed. The present work was made possible because the recent version of GAMESS has been extended to treat systems with as many as 500 atoms and 2047 atomic orbitals (AO). With the above selected methods, our system containing 27 Mo atoms and 54 S atoms with a total of 1188 AO's can be treated. The application of more accurate basis sets or high accuracy methods such as DFT approaches would exert an enormous demand on our available computers and make difficult or impossible further calculations necessary for the elucidation of catalytic mechanisms.

TABLE 1: Atomic Coordinates of the Initial and Optimized Structures of the $Mo_{27}S_{54}$ Slab with Optimized Total HF/MINI/ECP-SBK Energy of − 2325.3120515269 au (symmetrically unique atoms only)

unique atoms	charges	initial guessed coordinations			optimized coordinations		
		x	*y*	*z*	*x*	*y*	*z*
X	0.0	0.000000000	0.000000000	0.00000000	0.000000000	0.000000000	0.000000000
Mo	42.0	2.008000000	0.000000000	0.00000000	2.0190990562	0.000000000	0.000000000
S	16.0	4.050000000	0.000000000	1.57000000	4.0537427996	0.000000000	1.563488600
Mo	42.0	5.050000000	1.732050808	0.00000000	5.0322841892	1.7856478191	0.000000000
S	16.0	7.050000000	1.732050808	1.58000000	7.0944661853	1.9457208837	1.5442911731
Mo	42.0	8.050000000	0.000000000	0.00000000	7.7811529746	0.0000000000	0.000000000
Mo	42.0	8.050000000	3.464101616	0.00000000	7.7551901168	3.7503172478	0.000000000
S	16.0	−2.070000000	0.000000000	1.52000000	−1.9885430578	0.0000000000	1.5207509155
Mo	42.0	−4.050000000	0.000000000	0.00000000	−4.0016855812	0.0000000000	0.000000000
S	16.0	−5.050000000	−1.732050808	1.58000000	−5.0281134032	−1.6993217101	1.5029488830
Mo	42.0	−7.050000000	−1.732050808	0.00000000	−7.1703682594	−1.5665408293	0.000000000
S	16.0	−8.050000000	0.000000000	1.59000000	−8.0464680247	0.0000000000	1.6284634915
S	16.0	−8.050000000	−3.464101616	1.59000000	−7.9967901598	−3.2766032009	1.5719535610

The initial coordinates of the atoms were set using the structural parameters found in the Handbook of Crystal Structures.[8] The optimization was performed with the convergence accelerating option DIIS and with ETHRSH=10 and DAMP switched on in the direct SCF procedure (DIIS, ETHRSH, and DAMP are three control parameters that can be adjusted so as to accelerate and stabilize the computational process). The initial guess on coordinates was adjusted whenever divergence occurred. It should be noted that the unrestricted Hartree−Fock (UHF) procedure was found to be the most robust in the geometry optimization of the present slab, although no unpaired electrons were assumed for the molecular system (multiplicity was set at 1). Each resulting MO consisted of two distinct sets, α and β, each of which was filled with only one electron. In this scheme, the wave functions of the electron pair in each MO are separated into two Hartree−Fock equations without direct restriction of paired arrangement in the MO. The basic idea of this scheme and the techniques implemented in GAMESS can be found in ref 35 (and the references therein). Calculation results consistently showed that α and β sets were exactly identical in energy and AO populations. With the initial guesses of coordinates listed in Table 1, the final optimal structure can be obtained. Its equilibrium coordinates set is also listed in Table 1. The computational time for the optimization of the $Mo_{27}S_{54}$ cluster is approximately 2400 h for one continuous run.

The atomic orbital (AO) population distribution over the molecular orbitals and the corresponding orbital energies can be extracted from the GAMESS output. It should be noted that the original GAMESS output for d AO participation in MO's are represented by six linearly dependent AO's, namely the $\bar{d}_{x^2}$, $\bar{d}_{y^2}$, $\bar{d}_{z^2}$, $\bar{d}_{xy}$, $\bar{d}_{xz}$, and $\bar{d}_{yz}$. To obtain the five linearly independent d components, one should consider the following conversion from the six $\bar{d}$ AO's:

$$d_{x^2-y^2} = {}^1/_2(\bar{d}_{x^2} - \bar{d}_{y^2}) \tag{1}$$

$$d_{z^2} = \bar{d}_{z^2} - {}^1/_3(\bar{d}_{x^2} + \bar{d}_{y^2} + \bar{d}_{z^2}) \tag{2}$$

$$d_{xy} = \bar{d}_{xy} \tag{3}$$

$$d_{xz} = \bar{d}_{xz} \tag{4}$$

$$d_{yz} = \bar{d}_{yz} \tag{5}$$

The choice of our computational methods is dictated by the wish to approach the electronic structure of MoS_2 in the real conditions of catalysis. We therefore had to use methods necessitating additional, but acceptable, computational efforts, namely making calculations for several situations corresponding to a partial reduction characteristic of the working catalysts. We recognize that more reliable tools such as high level ab initio approaches (MP2, CI, and MCSCF, etc.) and more recently the elaborate DFT methods should be used for a better qualitative analysis.

The practical characteristics of real catalysts cannot be satisfactorily approached by any quantum mechanical tool, if such a tool applies to a state of matter which neglects changes due to the environment in the catalytic process. Qualitative clues found in theoretical calculations corresponding to the real catalysts and corroborated by experimental phenomena should be more helpful to our understanding of details of the catalytic process, especially in our case of HDS and HYD. We present here the first steps of an attempt in this direction.

Geometry and Bonding

The full D_{3h} symmetry of the current cluster is chosen to reduce the computational expenses. However one should be aware that the finite structure is different from the bulk, as reflected in crystal structure parameters. Consequently, it is possible that a lower symmetry be actually formed due to some extensive relaxation of all atoms in the finite cluster, namely a symmetry distortion, causing a slight shift of the S atoms from their D_{3h} symmetry positions. In this case, the full optimization of the structure becomes difficult for the presently available computational capabilities. This aspect definitely needs to be validated in the future, because all the theoretical calculations so far completely neglected this possibility.

Figure 1 presents the schematic bonding structure (drawn by using the MOLDEN program on a SGI Indigo 2 machine, ref 36) of the optimized slab with D_{3h} symmetry (each point corresponding to sulfur actually represents two atoms, situated respectively in the upper and lower plane). This finite slab represents both edges of MoS_2, namely $(\bar{1}010)$ and reduced $(10\bar{1}0)$ (actually $(30\bar{3}0)$; but for convenience, we will use "reduced $(10\bar{1}0)$" below). On the $(\bar{1}010)$ edges, six Mo atoms, atom 64 and similar positions obtained by symmetry considerations, hereafter designed as "reflections", and on the reduced $(10\bar{1}0)$ edges, three Mo atoms, atom 31 and its reflections, are represented, respectively. The remaining edge Mo atoms are those at the corner position (atom 37 and its reflections), which are more closely binding to vicinal Mo atoms sitting on $(\bar{1}010)$ edges than to those on the "reduced" $(10\bar{1}0)$ edges. This is due mainly to the pulling effect of the bridged S atoms between them (atom 82(73) and its reflections). Let us underline the fact that the corner Mo atoms (atom 37 and its reflections) and the

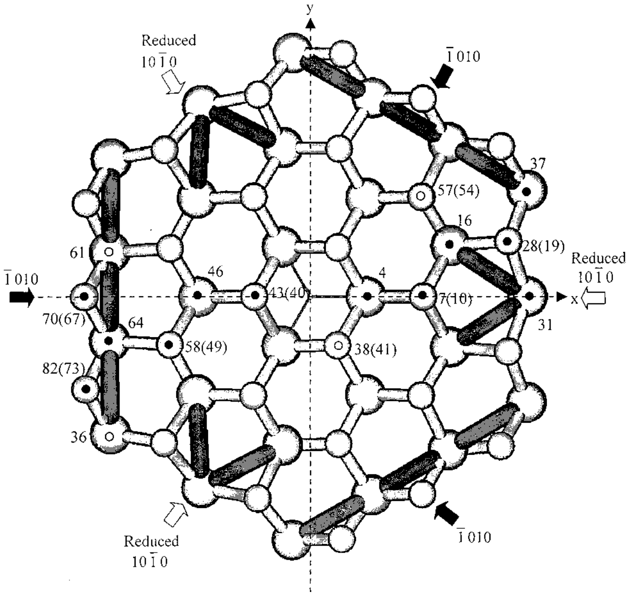

Figure 1. Optimized bonding structure of $Mo_{27}S_{54}$: unique atoms marked by filled circles.

TABLE 2: Bonding Properties

bonds	length A (order)	bonds	length A (order)
Mo(4)−S(7(10))	2.5315(0.675)	Mo(64)−S(58(49))	2.6202(0.574)
Mo(4)−S(38(41))	2.5157(0.696)	Mo(64)−S(70(67))	2.4235(0.863)
Mo(16)−S(7(10))	2.5328(0.678)	Mo(64)−S(82(73))	2.4655(0.778)
Mo(16)−S(28(19))	2.5813(0.658)	Mo(36)−S(82(73))	2.3828(1.077)
Mo(16)−S(57(54))	2.5119(0.722)	Mo(16)−Mo(37)	3.3577(0.093)
Mo(31)−S(28(19))	2.5772(0.473)	Mo(16)−Mo(31)	3.2779(0.095)
Mo(37)−S(28(19))	2.4653(0.826)	Mo(36)−Mo(64)	3.2748(0.147)
Mo(46)−S(43(40))	2.5230(0.654)	Mo(61)−Mo(64)	3.1331(0.279)
Mo(46)−S(58(49))	2.4899(0.720)		

3 Mo atoms on “reduced” edges (31 and its reflections) are 2-fold coordinatively unsaturated. The distinction between the atoms on corners from those on edges is necessary because all investigators agree in believing that the corner atoms are different from the other ones located on edges, both in their catalytic roles and electronic properties.

Metal−metal bonds with conspicuous characteristics are formed, especially on $(\bar{1}010)$ edges with bond orders of 0.147 for Mo(36)−Mo(64) (represented in the figure) and 0.279 for Mo(61)−Mo(64), respectively. This reflects the main different features of the $(\bar{1}010)$ edge Mo atoms compared with those in the basal plane (bulk Mo atoms) and on the reduced $(10\bar{1}0)$ edges, as listed in Table 2. The overall bonding structure can be understood considering three circles around the central “dumb atom” X as viewed perpendicularly to the basal plane.

The first circle consists of Mo(4) and its two reflections, and S(40) +S(43) and their reflections. The second circle consists of Mo(16) and its five reflections, Mo(46) and its two reflections, S(7)+S(10) and their reflections, and S(58)+S(49) and their reflections. The third circle consists of Mo(31) and its reflections, Mo(37) and its reflections, Mo(64) and its reflections, S(28)+S(19)) and their reflections, S(70)+S(67) and their reflections, S(82)+S(73) and their reflections.

The Mo−S bonds can be classified in two main families, the first comprising those linking S−Mo−S−Mo in three circles and the second one comprising those linking circles together through S−Mo bonding. The bond length values in Table 2 reflect the fact that lengths depend on the position in the slab, namely the circle where the bond is located. In the first circle, the D_{3h} symmetry nature of the structure ensures that only one kind of S−Mo bond exists with bond length and bond order of 2.5157 Å and 0.696, respectively. In the second circle, three kinds of S−Mo bonds exist with bond lengths (orders) of 2.5328 Å (0.678), 2.5119 Å (0.722), and 2.4899 Å (0.720) for Mo(16)−S(7) and its reflections, Mo(16)−S(57) and its reflections, and Mo(46)−S(58) and its reflections, respectively. In the third circle, five kinds of Mo−S bonds exist with bond lengths (orders) of 2.4653 Å (0.826), 2.5772 Å (0.473), 2.3828 Å (1.077), 2.4655 Å (0.778), and 2.4235 Å (0.863) for Mo(37)−S(28) and its reflections, Mo(31)−S(28) and its reflections, Mo(36)−S(82) and its reflections, Mo(64)−S(82) and its reflections, and Mo(64)−S(70) and its reflections, respectively. The Mo−S bonds connecting the first and second circles are Mo(46)−S(43) and its reflections and Mo(4)−S(7) and its reflections. Between the second and the third circles, the connecting bonds are Mo(16)−S(28) and their reflections and Mo(64)−S(58) and their reflections. The Mo−S bonds connecting the outer circles are longer (2.6207 Å toward the $(\bar{1}010)$ edges and 2.5813 Å toward the reduced $(10\bar{1}0)$ edges) than those connecting inner circles (2.5230 Å toward the $(\bar{1}010)$ edges and 2.5315 Å toward the reduced $(10\bar{1}0)$ edges).

It is clear that the bonding of a cluster/macromolecule with limited size cannot coincide with the experimental data available only for the bulk structures of MoS_2, which corresponds to arrangements one or 2 orders of magnitude larger in size than in the case of $Mo_{27}S_{54}$. However, the bonds of the inner circles of the $Mo_{27}S_{54}$ model are quite far from the boundaries. This suggests the origin of the difference between the calculated results with the ab initio MO method at the UHF level and the experimental bulk bond length. The Mo−S bond length in the bulk structure is 2.35 Å,[8] while we obtain a value of about 2.52 Å by using the current combination of ab initio methods. The deviation is as large as 0.17 Å. This is due to our choice of a computationally affordable method. Actually the currently applied AO functions are very simple compared to those based on larger sets or more precise methods (such as ab initio CI, MP2, and DFT). The current method predicts longer bond lengths than the real values, and this deviation may be still enlarged due to the limited cluster size compared to the infinite bulk crystal structure.

For the Mo−Mo distances, the experimental data for bulk MoS_2 structure is 3.16 Å, while the calculated value for the inner circle of $Mo_{27}S_{54}$ cluster is 3.4982 Å, with which no Mo−Mo bonding noticeably appears. However, Mo−Mo binding interactions are clearly formed, according to our calculation, between Mo(64)−Mo(36), Mo(64)−Mo(61), and Mo(31)−Mo(16) with bonding lengths of 3.2748 Å, 3.1331 Å, and 3.2779 Å, respectively, for the unique Mo atoms in Figure 1. The Mo−Mo bindings in the middle of the $(\bar{1}010)$ edges seem to be the strongest.

The bond orders reported in Table 2 show that the bonds between the Mo atoms and the bridged S atoms are stronger than the bonds between Mo atoms and basal plane S atoms. This means that the thermal stability of the simply bridging bonds is higher than the ones partitioned between S atoms and three Mo atoms. This is consistent with the results of the tight-binding MO calculations by Tan and Harris.[13] We must keep in mind that the structure of MoS_2 at temperatures corresponding to most catalytic processes is thermally stable. It is, however, clear that the bond orders deduced from theoretical calculations cannot directly be correlated to the stability during catalysis because a reduction of catalysts occurs through a reaction between MoS_2 clusters and hydrogen species rather than by a purely thermal process.[4,37]

TABLE 3: Mulliken Atomic Charges (symmetrically unique atoms)

atoms	charges	atoms	charges
Mo(4)	0.67209	S(43)	−0.359092
S(7)	−0.381691	Mo(46)	0.663765
Mo(16)	0.686797	S(58)	−0.374406
S(28)	−0.510899	Mo(64)	0.791058
Mo(31)	0.837614	S(70)	−0.234268
Mo(37)	0.892518	S(82)	−0.355724

Catalysis chemistry investigations have revealed that the HDS and HYD activities are mainly due to properly reduced edges, on which coordinatively unsaturated metal sites (up to 3- or 4-fold coordination unsaturation) play important roles, respectively, in the hydrogenation of −C═C− double bonds and in the hydrodesulfurization of sulfur containing compounds (in this latter case, probably through the formation of an ensemble of edge sites).[1−4,14,28,29,38] For highly reduced metal sites, it is clearly seen in Figure 1 that some S atoms on edges must be removed by reaction with hydrogen to leave 3- or 4-fold coordinated unsaturation sites (CUS's). These highly reduced sites can be easily formed on $(\bar{1}010)$ edges by removing bridged S atoms or opening the bridging S−Mo bonds. On the reduced $(10\bar{1}0)$ edges, the Mo sites can become highly unsaturated only if the S atoms bound to three Mo atoms are removed. This may create defective gaps in the structure (probably starting from the reduced edges), forming more corner sites under extreme conditions, for example under the action of atomic hydrogen or protons and/or at elevated temperature. This may even completely destroy the MoS_2 structure in the case of over-reduction.[4,14,37] The fact that the metal−metal binding on $(\bar{1}010)$ edges geometrically permits the formation of ensembles or pairs of Mo sites must be noticed, because such pair-type ensembles have been considered as essential for the hydrotreating reactions.[14,38]

Atomic Populations in HOMO and LUMO

The Mulliken atomic charge distributions are listed in Table 3. The two sides of the MoS_2 slab containing S atoms are negatively charged, forming two negatively protected electronic layers. The positively charged Mo plane is in the middle of the sandwiched structure, only exposing part of Mo atoms, and these are on the edges.

Surface science experiments showed that an MoS_2 slab can be destroyed (reduced) by the action of atomic hydrogen or protons at elevated temperatures.[37] According to our understanding of the electronic structure of the slab, the mechanism of this phenomenon may be explained more accurately by a mechanism in which protons attack the negatively charged S layers and get bound to S atoms on basal planes (due to chemical affinity between protons and S atoms), leading to the weakening or even cleavage of S−Mo bonds. This preferably occurs for the 3-fold coordinated S atoms close to the reduced $(10\bar{1}0)$ edges, namely S(28) and its reflections, because of their higher negative charges (as high as 0.5109). Taking into account the charges of the coordinatively saturated S atoms, the probability of interactions leading to reaction are larger for those sitting in the outer circles than those in inner circles of the cluster. Experimental observations have indicated that the bridged S atoms on $(\bar{1}010)$ edges are removed prior to the three coordinated S atoms.[1−4,14,37] These bridged S atoms on $(\bar{1}010)$ edges possess negative charges. These charges are, however, smaller than those carried by the S atoms in inner circles. This suggests that activated forms of hydrogen could modify the reactivity order for these different kinds of S atoms. In addition, the bridged S atoms close to corner positions carry much higher negative charges than the other ones on the $(\bar{1}010)$ edges. This again suggests that the atoms on the corners of a real MoS_2 cluster have exceptionally reactive features. This was not shown in recent DFT calculations with periodic geometric structures made of MoS_2 units.

The positive charge distribution on the Mo atoms reflects the fact that the 2-fold coordinatively unsaturated Mo atoms, namely Mo(37) (corners) and Mo(31) ('reduced' edges) and their reflections, carry more positive charges than the saturated Mo atoms (Mo(4) and Mo(43), and their reflections). The Mo atoms on corner positions possess the largest charge values. These Mo atoms should be distinguished from the other Mo atoms on the edges.

The HOMO−LUMO gap in energy amounts of 0.2154 au (5.8614 eV), namely the electrons in the frontier MO, are strongly bonded in the HOMO, in which the major contribution comes from the $3p_y$ of S(28) and its 11 equivalents and Mo(31) and its two reflections. This strong binding feature indicates that the MoS_2 phase is very stable at high temperature in the absence of reactive agents. There are two degenerated MO's as HOMO and HOMO-1, while no degenerated MO is found for LUMO.

For describing the atoms (sites) sitting on the edges and corners of the structure, the AO distributions on the MO's are shown in Figure 2. In this figure, the scale in the vertical axis corresponds to the square of the coefficients of AO's distributed on MO's with the different energy levels indicated on the other axis. From Figure 2, it can be seen that the AO distribution of the Mo(31) site on the reduced $(10\bar{1}0)$ edge is mainly on the occupied MO's, and only a very low proportion on the unoccupied MO's. This indicates that the sites sitting on the reduced $(10\bar{1}0)$ edge (Mo(31) and its equivalents) act as electron donors rather than acceptors. This donation dominantly comes from the $4d_{xy}$ orbital of the Mo(31) site (Figure 2a). This may suggest a catalytic action of these sites for the activation of π-bonds of potential reactants in HDS and CO hydrogenation. These sites likely provide electrons to the antibonding π^* of the reactants. This initial process is essential in CO activation on transition metals.[39]

For the HDS/HYD catalysis, the situation is more complicated because various reactants with completely different electronic structures have to be considered. In the case of thiophene, for example, the extended Huckel approach[40] and that based on the DFT band structure[17] show that π−bonds over the carbon atoms may be activated on this kind of electron-donating sites in the first activation step. However, other MO based approaches have drawn different conclusions[12,41] due to, besides the variety of theoretical methods used, different assumptions on (i) the type of adsorption (e.g., the S atom), (ii) the choice of a given small cluster as model and/or the chemical composition of edges. A recent publication[42] mentioned a type of *supported* triangular MoS_2 cluster detected by STM at high resolution. This structure exhibits $(\bar{1}010)$ edges and three corner Mo sites. Although it is questionable whether a cluster in strong interaction with a support different from the normal one (alumina) is really representative, it is interesting to note that the $(\bar{1}010)$ edges have been considered to be active for HDS when in a reduced state. Nevertheless, our calculations show that the sites on "reduced" $(10\bar{1}0)$ (Mo(31) in our case) may not be sufficient for C−S bond cleavage. We shall briefly allude to the possibility of removing bridged S atoms from the coordination sphere of Mo(64) in the discussion. We hope that the present work will permit to extend these calculations and provide more detail on

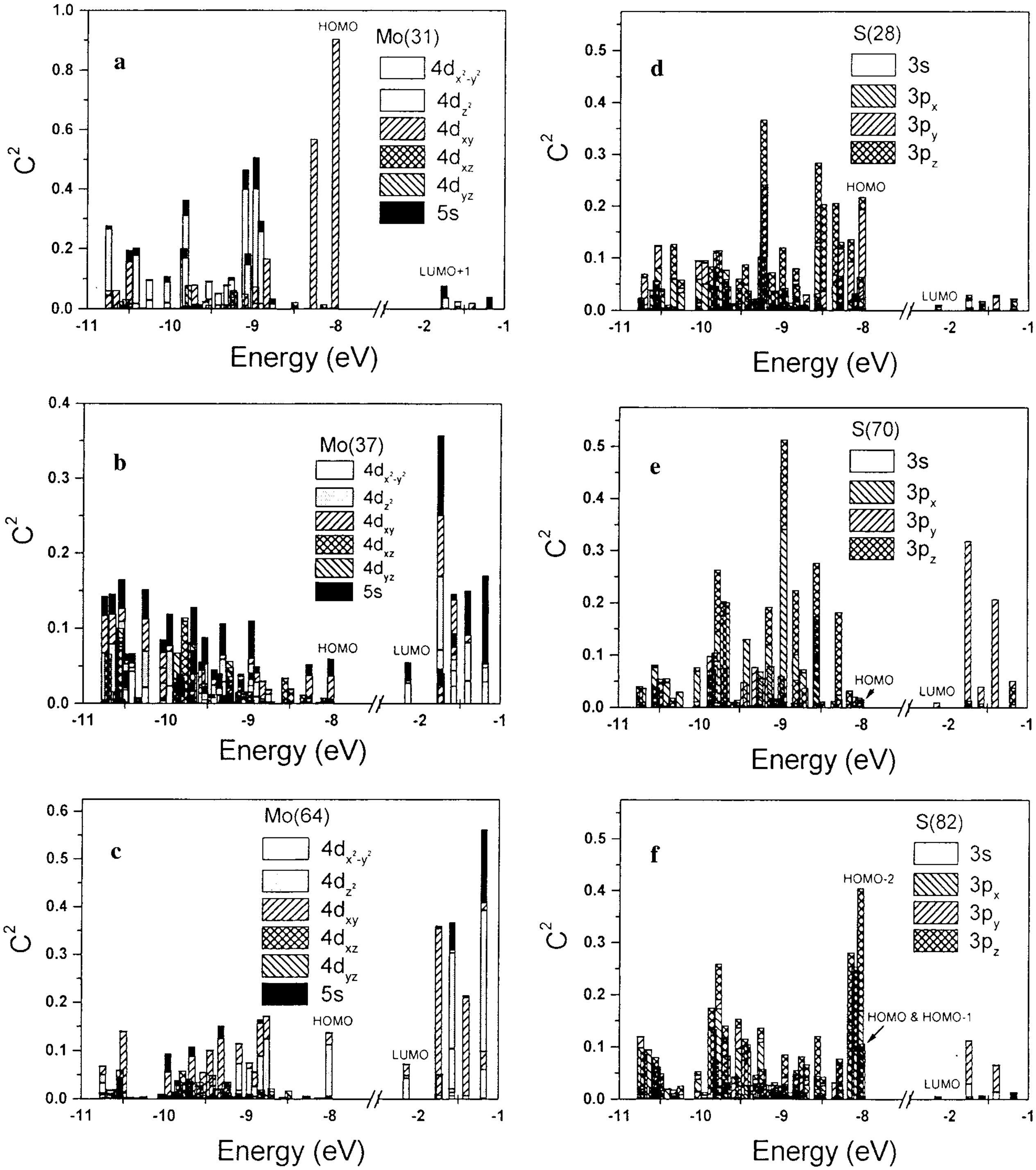

Figure 2. Relative densities of AOs on MOs for different edge atoms: AO participation in degenerated MOs is also included ($E_{\mathrm{HOMO}} = E_{\mathrm{HOMO-1}} = -8.014$ eV; $E_{\mathrm{LUMO}} = -2.152$ eV; $E_{\mathrm{HOMO+1}} = -1.755$ eV).

the effect of a further reduction of $(\bar{1}010)$ edges (a point to be discussed in a separate article). The energy changes in partial reduction of edges have been discussed in a recently submitted article.[43]

For other sulfur-containing species, for example for dibenzothiophene, the hydrogenation of benzene rings may also need electron-donating properties of the metal sites, but the cleavage of S−C bonds demands the interaction of the HOMO portion of the S atom with the LUMO of the metal site,[12,44] which is hardly observed in Figure 2 for the 2-fold CUS Mo(31). For the Mo(37) site on the corner, also with a 2-fold coordination unsaturation, the AO's are distributed on both occupied and unoccupied MO's. The density on HOMO is significantly smaller than the corresponding one for Mo(31). The distribution on LUMO, however, is more siginificant (Figure 2b) than in the case of Mo(31). The AO distributions on HOMO come mainly from 4d$_{xy}$ and 5s atomic orbitals. On the LUMO, the AO distributions are mainly from 4d$_{x^2-y^2}$ and 5s atomic orbitals.

These features of the Mo(37) site indicate that the Mo sites on corners possess both eletron-donating and electron-accepting properties to a mild degree. This and a former remark on Mo(37) confirm literature conclusions that the corner sites of MoS$_2$ clusters generally have distinct activities for both HYD and HDS compared to the other edge sites.[4,25−34] Our results offer an in-depth understanding of this difference, namely that the Mo(37) site possesses both the electron-donating and -accepting properties which are required, especially for HDS reactions. But we must admit that, at this stage, our work only provides part of the necessary pieces of information. Conclusions concerning the reaction of molecules which may need HYD and/or direct HDS mechanisms to react demand a more complete examination of the possibilities, both from the theoretical and experimental points of view. Correct electronic pictures of all the possible sites sitting on the edges of a MoS_2 slab of a working catalyst are necessary. At this point, any preassumption for catalyst sites may be misleading. For the Mo site (Mo(64)) sitting on $(\bar{1}010)$, the AO distributions on the MO's show that this site contributes to both HOMO and LUMO in noticeable proportions although Mo(64) is saturated in the current structure. The distribution on HOMO mainly comes from $4d_{z^2}$, and a very small portion comes from $4d_{xy}$. The contribution to LUMO is smaller than on HOMO, mainly from $4d_{xy}$ and $4d_{x^2-y^2}$. This suggests that the Mo(64) site, although on unreduced $(\bar{1}010)$ edges, possesses features of high energy states. However, the $4d_{z^2}$ character due to Mo(64) on HOMO and the $4d_{xy}$ and $4d_{x^2-y^2}$ on LUMO may not be useful for catalysis, because the outer S layers may block the access of reactants to sites in a coordinatively saturated environment, namely without removal of the bridged S stoms. This suggests that the activation of reactants on this site requires a more accessible environment in order to have siginificant interactions with reactant molecules. This can be realized by removing the bridged S atoms, which may lead to further enhancement of the electronic fingerprint of the Mo(64) site on HOMO and LUMO. This confirms previous opinions concerning edges, from which sulfur atoms had been removed. They are necessary for a significant catalytic activity in HYD and HDS. Because very considerable computational efforts are needed for the calculation of such large slabs with the reduced $(\bar{1}010)$ edges (where the bridged S atoms on the edges have been removed), we could not examine this point more in detail. Further calculations are certainly necessary to explain the HDS activity of reduced $(\bar{1}010)$ edge Mo sites. This is one of the objectives of our ongoing computations.

The AO distributions of 3-fold bonded S atom (S(28)) in Figure 2 show that they possess a high portion of $3p_y$ orbitals on HOMO, but no significant contribution to LUMO and other low energy unoccupied MO's. This again suggests that the removal of this kind of S atom may need a reactive species produced catalytically, e.g., a proton species, to react at temperatures far below the decomposition of the MoS_2 structure. For the bridging S atoms on the $(\bar{1}010)$ edges, unoccupied MO's are observed as well as much weaker contributions to the HOMO, compared to S(28). This probably implies that these S atoms are able to interact with atomic hydrogen. Especially when high energy situations are established, as during catalyst reduction, these S atoms may be removed by atomic hydrogen (or rather, protonic hydrogen) to form the reduced sites accessible to reactants.

Discussion

Like nearly all attempts to use theoretical chemistry in heterogeneous catalysis, this work has to take into account present computational constraints. The basis chosen is admittedly not a high level set. We did not find in the literature mention of the use of higher level basis sets for problems of similar complexity. More specifically, no relaxed bond lengths have been calculated when using higher level theories. Our attempts using frozen structures (bulk crystal parameters) did not lead to convergent results in SCF using hybrid DFT proposed in some softwares. The compromise we have selected permits to detect features due to relaxation. These are possibly exaggerated with respect to reality. But, taking these relaxation phenomena into account is recognized as absolutely necessary for obtaining significant results. Our data are only qualitative. But they show that we can describe quite in detail the electron densities of *several* types of sites (edge and corner) using an identical approach for all. This leads to interpretations that coincide with experimental observations and predictions that could stimulate further research.

As indicated above, MoS_2 (or sometimes WS_2) is the essential, and sometimes the only, active component in catalysts active for HDS/HYD reactions. Although we cannot quantitatively appreciate the effect of removal of S atoms from our $Mo_{27}O_{54}$ cluster, our work suggests a few remarks concerning this point. HDS and HYD take place at relatively high temperatures (typically 280−400 °C), and high H_2 pressures are absolutely necessary (30−100 bar). In addition, a small amount of H_2S has to be present, to avoid deep reduction of MoS_2 (or WS_2) and to maintain catalyst activity. The relatively strong, but limited, reduction of the stacks of MoS_2 slabs (actually piles of two or several superposed slabs) is a fundamental feature of the last stage of catalyst activation.[1−4,25−34] Some S atoms must be removed from MoS_2 slabs. It has been shown experimentally, in surface science type experiments and by thermo-chemistry calculations, that the removal of S atoms from a MoS_2 slab starts from the edges.[37,45] Theoretical calculations show that this removal starts with the terminal S atoms originally bound on the 2-fold unsaturated Mo atoms, for example in our case, on the $(10\bar{1}0)$ edges (that we called "reduced"). These terminal S atoms could be removed even by molecular hydrogen, but this is much easier in the presence of activated hydrogen. In more severe conditions (e.g. elevated temperature in the presence of hydrogen), the bridged S atoms sitting on the $(\bar{1}010)$ edges can also be removed. Finally, the removal of the S atoms on the basal plane, which are bonded with three Mo atoms, is possible, but under quite extreme conditions, namely much higher temperatures and/or thanks to the action of atomic/protonic hydrogen.[37,45]

With the corresponding experimentally proven facts in mind, a picture of the edges on MoS_2 slabs under the HDS/HYD conditions can be given. The reduced $(10\bar{1}0)$ edges will remain the same as those shown in Figure 1 for our $Mo_{27}S_{54}$ crystallite. But the Mo sites on the $(\bar{1}010)$ edges will acquire a different (higher) reduction state. This occurs as a consequence of a dynamic reduction-sulfidation equilibrium with the gas phase, whose composition is imposed by the operation conditions, namely a high hydrogen pressure, the presence of hydrogen sulfide, and elevated temperatures. The result is a partially reduced catalyst surface. In structural terms, a few possibilities can be contemplated. Possible states are as follows: (i) 2-fold CUS's formed by breaking two Mo−S bridging bonds or removing two bridging S atoms between two Mo atoms on the edges or other similar combinations leading to reduction, (ii) 3-fold CUS's formed by further reduction of 2-fold CUS's, and finally (iii) 4-fold CUS's formed by removing all bridging S atoms on the $(\bar{1}010)$ edges of the MoS_2 slabs (Figure 3). However, the loss of S atoms in processes (ii) and (iii) may lead to the destruction of the MoS_2 structure, implying a deep reduction of catalyst, which could also destroy the adequate geometry of the catalyst surface. This should be avoided.

A correlation between catalytic activity and the extent of reduction of MoS_2 catalysts has been elegantly established experimentally by Kasztelan et al.[25,26] This concerned the HYD activity and included a detailed analysis of the mechanism.

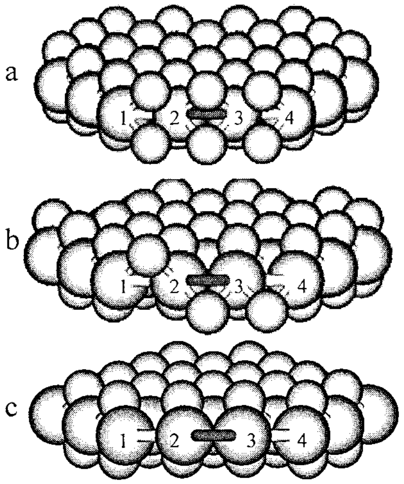

Figure 3. Different reduced states of Mo sites on $(\bar{1}010)$ edges of $Mo_{27}S_{54-x}$ slabs: the bridged S atoms are removed to schematically represent various coordinated unstauration sites. (a) Original $Mo_{27}S_{54}$ slab: Mo(1) and Mo(4) are two corner sites with 2-fold coordinated unsaturation characters, and Mo(2) and Mo(3) are two fully saturated sites. (b) Mo(1) and Mo(4) are two 3-fold coordinated unsaturation sites, and Mo(2) and Mo(3) are two 2-fold coordinated unsaturation sites, respectively. (c) Mo(1) to Mo(4) are all fully reduced into 4-fold coordinated unsaturation sites, and further reduction in this case will destroy the MoS_2 structure.

These results were further discussed taking into account all the aspects of the HDS and HYD reactions reported since. The conclusions confirm that the CUS's on the reduced $(\bar{1}010)$ edges of MoS_2 slabs play an essential role. More specifically, 3-fold CUS's may be dominant for HYD and some kind of arrangement of paired sites probably involving SH groups would be the main active sites for HDS catalysis.[14,38] Our theoretical calculations in the present paper suggest that the reduced $(10\bar{1}0)$ edges may not play any significant role, especially in the cleavage of S−C bonds. This is due to an insufficient population of split d valence orbitals of Mo atoms in the frontier MO's (LUMO) of the real structure of MoS_2, while they are probably useful for the activation of π-bonds, which are needed in CO hydrogenation and double bond hydrogenation. Extrapolating our results, we can explain the effect of the removal of the bridged S atoms on $(\bar{1}010)$ edges or the cleavage of bonds between Mo and bridging S atoms during reduction, which will certainly change the MO distributions on the reduced Mo sites on the edges. This could create the characteristics of the edge Mo orbital distribution (especially 4d proportions) on HOMO/LUMO of the cluster expected to be necessary for the cleavage of S−C bonds of reactants in HDS.

However, additional computational efforts are still necessary to get a more exact picture of the catalytic sites in HDS/HYD. The current work provides directing lines toward a better understanding of the nature of HDS and HYD catalysis over MoS_2-type catalysts. For CO hydrogenation reactions over MoS_2, the situation is simple compared to HDS/HYD, but comparatively less experimental information exists, which could suggest sufficiently detailed mechanisms. It is hoped that detailed calculations on the activation of the CO over various candidate sites on the MoS_2 structure could contribute to the elucidation of this mechanism.

Conclusion

The electronic structures of a real size MoS_2 slab have been calculated by using ab initio MO approaches at a computationally affordable level of theory. Thanks to a compromising choice of theoretical methods, the structure of $Mo_{27}S_{54}$ can be fully optimized. The calculation provides detailed information on the electronic properties of the structure and the individual sites. By analyzing this information, the different contributions of edge sites to the frontier MO's of the structure can be clearly distinguished. This can further be related to the different catalytic roles of these sites, especially in HDS/HYD for which a detailed experimental basis is available. On the basis of the theoretical results and those from experiments, the situation can be summarized as follows:

(1) The structure of a finite slab of MoS_2 is more relaxed toward the boundaries, a fact which had not been fully considered in previous theoretical studies at the first principle level.

(2) The distinction between different sites on or near edges and on corners has been achieved on a cluster of size representative of the size in real catalysts, namely $Mo_{27}O_{54}$. This indicates that the 2-fold CUS's on corners have both electron-donating and electron-accepting properties, and hence are potentially active sites for HDS reactions, while the 2-fold CUS's on so-called 'reduced' $(10\bar{1}0)$ edges possess only the electron donation features permitting π-bond activation for the HYD reaction or CO hydrogenation reactions. These sites are probably not sufficiently active for the C−S bond cleavage necessary in HDS reactions. This is due to the lack of electron-accepting features.

(3) The removal of basal plane S atoms requires protonic hydrogen species, and the reaction probably starts from the S atoms (bonded with three Mo atoms) close to a corner and sitting on the "reduced" $(10\bar{1}0)$ edges.

(4) The unreduced $(\bar{1}010)$ edges do not seem to have the possibility to possess active sites.

The corresponding reduced states need to be further analyzed to get a complete picture of the catalytic roles of the edges sites on MoS_2 structures with finite size.

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