

Vacancy Formation on MoS₂ Hydrodesulfurization Catalyst: DFT Study of the Mechanism

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In this work is reported a periodic density functional theory study of the vacancy formation mechanism on the [10–10] and the [–1010] edges of MoS₂ nanocrystallites that are the active phases in hydrodesulfurization catalysis. It has been previously shown that, from a thermodynamic point of view, there should be only very few vacancies on these edges and that their number is only slightly influenced by an increase in the hydrogen partial pressure. The kinetics of the vacancy creation is now considered through a detailed analysis of the intermediates and transition states found on the different pathways for the extraction of a surface sulfur atom by a hydrogen molecule of the gas phase. Only on one of the crystallite edges, the (10–10) (metallic edge), does the activation energy of the rate determining step of the vacancy formation remain smaller than 1 eV. This value allows us to consider that a dynamic equilibrium takes place on this edge. The rate-determining step is the heterolytic dissociation of the H₂ molecule, leading to the formation of one S–H and one Mo–H group. The activation energy for the H₂S departure is estimated to be 0.50 eV, in nice agreement with the value deduced from sulfur exchange experiments. The vacancy formation is possible on the [–1010] edge of the crystallite (the sulfur edge) but the rate determining step, which is the displacement of one S–H group on the surface, has an activation energy of 1.25 eV. This kind of vacancy formation on the sulfur edge does not imply the departure of one H₂S molecule from the surface.

I. Introduction

Diesel fuel specifications will soon impose a drastic diminution of their sulfur content. The active phases of the hydrodesulfurization (HDS) catalysts are the molybdenum disulfide nanocrystallites, promoted by cobalt or nickel atoms and deposited on a high specific surface area alumina.¹ This industrial pressure has induced an increase in the number of studies dealing with theoretical investigations of the MoS₂ surfaces^{2–17} under various conditions. Correlations between the experimental and theoretical studies have given a better insight into the catalyst's behavior under in situ working conditions. For example, the shape of MoS₂ platelets deposited on gold have been investigated recently by STM studies,^{18,19} whereas theoretical studies^{20,21} have demonstrated that this shape is dependent on the sulfiding conditions and that under the catalytic conditions, the crystallites will be almost hexagonal, as was previously proposed by Kasztelan et al.²² These hexagonal platelets exhibit two kinds of edges (Figure 1a), that is, the (–1010) and the (10–10) named respectively the metallic and the sulfur edges. It have been demonstrated experimentally²³ and theoretically^{2–5} that the sulfur stoichiometry of the edges is strongly dependent on the H₂/H₂S partial pressure ratio in the surrounding gas phase. Starting from the stable edges determined in previous studies, we are now able to investigate the reactivity of these systems. Whatever the reaction pathway considered for the HDS, the proposed mechanisms^{1,24,25} require the participation of coordinatively unsaturated sites (CUS) on the edges of the MoS₂ active phase, on which the sulfur-containing molecule may adsorb and react. Experimental evidence for the vacancy formation has been given by Kabe et al.^{26–31} by the ³⁵S exchange method. These authors showed that

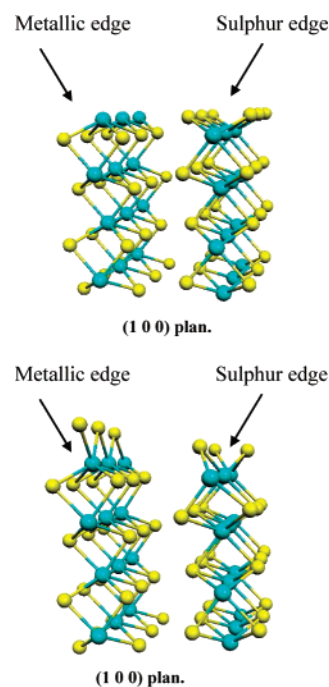


Figure 1. (a) Representation of the crystallographic (100) plan. Mo atom in blue, S atom in yellow, and H atom (not represented on this figure) in white. (b) Representation of the stable edges within the catalytic conditions.

the number of vacancies created is very small and that their number is only slightly influenced by an increase in the H₂ partial pressure. These results are in agreement with the thermodynamic data deduced from previous DFT calculations, in which we showed that the stable surfaces do not present any vacancies.^{3,4} The vacancy formation mechanism may have a large influence over the overall desulfurization reaction. More-

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over, depending on the size and location of the most rapidly created CUS, the adsorption mode of the organic molecule may change. These differences are crucial for large molecules, such as the dimethyldibenzothiophenes that are known to be refractory to the HDS process performed with classical catalysts.¹

The discrepancies among the theoretical calculations that show there are no vacancies and experimental studies showing that the vacancies can be created during the S exchange reaction may be due to a kinetic phenomenon. A detailed description of the intermediates and transition states of the reaction of extraction of an S atom by hydrogen molecules of the gas phase can give new hints to explain the experimental data. In this work, we therefore investigated the vacancy formation mechanism over the (100) MoS₂ surfaces, starting from the stable surfaces within the HDS reaction conditions. We have computed the activation energies of the various possible elementary steps that is, H₂ adsorption and dissociation, hydrogen atom migration on the edges of the particles, H₂S formation on the surface, and H₂S desorption. The results are compared directly with experimental data and allow us to explain some results of radioactive sulfur exchange experiments.

After a presentation of the computational methods in Section II, the mechanism of the sulfur departure from the metallic edge and from the sulfur edge will be presented in Sections III and IV, respectively. A general discussion and the comparison with the experimental data will then be carried out in Section V.

II. Computational Methods

The ab initio calculations were performed with the Vienna ab Initio Simulation Program (VASP).^{32,33} It is based on Mermin's finite-temperature local density functional theory.³⁴ The calculations use a plane wave basis set and the electron-ion interactions are described through optimized ultrasoft pseudopotentials.^{35,36} The resolution of the Kohn-Sham equations is performed using an efficient matrix diagonalization routine based on a sequential band-by-band residual minimization method for the one-electron energies. An improved Pulay mixing is used to update the charge density. The optimization of the atomic positions is performed via a conjugate gradient minimization of the total energy using the Hellmann-Feynman forces on the atoms.

Throughout this work, we used a large supercell ($9.48 \times 20 \times 12.294$ Å³) containing three elementary MoS₂ asymmetric units in the *x* direction, four in the *z* direction and two layers along the *x* axis (Figure 1a). Previous studies²⁻⁵ showed that this model was suitable for prediction of the electronic and structural properties of the MoS₂ perfect surface. The two upper rows were allowed to relax, while the two lower layers were kept fixed at the bulk geometry in order to simulate bulk constraints. The calculations were performed at Γ point with a cutoff energy of 210 eV, a Methfessel-Paxton³⁷ smearing with $\sigma = 0.1$ eV. The exchange-correlation function developed by Ceperley and Alder and parametrized by Perdew and Zunger³⁸ was used with the generalized gradient corrections introduced as proposed by Perdew et al.³⁹

To localize the various transition states (TS), we have used the nudge elastic band (NEB)⁴⁰ method implemented in the program, modified following the Johnson group method⁴¹ in order to have a significant image density near the transition state. Frequency calculations have been performed through numerical differentiation of the force matrix, including all of the optimized degrees of freedom (i.e., the coordinates of the molecule and of the atoms of the two upper rows of the slab) in order to characterize the transition states. It has thus been checked that

all the TS presented in this study have one, and only one, imaginary frequency.

III. Vacancy Formation on the Metallic Edge

The perfect (100) surface of the active MoS₂ crystallites, now well accepted as the active surface, exhibits two types of edges, one exposing unsaturated molybdenum atoms (10–10 edge), the other one exhibiting sulfur-saturated Mo atoms ($\bar{1}010$ edge) (Figure 1a). These two surfaces will be labeled hereafter metallic and sulfur edges, respectively. Previous^{2-5,20,21} DFT studies have shown that the sulfur coverage of the stable surfaces within the catalytic reaction conditions is different from the perfect crystallographic one. Formally, for each Mo atom, a sulfur atom is transferred from the sulfur edge to the metallic one. The geometry of this stable surface is represented in the Figure 1b. The aforementioned DFT studies also showed that the vacancy formation is a strongly endothermic process, the CUS being unstable on the edges, even under high hydrogen partial pressures. However, it has been shown experimentally^{26-31,42} that some sulfur atoms are exchangeable. In a first step, we have, therefore, investigated the vacancy formation mechanism on the metallic edge, starting from a surface that is stable under the reducing conditions corresponding to the catalytic HDS conditions. The mechanism of H₂S removal from the surface has been divided into elementary steps. The results of the calculations will be given as energy diagrams on which are represented the geometry of the intermediates and of the transition states (TS).

III.1. Departure of a First H₂S Molecule from the Metallic Edge Surface. Figure 2 shows the reaction energy diagram for the elimination of one H₂S molecule from the metallic edge. As previously mentioned, the overall reaction is strongly endothermic ($\Delta E = 1.40$ eV). Because no H₂ physisorption occurs on the edge, the reaction is directly initiated by the heterolytic dissociation of the H₂ molecule, leading to the formation of one Mo–H group and one S–H group. The activation energy of this elementary step is $E_{\text{act}} = 0.97$ eV. The geometry of the transition state, labeled TS2a, is represented on Figure 2. The bond distances of this TS2a are 1.05, 1.62, and 1.72 Å for the H–H, the H–Mo, and H–S bonds, respectively. Other dissociation modes of the H₂ molecule into two S–H or one H₂S group were also investigated. The activation energies are more important, i.e., 1.47 and 1.63 eV for the direct formation of one SH₂ group and two S–H groups, respectively, results which allow us to reject these hypothesis.

Then in order to permit the further displacement of the hydride-type hydrogen atom to the sulfur atom, leading to the formation of one SH₂ group, the displacement of the proton from one side of the slab to the other one is required. This displacement is similar to the well-known ammonia inversion. The hybridization of the S atom in the transition state TS2b is almost sp², and the S–H bond distance is 1.36 Å, a value comparable to the classical S–H distance. The activation energy of this second step is $E_{\text{act}} = 0.66$ eV. After this step, the adsorbed H₂S molecule is obtained by the migration of the hydride hydrogen atom through TS2c, where the S–H distances are 1.59 and 1.36 Å. The activation energy of this strongly endothermic step is 0.79 eV.

The last step of the reaction is the H₂S desorption, with creation of a CUS on the Mo atom on the edge. This step is endothermic (0.45 eV), and the activation energy is 0.52 eV. Because of the microreversibility principle, the diagram depicts also the adsorption and the dissociation of the H₂S molecule

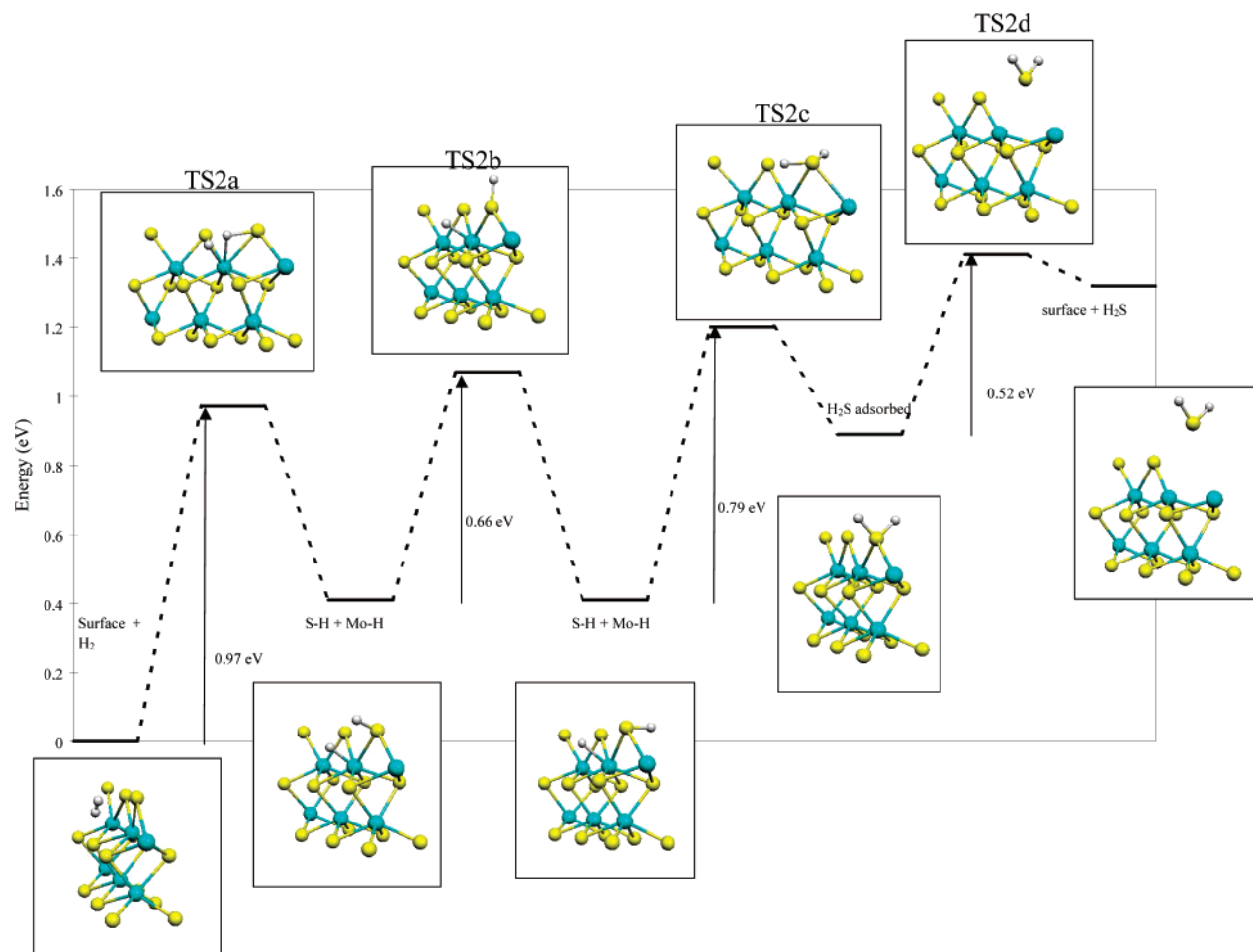


Figure 2. Energy diagram of the departure of the first sulfur atom from the metallic edge ($\Delta E = 1.4$ eV). The geometries of the various transition states and intermediates are also represented.

on the vacancy. The small difference (0.07 eV) between these kinetic and thermodynamic values of the final step of the H₂S desorption shows that the adsorption of the hydrogen sulfide on this CUS is only weakly activated. The presence of H₂S in the gas phase will, therefore, have a strong inhibiting effect on the vacancy formation on the metallic edge. Furthermore, this adsorption will be irreversible, because the dissociation of the H₂S on the surface is exothermic and weakly activated ($E_{\text{act}} = 0.31$ eV).

III.2. Departure of a Second H₂S Molecule from the Metallic Edge. Once this defective surface is created, it is possible to remove a second sulfur atom in order to increase the size of the vacancy, which will permit the adsorption of large molecules. Indeed, this new vacancy would allow the adsorption through the benzene ring of molecules such as dibenzothiophene.^{25,43} In contrast with the adsorption on the stable edge (Section III.1), the reaction is initiated with the H₂ physisorption onto the vacancy, which is a slightly exothermic step (0.1 eV). In this geometry, the H–H bond is slightly activated. Indeed, the H–H distance is increased (0.85 Å) by comparison with the distance in the gas phase (0.77 Å). The activation energy for this elementary step is very low (0.1 eV); it does not lead to any bond creation or deletion. In contrast to the H₂ molecule behavior on the stable surface, two dissociation mechanisms are equally possible on the vacancy. The first one leads to the formation of one Mo–H and one S–H ($E_a = 0.55$ eV, TS3a), while the second one leads to the formation of two Mo–H species ($E_a = 0.60$ eV, TS3a', not reported here). Both geometries will evolve rapidly to give the most stable geometry,

consisting of one S–H group and one hydride in a bridging position between the two molybdenum atoms of the vacancy, as shown in Figure 3. The activation energy for the hydrogen migration on the surface from the Mo–H position to the bridging position is ~ 0.05 eV. This step, corresponding to the hydrogen migration on the surface, has been omitted for clarity of the figure. The formation of the H₂S group is then achieved by migration of the bridging hydride toward the SH group. The activation energy of this step is large ($E_a = 1.80$ eV, TS3b), and its transition state is located on the last part of the reaction path, in agreement with the Hammond principle. The S–H distances in this TS3b are 1.37 and 1.36 Å, as in the H₂S molecule, whereas the Mo–S ones are 2.67 and 2.72 Å. The S–H bond is already formed in the TS, and the end of the reaction path is only a rotation of the H₂S molecule to increase the Mo–S bond strength (Mo–S = 2.45 and 2.51 Å). The final step corresponding to the departure of the H₂S molecule is less activated ($E_a = 1.05$ eV). This activation energy is very close to the energy variation for the H₂S molecule departure ($\Delta E = 0.95$ eV), and so it can be considered that the reverse reaction is almost not activated. The rate-determining step of the second S atom departure is, thus, the formation of the H₂S molecule. Considering only the activation energies, the formation of a double vacancy from the single one is very unlikely because the dissociative adsorption of the H₂S molecule on this single vacancy ($E_{\text{act}} = 0.09$ eV) would be faster than the removal of a second sulfur atom from the surface.

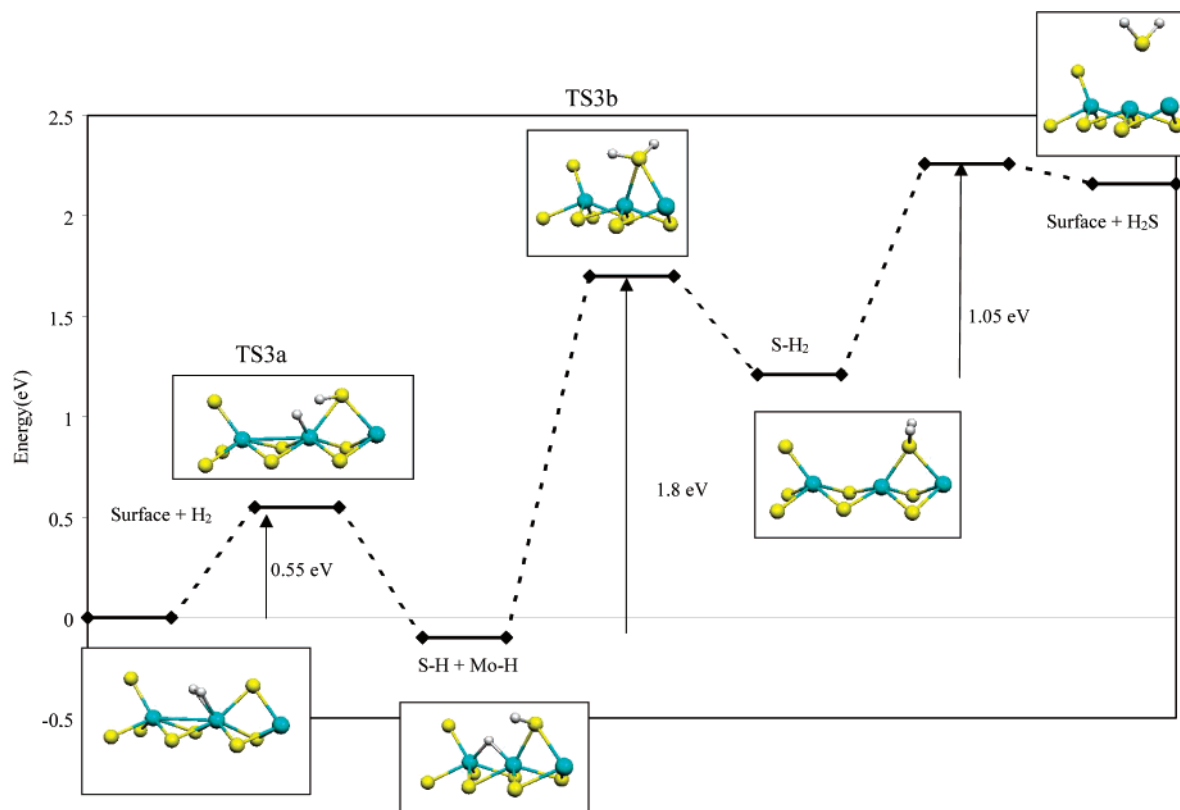


Figure 3. Energy diagram of the second S departure from the metallic edge ($\Delta E = 2.16$ eV).

IV. Vacancy Formation on the Sulfur Edge

In previous studies,^{3,4} we have shown that the coordination of the Mo atoms in the catalyst working conditions is four. However, the formation of a vacancy is also possible on the sulfur edge. Different mechanisms are possible that will be considered successively.

IV.1. Departure of the First H₂S Molecule from the Sulfur Edge. We first investigated the most straightforward mechanism, which consists of the departure of one H₂S molecule from the sulfur edge following the dissociative adsorption of a hydrogen molecule. The successive steps of this endothermic reaction ($\Delta E = 1.89$ eV), which have been considered here, are presented in Figure 4. Because of the low coordination number of the molybdenum atoms (4 on the sulfur edge), the reaction is first initiated with the H₂ physisorption onto the Mo atoms. This step is weakly activated ($E_{\text{act}} = 0.09$ eV, TS4a) and almost athermic ($\Delta E = 0.03$ eV). This physisorption induces an activation of the H₂ molecule shown by the increase in the H–H distance ($d_{\text{H-H}} = 0.80$ Å, $d_{\text{Mo-H}} = 2.00$ Å). The hydrogen molecule may then be easily dissociated ($E_a = 0.60$ eV) through the TS4b into a stable intermediate with one S–H and one Mo–H group. The hydrogen dissociative adsorption on the sulfur edge is exothermic ($\Delta E = -0.21$ eV), although the large entropy decrease makes the dissociated state an unstable one.³

The formation of the adsorbed H₂S then requires an inversion of the SH group, followed by a diffusion of the hydrogen atom on the surface. The first process is fast; the activation energy to reach TS4c is $E_a = 0.62$ eV, whereas the activation energy of the migration is $E_a = 1.69$ eV (TS4d). This first endothermic step ($\Delta E = 1.22$ eV) appears to be the rate-determining one for the vacancy formation on the sulfur edge. During this step, two Mo–H bonds are broken, while one S–H bond is created. The desorption of the H₂S molecule from this surface is

endothermic. Similarly to the adsorption of the H₂S molecule on the vacancy of the metallic edge, the adsorption of an H₂S molecule is almost not activated, and the dissociation of the molecule to form one Mo–H and one S–H is exothermic and weakly activated ($E_a = 0.47$ eV).

H₂S desorption of the molecule from this surface is slower than on the metallic edge and also more unlikely from the thermodynamic point of view. The Mo–S bonds are stronger than on the metallic edge, which is in agreement with the bond order conservation principle, because the coordination of the molybdenum atom on the sulfur edge is lower than on the metallic edge, as shown on Figure 1b.

IV.2. Vacancy Formation without H₂S Departure. On the sulfur edges, CUS can also be formed by an isomerization of the surface without departure of any H₂S molecule, as shown in Figure 5. Indeed, on the sulfur edge, the isomerized surface is only slightly less stable (1.21 eV) than the most stable one. The energetic cost of the vacancy formation is reduced from 1.89 eV in the previous mechanism to 1.21 eV. However, the activation energy is greater than for the previous reaction path ($E_a = 1.96$ eV). This simple mechanism, which should have led to the creation of an S–S bond on the edge, as shown in Figure 5, can be ruled out.

However, taking into account the participation of an H₂ molecule during the migration of the S atom, it should be possible to decrease the activation energy of the vacancy formation. Indeed, the formation of a S–H bond should decrease the strength of the Mo–S one. The reaction energy diagram of this mechanism is shown in Figure 6. It first requires H₂ physisorption, as in the mechanism presented in Figure 4. Then the dissociation leading to the formation of one S–H and one Mo–H group is slightly activated (TS6b, $E_{\text{act}} = 0.42$ eV). A migration of the hydride species, which should proceed in at

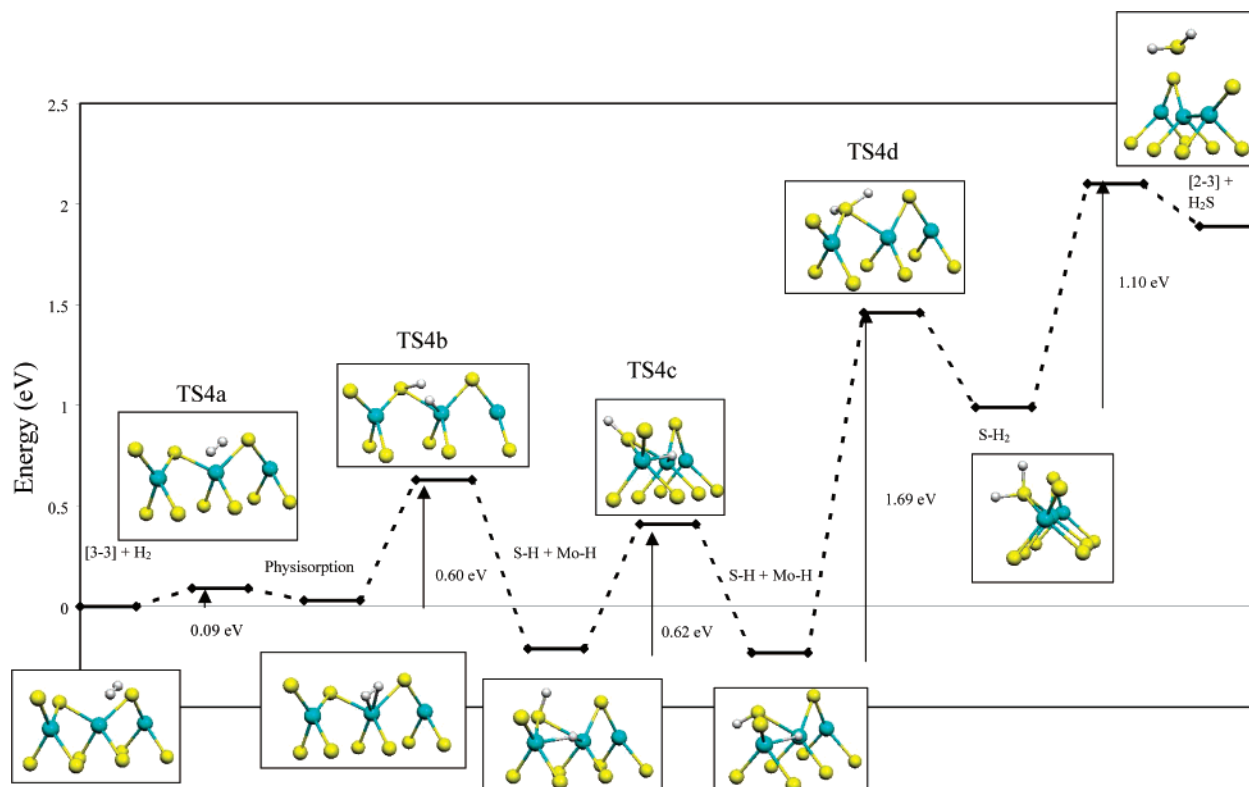


Figure 4. Energy diagram of the vacancy formation on the sulfur edge ($\Delta E = 1.89$ eV).

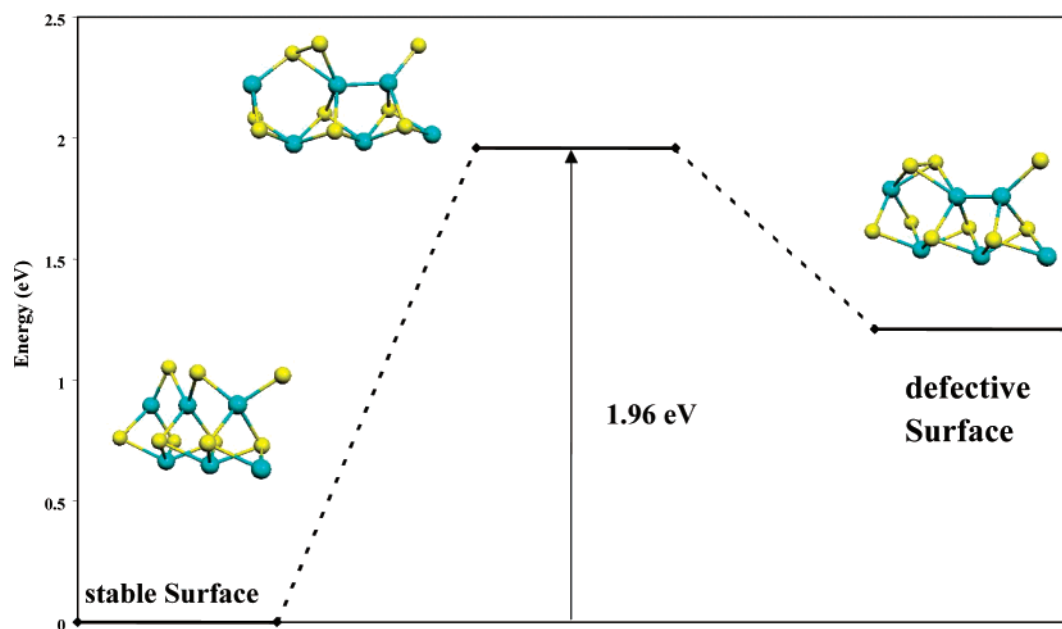


Figure 5. Energy diagram of the vacancy formation without hydrogen molecule ($\Delta E = 1.21$ eV).

least into two steps, is also required through two different transition states (TS6c and TS6d), the activation energies of which are 0.79 and 0.26 eV, respectively. These two steps, which correspond, respectively, to the sulfur inversion and the hydride migration can be inverted. The activation energy of the final step, that is, the S-H group migration, is 1.25 eV. This value is smaller than the one obtained for the direct sulfur migration (1.96 eV). The vacancy formation remains more difficult on the sulfur edge than on the metallic one, but the difference in activation energy is strongly reduced with the participation of hydrogen atoms.

Furthermore, the presence of hydrogen also reduces the energy loss during the vacancy formation from 1.21 to 0.75

eV. Indeed, the isomerization of the surface leads to the formation of one S-S bond, and the adsorption of the H₂ molecule on this S-S bond is exothermic.² The least unstable vacancy is, thus, located on the edge containing the most unsaturated molybdenum atoms.

IV.3. H₂S Departure from the Isomerized Surface. To carry out a complete comparison with the sulfur exchange experiments,^{27-31,42} we also investigated the H₂S departure from this isomerized surface (last step of the Figure 6). The mechanism can be decomposed into the following steps shown in Figure 7: (i) inversion of one of the S atoms to place one H atom above the sulfur atom, (ii) hopping of the hydrogen atom to form the adsorbed H₂S group, and (iii) departure of the H₂S

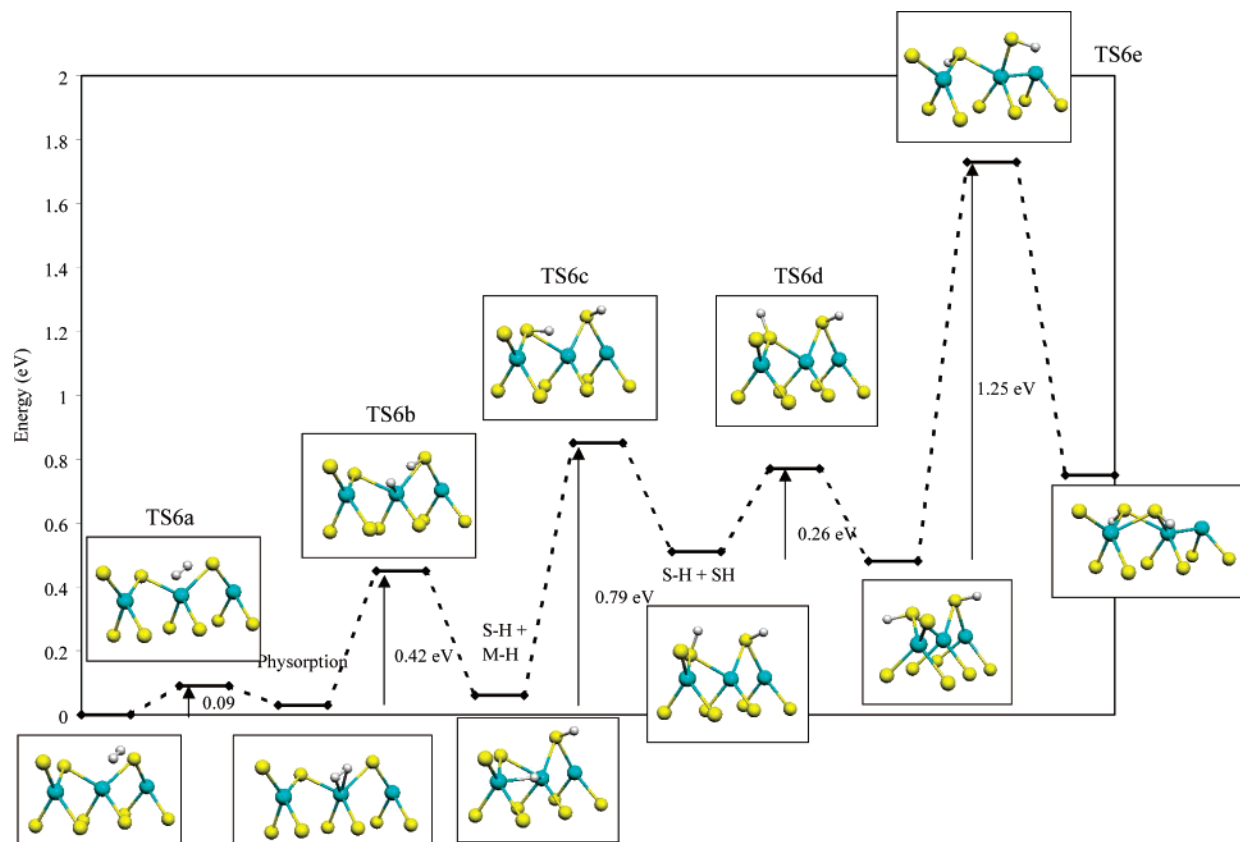


Figure 6. Energy diagram of the vacancy formation on the sulfur edge with the participation of one H_2 molecule ($\Delta E = 0.75$ eV).

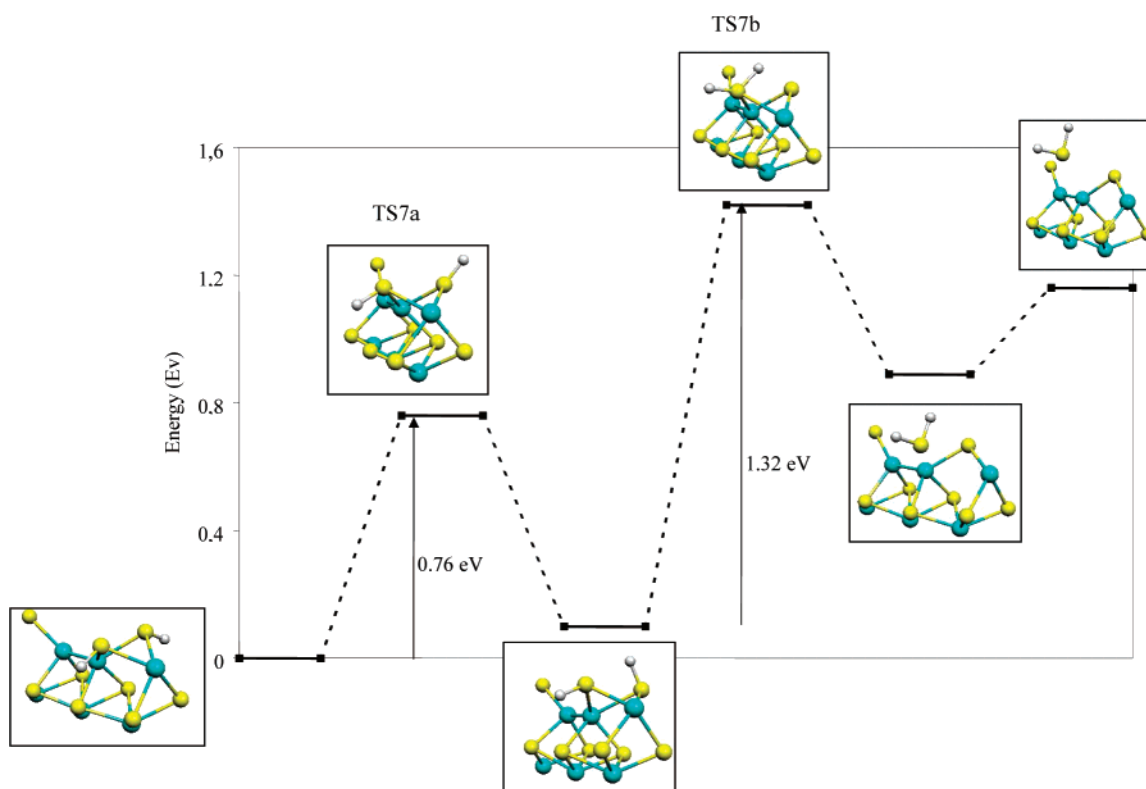


Figure 7. Energy diagram of H_2S departure from the defective surface of the sulfur edge ($\Delta E = 1.14$ eV).

molecule. This process is endothermic with two transition states (TS7a and TS7b), the activation energies of which are 0.76 and 1.32 eV, respectively. The departure of the H_2S molecule from the surface is a nonactivated process. Following this reaction path, the highest activation energy is the creation of the H_2S

group on the surface, as previously observed for the formation of a double vacancy on the metallic edge. Starting from the most stable surface (Figure 1b), the cost of the S atom's departure from the S edge remains high (1.89 eV, see Section IV.1), but it is possible to decompose this departure into steps

for which the highest activation energy is ~ 1.3 eV. The departure seems possible, but considering the large energy cost, the number of vacancies will remain very small.

V. Discussion

Theoretical calculations suggest that, from the thermodynamic point of view, the vacancy creation is an unfavorable process on the edges of the MoS₂ particles. But experimental results clearly demonstrated that there are labile S atoms on the edges of the MoS₂ active phase. The present kinetic modeling of H₂S removal from the surface will allow us to understand this discrepancy. Indeed, this study shows that it is possible to extract one S atom per unit cell that contains three S atoms per metallic edge of the MoS₂ nanocrystallites. The activation energy of the most difficult step (TS2a) is ~ 1 eV on the metallic edge. The extraction of a sulfur atom is, therefore, possible on the metallic edge. The kinetic of the exchange reaction should be first-order to the H₂ partial pressure, because the rate-determining step (RDS) is the dissociation of the H₂ molecule, leading to the formation of one Mo–H and one S–H group.

The departure of a second sulfur atom from the metallic edge is much more difficult from a thermodynamic point of view as well as from a kinetic point of view ($E_{\text{act}} = 1.8$ eV). The formation of this type of vacancy will also be greatly inhibited by the presence of H₂S in the gas phase. Indeed, the adsorption of this molecule on the vacancy is almost not activated. Its adsorption and its further dissociation should, therefore, be faster than the desorption of a second sulfur atom from the edge. This conclusion is in agreement with the experimental results that show that the number of exchanged sulfur atoms is very low unless a sulfur source is available in the gas phase. Indeed, the number of removed atoms under pure H₂ is very small, but the presence of S atoms in the gas phase (H₂S or thiol) allows the exchange of most of the atoms located on the edges through the dissociative adsorption of the molecule, thus limiting the vacancies to a small number. We can conclude that the departure of a sulfur atom is a dynamic equilibrium process that is strongly displaced toward the formation of the saturated surface. But this dynamic process allows the presence of a very small number of vacancies that are located on the edge of the nanoparticles. The mean lifetime of the vacancies should be small, because the H₂S adsorption is a nonactivated reaction. This may explain why, to the best of our knowledge, there is no direct physical experimental evidence of vacancies on the MoS₂ catalyst under *in situ* conditions.

The present calculations allow us to explain the measured activation energy deduced from the S-exchange experiments. Indeed, the H₂/D₂ exchange is possible on MoS₂ catalyst for temperatures higher than 150 °C.^{44–47} We can, therefore, consider that the equilibrium between H₂ molecules in the gas phase and the H atoms on the surface is achieved. The radioactive sulfur exchange reaction is carried out at high temperature (i.e., 350 °C), and so an equilibrium between the H₂ molecules and the adsorbed H₂S molecule on the surface will also be achieved. The activation energy deduced from the S exchange experiments²⁵ (0.4 eV) corresponds to that of the irreversible H₂S desorption step that we have computed to be 0.5 eV. An increase in the H₂ partial pressure will increase the concentration of the H atoms on the surface, leading to an increase in the rate of the H₂S departure, but it will not change the measured activation energy. The effect of the temperature is more difficult to predict. Indeed, the rate of the last step of the reaction will increase, but the concentration of H atoms on the surface will decrease, because the entropy of H₂ in the gas

phase will be greater. However, it could be assumed that the overall effect will be relatively small.

The direct departure of the sulfur atoms located on the sulfur edge is in principle possible, but the reaction path had to be modelled by two successive strongly endothermic and highly activated steps. Furthermore, the activation energy of the H₂S departure following the simplest mechanism is higher than 1 eV, a value that is not compatible with the aforementioned experimental results. Indeed, the mechanism involving the isomerization of the surface presents an activation energy for the H₂S departure smaller than the experimental one (0.25 versus 0.4 eV); however, the activation energy of the regeneration of the stable surface (exothermic step) is smaller than the formation of the adsorbed H₂S molecule, and so, the overall rate of S departure from the sulfur edge will be small.

Some other conclusions on the HDS catalytic mechanism can also be drawn from these calculations. There will be only a very low number of CUS at any time, and they will subsist on the edge of the catalyst for a very short time. Indeed, the H₂S adsorption on the vacancies is almost a nonactivated process, and there will be a competitive adsorption of the H₂S and organic molecule on the surface during the HDS reaction. This is in agreement with the strong inhibiting effect of the H₂S molecule previously reported.¹ Furthermore, the dissociation of the H₂S molecule is a weakly activated process, giving an irreversible adsorption that will inhibit the adsorption of other molecules. The adsorption of molecules such as DBT and DMBT through one of the aromatic rings will be difficult, because these particular adsorption modes require the departure of two neighboring sulfur atoms from one edge.^{25,43}

VI. Conclusion

From a thermodynamic point of view, the formation of vacancies on the edges of the MoS₂ nanocrystallites is an unfavorable process. However, it is possible to decompose this endothermic reaction into several elementary steps, the activation energies of which are below 1.5 eV. These relatively small values will allow the transient formation of vacancies at 623 K on the catalyst through a sulfur exchange with the S atoms of S-containing molecules in the gas phase. The direct departure of one sulfur atom from the sulfur edge is very unlikely ($E_{\text{act}} = 1.8$ eV). Creation of a coordinatively unsaturated site on this edge through an isomerization mechanism requires a lower activation energy, but the values remain high, whatever the mechanism considered ($E_a = 1.2$ or 2.0 eV with and without an adsorbed hydrogen atom).

On the metallic edge, the rate-determining step ($E_{\text{act}} = 1.0$ eV) for the vacancy formation is the dissociation of the hydrogen molecule into one Mo–H and one S–H group. Once an H₂S group is formed on the metallic edge through the diffusion of hydrogen atoms on the edge, the activation energy of its departure, giving rise to the formation of a vacancy, is only 0.5 eV. This last value is in nice agreement with the value deduced from the sulfur exchange experiments.

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