

Theoretical Study of the MoS₂ (100) Surface: A Chemical Potential Analysis of Sulfur and Hydrogen Coverage. 2. Effect of the Total Pressure on Surface Stability

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We investigate theoretically, by quantum DFT calculations, the adsorption of H₂ molecules on the [100] MoS₂ surfaces, considering various edge sulfur stoichiometries. Depending on the nature of the gas phase, the adsorption energies vary from strongly positive values to strongly negative ones. Using these energies, we have constructed a thermodynamic diagram, which gives the stoichiometry of the edges and the nature of the adsorbed hydrogen atoms as a function of the total pressure and of the $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ partial pressure ratio and determines the best conditions to examine the S–H groups using spectroscopic techniques.

I. Introduction

Alumina-supported MoS₂ nanocrystallites promoted or not by cobalt or nickel atoms are the active phases of the hydrodesulfurization (HDS) catalysts. The HDS operation is the most important process of the fuel treatment used to remove the sulfur atoms from the hydrocarbon molecules present in the petroleum fractions. The new specifications on automobile gas emission has increased the interest on the research for more active HDS catalysts. Indeed, it will soon be need to remove sulfur atoms from molecules which are very difficult to treat, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) and other substituted dibenzothiophene molecules.^{1,2} The determination of the HDS reaction mechanism and of the rate-limiting step will give hints to find more efficient catalytic systems. One important step in the elucidation of the mechanism is the determination of the chemical nature and of the stoichiometry of the catalyst surfaces under the industrial operation conditions. In a previous paper,³ we have shown that ab initio calculations are a very useful tool for this purpose. We demonstrated, in agreement with other authors,^{4,5} that the surface sulfur stoichiometry is strongly dependent on the H₂/H₂S gas ratio of the surrounding atmosphere and that the more stable surfaces of the active phase do not correspond to the stoichiometric one. Moreover, these surfaces do not present coordinative unsaturated molybdenum atoms (CUS), which are generally considered in the description of the mechanism.^{2,6} Whatever the mechanism proposed, the presence of adsorbed hydrogen molecules that may create S–H and Mo–H groups is required. Despite numerous experimental studies,^{7–11} direct evidence of the existence of hydrogen on the catalyst has never been clearly established. However, the existence of S–H groups has already been suggested¹¹ on bulk MoS₂ by an inelastic neutron

spectroscopy (INS) through the observation of the Mo–S–H deformation mode, but no information was deduced on the precise location of the hydrogen atom, i.e., on the basal or the edge planes of the MoS₂ crystallites. As the HDS reaction is achieved within H₂ molecules acting on the feed in the gas/liquid phase, it is also important to determine the influence of the hydrogen partial pressure (P_{H_2}) on the sulfur surface coverage and to study the hydrogen dissociation on these MoS₂ surfaces. After a brief presentation of the method used previously for the determination of the stable MoS₂ surfaces,³ we discuss the dissociative adsorption of H₂ on these surfaces. Attention has been addressed to defectives surface in order to determine whether they can be stabilized by an increase of the H₂ pressure. In a second part, we construct a diagram that gives the nature of the “thermodynamically stable hydrogenated surface” as a function of the total gas-phase pressure for various partial pressure ratios ($P_{\text{H}_2}/P_{\text{H}_2\text{S}}$). Using this diagram, we will be able to predict the chemical conditions needed to create thermodynamically stable S–H and Mo–H groups on the surface.

II. Calculation Methods

The ab initio calculations were performed with the Vienna Ab initio Simulation Program (VASP).¹² It is based on Mermin's finite-temperature local density functional theory.¹³ The calculations are performed in a plane wave basis set and the electron–ion interactions are described using optimized ultra soft pseudopotentials.¹⁴ The resolution of the Kohn–Sham equations is performed using an efficient matrix digitalization 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

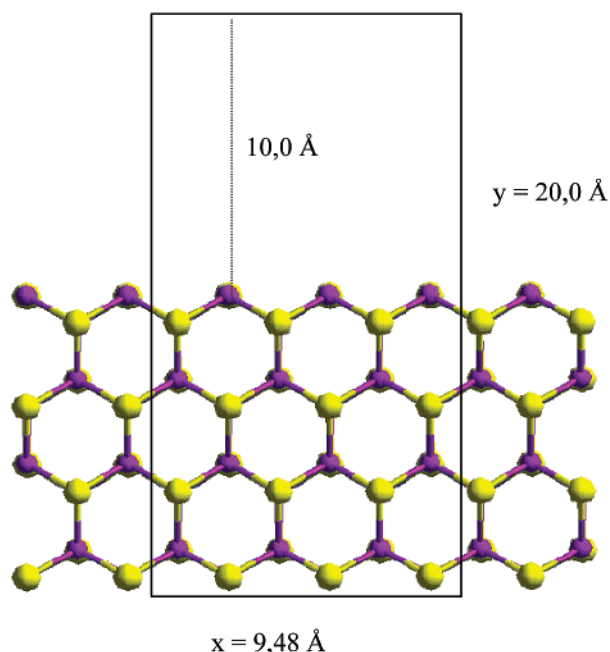


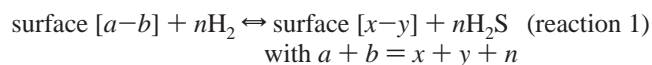
Figure 1. Unit cell used during the calculation ($x = 948$ pm, $y = 200$ pm, $z = 122.9$ pm), yellow circles: sulfur atoms; purple circles: molybdenum atoms. The structure is periodic along the x and z directions.

atomic positions is performed via a conjugate gradient minimization of the total energy using the Hellmann–Feynman forces on the atoms. Reference 12 gives a more detailed description of the technique.

All over this work, we used a large super cell ($9.48 \times 20 \times 12.294$ Å³) containing three elementary MoS₂ asymmetric unit in the x direction, four in the y direction, and two layers along z axis (Figure 1). Previous studies^{15,16} showed that this model was suitable to predict the electronic and structural properties of the MoS₂ perfect surface. The two upper rows were allowed to relax while the two lower 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–Paxton¹⁷ smearing with $\sigma = 0.1$ eV, and the exchange–correlation functional developed by Ceperley and Alder and parametrized by Perdew and Zunger.¹⁸ Generalized gradient corrections are introduced as proposed by Perdew et al.¹⁹

III. Surface Stability Without Hydrogen

The perfect [100] MoS₂ surface exhibits two types of edge, one exposing unsaturated molybdenum atoms ($10\bar{1}0$ edge), the other one exhibiting sulfur saturated Mo atoms ($\bar{1}010$ edge); we name them hereafter molybdenum edge and sulfur edge, respectively. They will be referred according to the number of sulfur atoms present on each edge. For example, the perfect [100] surface will be noted [6–0] as there are six sulfur atoms on the sulfur edge and no sulfur atom on the molybdenum one. In industrial working conditions, involving the presence of H₂ and H₂S in the gas/liquid phase, a variation of the sulfur coverage should occur according to reaction 1.



The calculated electronic³ energy of each surface shows that the most stable surface according to reaction 1 is the [6–3]

surface with six adsorbed sulfur atoms on the sulfur edge and three on the metallic one. However, the relative surface stability is affected by the composition of the gaseous mixture, which can be taken into account by calculating the affinity of the reaction 2 ($A = -\Delta rG$)



The method is described in ref 3, and the key points of the calculation are reported here. The [6–3] surface is used as reference in this calculation and ΔrG is deduced as follows:

$$\Delta rG = \mu(\text{surface}[x-y]) - \mu(\text{surface}[6-3]) + n(\mu(\text{H}_2\text{S}) - \mu(\text{H}_2))$$

(n may be negative to represent sulfur atoms deposition on the surface).

Assuming that the difference between the chemical potential of solid phases can be approximated by the difference in their electronic energy, we can compute

$$\Delta rG = \Delta E^\circ + n\Delta\mu$$

$$\Delta\mu = \mu(\text{H}_2\text{S}) - \mu(\text{H}_2) = \Delta\mu^\circ(T) + RT \ln \frac{P(\text{H}_2\text{S})}{P(\text{H}_2)}$$

with

$$\Delta\mu^\circ(T) = \Delta E_{\text{el}} + \Delta ZPE + \Delta H_{\text{vib}} + \Delta H_{\text{rot}} + \Delta H_{\text{tr}} - T(\Delta S_{\text{vib}} + \Delta S_{\text{tr}} + \Delta S_{\text{rot}})$$

The enthalpic and entropic parts of the previous expression are computed using statistical thermodynamic and standard partition function expression.

In all the thermodynamic calculations, the temperature is fixed at 623 K, which is the usual temperature in the catalytic reactor during the hydrodesulfurization reaction. However, we showed that this parameter does not change the conclusion although the limits of the various stability regions are slightly changed. Within the H₂/H₂S ratio compatible with the MoS₂ stability, only three kinds of surfaces are stable (see Figures 2, 4, and 5 in ref 3). The [6–6] surface is stable for $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ partial pressure ratio greater than 10000, while the [3–3] is stable for $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ smaller than 0.05. For the intermediate values ($10000 > P_{\text{H}_2\text{S}}/P_{\text{H}_2} > 0.05$), the most stable surface is the [6–3] one. Although the formal oxidation number of the atoms located on the edge of the solid is difficult to estimate, the transformation of the [6–3] surface into the [3–3] one may be considered as a global reduction of the sulfur edge, and more probably of the molybdenum atoms of this edge even if a small variation of the formal oxidation number of the sulfur atoms cannot be excluded. Indeed during the previous reaction, three H₂ molecules are transformed into three H₂S ones. Six H atoms are then oxidized. As the formal oxidation number of the sulfur atoms is only slightly changed during the reaction, the slab needs to be reduced to balance the oxidation of the H atoms. Similarly, one can see the formation of the [6–6] surface starting from the [6–3] one as the oxidation of the molybdenum edge.

The second important conclusion of the aforementioned study is that the stable surfaces are regular and do not present any unsaturated sites allowing the adsorption of large molecules. As these results do not consider the presence of hydrogen on the surface, the computation of H₂ adsorption and/or dissociation

TABLE 1: Adsorption Energy (eV), on the Metallic Edge, of the First H₂ Molecule for the Most Stable Geometry of Each Dissociation Reaction: A Positive Value Corresponds to an Exothermic Adsorption

edge	surface	S-H/S-H	S-H/Mo-H	Mo-H/Mo-H	Mo-SH ₂
Mo edge	[X-6]	+0.27	-0.03	-0.28	-0.68
	[X-3]	-0.37	-0.27	not stable	-0.89
	[X-2]	-0.59	+0.10	+0.06	-1.21

energies on both edges of the [100] surface for various sulfur stoichiometries is needed to investigate the influence of hydrogen on the aforementioned equilibrium.

IV. H₂ Addition on the Surfaces

Hydrogen atoms may be present as hydride (Mo-H) or proton (S-H) groups or even as nondissociated hydrogen molecules. This last possibility may be considered as a strong physisorption. Taking into account the lack of experimental evidences, various configurations of dissociative and nondissociative adsorption of a dihydrogen molecule have therefore been considered. For example, for the addition of the first hydrogen molecule on the surface, a systematic calculation of all the possible configurations have been performed i.e., two S-H groups, two Mo-H groups, one S-H, and one Mo-H group, and even Mo-SH₂ group. This later should likely correspond to the final adsorption geometry of one H₂S molecule. All the adsorption energies given in this part include the ZPE correction which is relatively small (i.e., smaller than 0.05 eV) as the energy variation due to the X-H stretching mode balances the ZPE of the gaseous H₂ molecule.

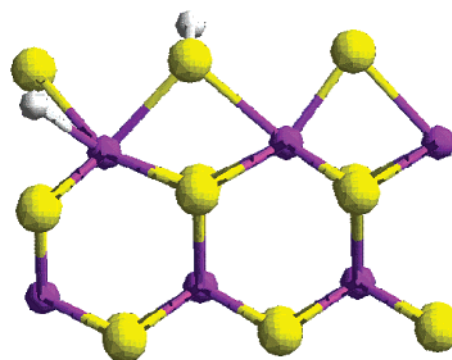
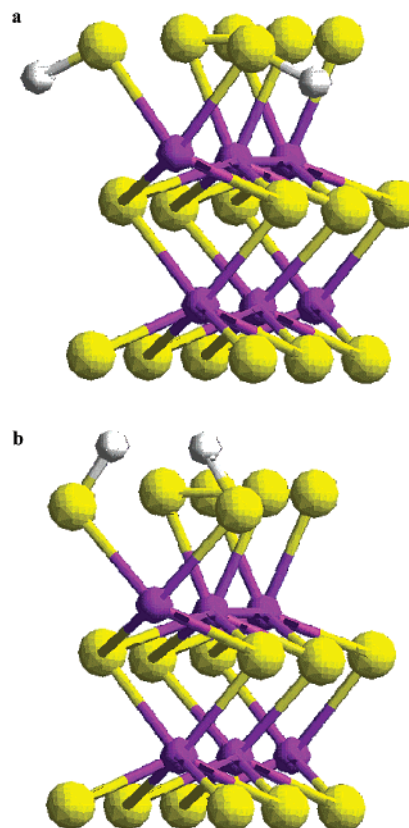
The interactions between one edge and the gas phase molecule above the second edge are small, we therefore can consider that the adsorptions on the two edges of the system are independent. This allows a significant reduction of the number of configurations to be computed. Furthermore only configurations corresponding to an even number of hydrogen atoms on each edge have been considered, as they do not require spin-polarized calculations.

The calculated surfaces will be noted [X-y] or [y-X] to indicate that the treated edge carries y sulfur atoms, while the second one is undefined.

IV.1. Adsorption on the Molybdenum Edge. We first studied the adsorption of H₂ on the stable surfaces, i.e., the [X-6] and [X-3] surfaces. The adsorption energies corresponding to the most stable geometry for each adsorption configuration i.e., two S-H, two Mo-H, one S-H, and one Mo-H, or even Mo-SH₂, are reported in Table 1. Second, the adsorption on the [X-2] surface has also been considered in order to investigate the effect of a large H₂ partial pressure on the stability of this defective surface.

IV.1.1. Adsorption on the [X-3] Surface. The H₂ addition on the [X-3] surface has been previously described in detail in ref 3. We will only summarize here the main results. Whatever the dissociative adsorption mode of one H₂ molecule per unit cell (i.e., one H₂ for three Mo atoms) the reaction is endothermic as shown in Table 1. Among all the tested geometries, the most stable one is achieved through the formation of one bridging Mo-H-Mo group and one S-H group. Figure 2 shows the geometry of this latter adsorption configuration. Further additions have also been considered but these additions are always endothermic.

IV.1.2. Adsorption on [X-6] Surface. The addition on the [X-6] surface is also considered in this work in order to have a complete picture of the H₂ adsorption on the surfaces even if

**Figure 2.** Most stable H₂ adsorption geometry on the [X-3] edge ($E_a = -0.27$ eV).**Figure 3.** Addition on the [X-6] edge: (a) most stable geometry ($E_a = 0.27$ eV), (b) after rotation of the two S-H bonds ($E_a = -0.02$ eV).

this surface, only stable for very high PH₂S/PH₂ partial pressure ratios, should not be present in catalytic reaction conditions. On this surface, S-S disulfur bonds are present, on which H₂ may dissociatively adsorb giving two S-H groups.²⁰

Addition of the First H₂ Molecule. Opposite to the results concerning the [X-3] surface, the addition of the first H₂ molecule on the surface leading to the formation of 2 S-H groups is exothermic. The [X-6] surface may be considered as an oxidized one, so it not surprising that the reduction by H₂ restoring the original oxidation states (formally S -II and Mo +IV) is an exothermic reaction. Among more than 10 checked adsorption configurations, the addition of H₂ inducing the breaking of the S-S bond present on this edge is the most stable one ($E_a = 0.27$ eV, Figure 3a). It results in two S-H groups, interacting with the edges of the neighboring slabs through weak hydrogen bonds. To estimate this interaction energy, one H atom

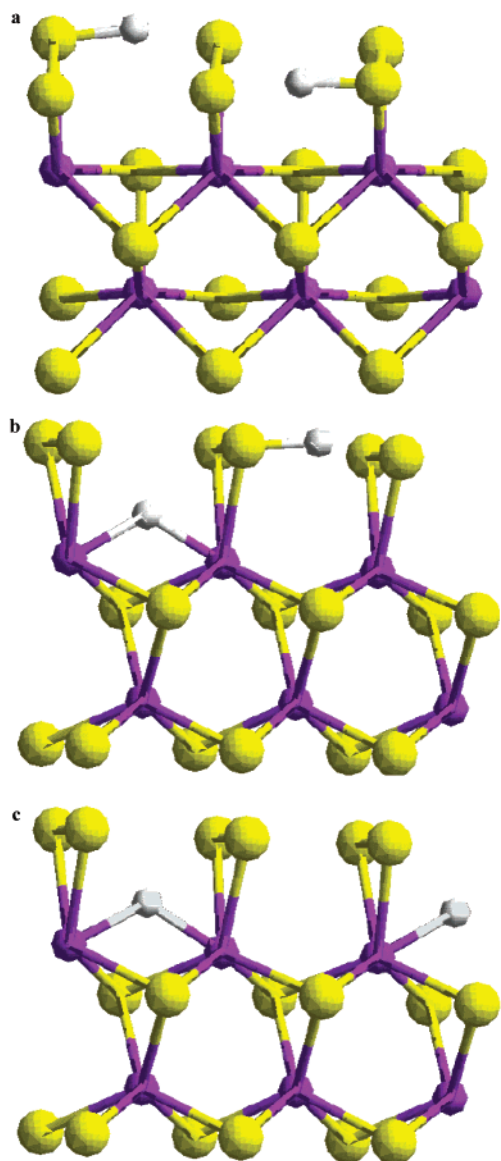


Figure 4. Addition on the [X-6] surface without S-S bond breaking: (a) formation of two S-H ($E_a = -0.30$ eV), (b) formation of S-H and Mo-H ($E_a = -0.03$ eV), (c) formation of two Mo-H ($E_a = -0.28$ eV).

has been rotated by 180° around the Mo-S bond. This displacement induces a decrease of the adsorption energy by 0.07 eV, a value that is in the range of hydrogen bond energy. If the second hydrogen atom is similarly rotated (Figure 3b), the adsorption energy is lowered by 0.22 eV. The energetic cost of the second displacement is more important than the first one, as some steric repulsion between the protons exist within the final geometry. The resulting geometry corresponds to an athermic adsorption ($E_a = -0.02$ eV).

All the other adsorption geometries that have been computed retain the S-S bond and correspond to less stable configurations. The adsorption energy is -0.03 eV for the formation of one S-H and one Mo-H group (Figure 4b), -0.28 eV for the formation of two bridging Mo-H groups (Figure 4c), and -0.30 eV for the formation of two S-H (Figure 4a).

Addition of a Second Molecule on the Most Stable Mono-hydrogenated Surface. As the first addition on this surface is exothermic, further additions of H_2 have been tested. The addition of a second H_2 molecule in a geometry similar to the

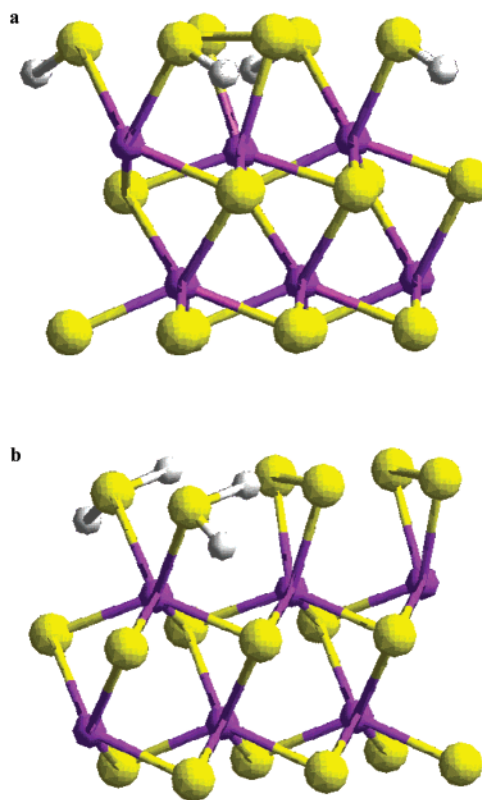


Figure 5. Addition of two H_2 molecules on the [X-6] surface. (a) Breaking of two S-S bonds ($E_{a1} = 0.27$ eV and $E_{a2} = -0.02$ eV). (b) Most stable geometry ($E_{a1} = 0.27$ eV and $E_{a2} = 0.24$ eV).

most stable one is possible ($E_{a2} = -0.02$), (Figure 5a) but this geometry is does not correspond to the most stable configuration, indeed the formation of two H_2S groups adsorbed on the surface as shown in Figure 5b is exothermic ($E_{a2} = 0.24$ eV).

This last geometry is interesting, as it should correspond to the elementary step of the sulfur adsorption-desorption mechanism. We did not check the effect of the addition of a third molecule on the surface, but it should be endothermic or athermic and lead to geometries similar to the previous ones. Furthermore the conditions for which such highly hydrogenated surface would be stable are difficult to obtain experimentally, as they will involve simultaneously a large H_2 partial pressure and a very large P_{H_2S}/P_{H_2} partial pressure ratio.

IV.1.3. Adsorption on the [X-2] Surface. To check the influence of the H_2 partial pressure on the vacancy formation, we studied the adsorption of H_2 on the [X-2] defective surface. Indeed, a large H_2 adsorption energy on this surface may balance the energetic cost of the sulfur removing and stabilize the vacancy. Several geometries of adsorption have been checked but they all lead to almost a same small adsorption energies of about 0.1 eV. The most stable geometry, which is represented in Figure 6a, corresponds to the formation of one bridging hydride and one S-H group ($E_a = 0.10$ eV). Another adsorption configuration with a small, but positive, adsorption energy is also observed and corresponds to a nondissociative adsorption ($E_a = 0.07$ eV) (Figure 6b). However, this mode induces a large destabilization of the H_2 molecule as the H-H distance is increased to 1.0 \AA . So, this geometry is likely a starting point of the H_2 dissociation on the surface. The last exothermic adsorption geometry that we found corresponds to the formation of two Mo-H groups ($E_a = 0.07$ eV), one of them being in a bridging position as shown in Figure 6c.

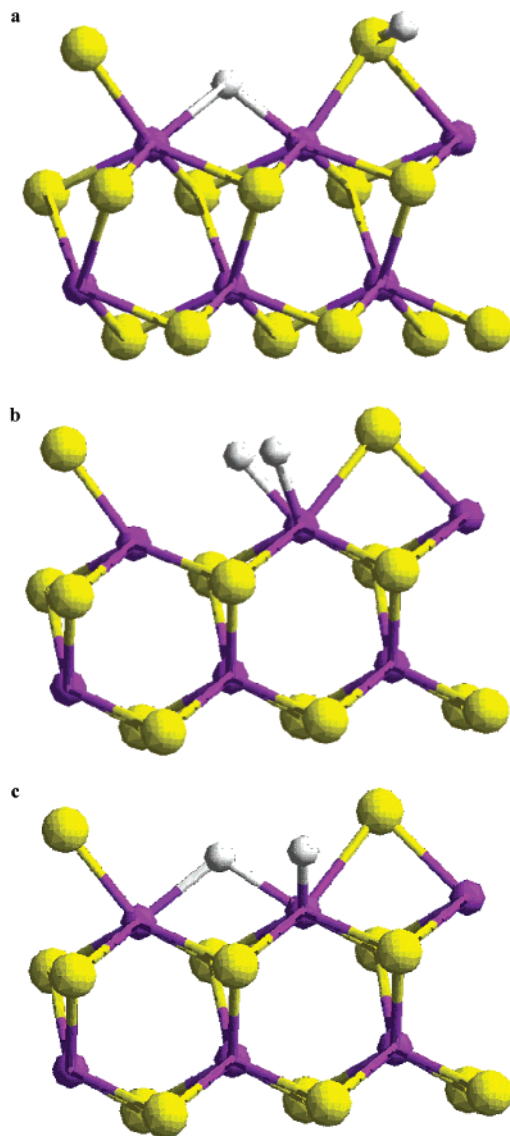
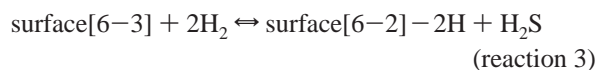


Figure 6. Most stable adsorption geometries on the [X-2] surface. (a) Formation of one S-H and one Mo-H ($E_a = 0.10$ eV). (b) Nondissociative adsorption ($E_a = 0.07$ eV). (c) Formation of two Mo-H ($E_a = 0.10$ eV).

Whatever the geometry considered, the adsorption energy of the H₂ molecule on the [6-2] surface is small and the reaction 3 remains highly endothermic ($\Delta_r E = 1.13$ eV).



The creation of a stable vacancy on the metallic edge of the [X-3] surface is only possible under a very high H₂ partial pressure. Under catalytic conditions, the [X-3] surface remains the only stable open surface on the metallic edge of the [100] surface.

IV.2. Adsorption on the Sulfur Edge. The [100] surface of the MoS₂ nanocrystallites exhibits also sulfur edges on which the H₂ molecules may adsorb. Under the HDS conditions, only the [6-X] and the [3-X] surfaces are stable. As for the metallic edge, adsorption on the defective [2-X] surfaces has also been considered in order to determine whether an unstable defective surface may become stable under large H₂ partial pressure. The study of the two last surfaces was discussed in a previous paper,³

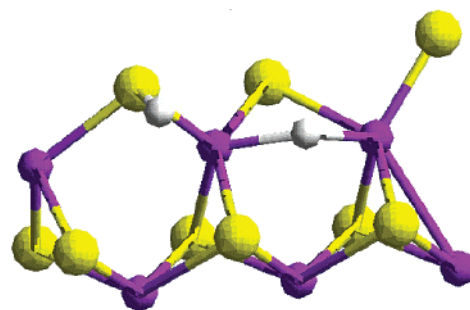


Figure 7. Addition on the [3-X] surface: most stable geometry for the first adsorption ($E_a = -0.01$ eV).

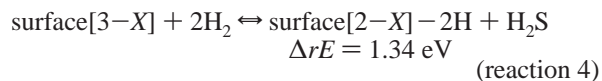
TABLE 2: Adsorption Energy (eV), on the Sulfur Edge, of the First H₂ Molecule for the Most Stable Geometry of Each Dissociation Reaction: A Positive Value Corresponds to an Exothermic Adsorption

	edge	surface	S-H/S-H	S-H/Mo-H	Mo-H/Mo-H	Mo-SH ₂
sulfur		[6-X]	+1.38	-0.32	-0.46	-0.10
	edge	[3-X]	-0.43	-0.01	-0.53	-1.21
		[2-X]	-1.22	+0.01	+0.62	-1.23

and only the main results are summarized here. Table 2 gives the adsorption energy of the most stable geometry of each adsorption configuration on the sulfur edge with the same convention as in Table 1.

IV.2.1. Adsorption on the [3-X] Surface. The H₂ adsorption energies on the [3-X] surface are reported in Table 2. Whatever the dissociative adsorption considered, i.e., formation S-H or/and Mo-H groups, the reaction is athermic or endothermic. The less unfavorable mode ($E_a = -0.01$ eV) relates to the formation of one S-H and one Mo-H group. The latter is located in a bridging position between two Mo atoms as shown in Figure 7. Because the Mo coordination number remains lower than 6, the addition of a second H₂ molecule has been checked. This second addition is also slightly endothermic, as well as is the third one.

IV.2.2. Adsorption on the [2-X] Surface. The addition on the [2-X] surface has been computed in order to check if an important hydrogen partial pressure can stabilize this defective surface, as it has been done for the [X-2] surface. The energies of the various modes of adsorption are reported in Table 2, which shows that the most stable configuration corresponds to the formation of two bridging Mo-H groups. The adsorption reaction is exothermic ($E_a = 0.62$ eV) but cannot stabilize the defective surface. Indeed, the overall reaction 4 corresponding to the vacancy creation and simultaneous H₂ addition remains endothermic. Considering furthermore the large entropy decrease due to the H₂ adsorption, the surface [2-X]-2H will be unstable from the thermodynamic point of view.



IV.2.3. Adsorption on the [6-X] Surface. The [6-X] surface is an oxidized one if we consider that the -II sulfur atoms are only bonded to two molybdenum atoms instead of three in the solid. A reduction of the surface should thus be possible and an exothermic adsorption can be expected.

Addition of the First H₂ Molecule. The adsorption energy of one H₂ molecule creating two S-H groups is exothermic ($E_a = 1.38$ eV). This adsorption energy is achieved for various adsorption geometries, which are represented in Figure 8a,b. The figures also show that the two protons are in interaction

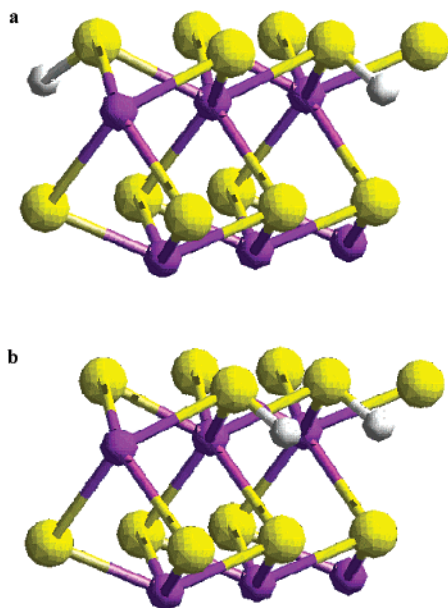


Figure 8. Most stable adsorption geometries on the [6-*X*] surface: (a) and (b) $E_a = 1.38$ eV.

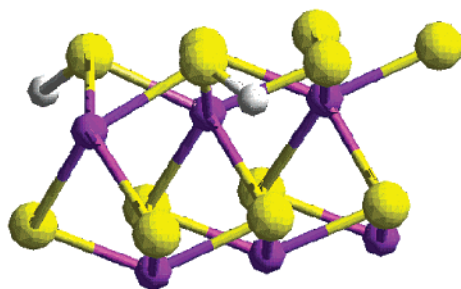


Figure 9. Adsorption on face to face sulfur atoms ($E_a = 0.78$ eV).

with the neighboring slab by hydrogen bonding. The adsorption energy is reduced to 0.99 eV when the hydrogen bonds are removed by a rotation around the Mo-S bond. The adsorption on “face-to-face” S atoms (i.e., with the same *x* coordinate and so bound to the same Mo atoms) induces a decrease (0.6 eV) of the adsorption energy ($E_a = 0.78$ eV) (Figure 9). This shows that the electrons added to the surface by the reaction with hydrogen atoms are not delocalized on the surface but that they are only shared with the sulfur atom that carries the proton and its two neighboring Mo atoms.

The adsorption energies of the other adsorption configuration are less stable. For example, the formation of two Mo-H groups is unlikely, as the adsorption energy is $E_a = -0.46$ eV (Figure 10a). The heterolytic dissociation (one Mo-H and one S-H) on this surface is improbable with a strong endothermic reaction energy ($E_a = -0.32$ eV) (Figure 10b).

Further Addition on the Most Stable Nonhydrogenated Surface. Further addition on the most stable monohydrogenated surface is also exothermic ($E_a = 0.43$ eV) (Figure 11a). Due to the size of the cell, two hydrogen atoms have to be added on “face-to-face” sulfur as shown in Figure 11a. This type of geometry is unfavorable and reduces the adsorption energy by around 0.6 eV (cf. previous paragraph). We can estimate the adsorption energy of the second molecule in a larger cell (that will avoid this “face-to-face” interaction) to 1.0 eV ($0.43 + 0.6$ eV). The addition of a third H_2 molecule creating a fully hydrogenated surface is endothermic ($E_a = -0.41$ eV) (Figure 11b).

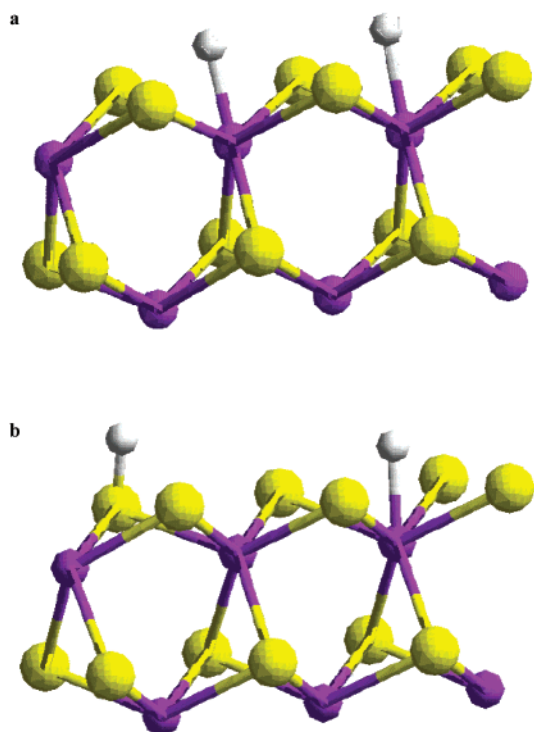


Figure 10. Other less stable adsorption modes: (a) formation of two Mo-H groups ($E_a = -0.46$ eV) and (b) formation of one S-H and one Mo-H group ($E_a = -0.32$ eV).

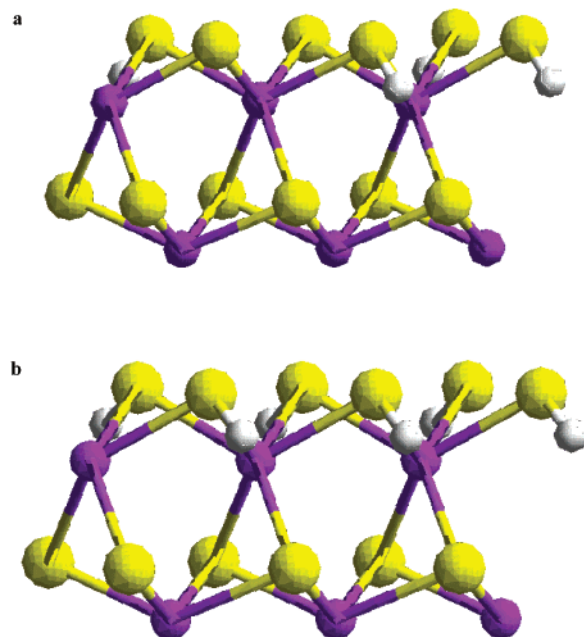


Figure 11. Further addition on the [6-*X*] surface: (a) addition of a second H_2 molecule ($E_{a1} = 1.38$ eV and $E_{a2} = 0.43$ eV) and (b) addition of a third one ($E_{a3} = -0.41$ eV).

From the above results we can expect that the most stable surface should correspond to a coverage of one H atom per Mo atom, taking into account only the electronic contributions to the enthalpy.

V. Hydrogen Coverage

To determine the nature of the stable surface in the presence of H_2 and H_2S molecules in the gas phase, we have to take into account the entropic and enthalpic contributions in hydrogen

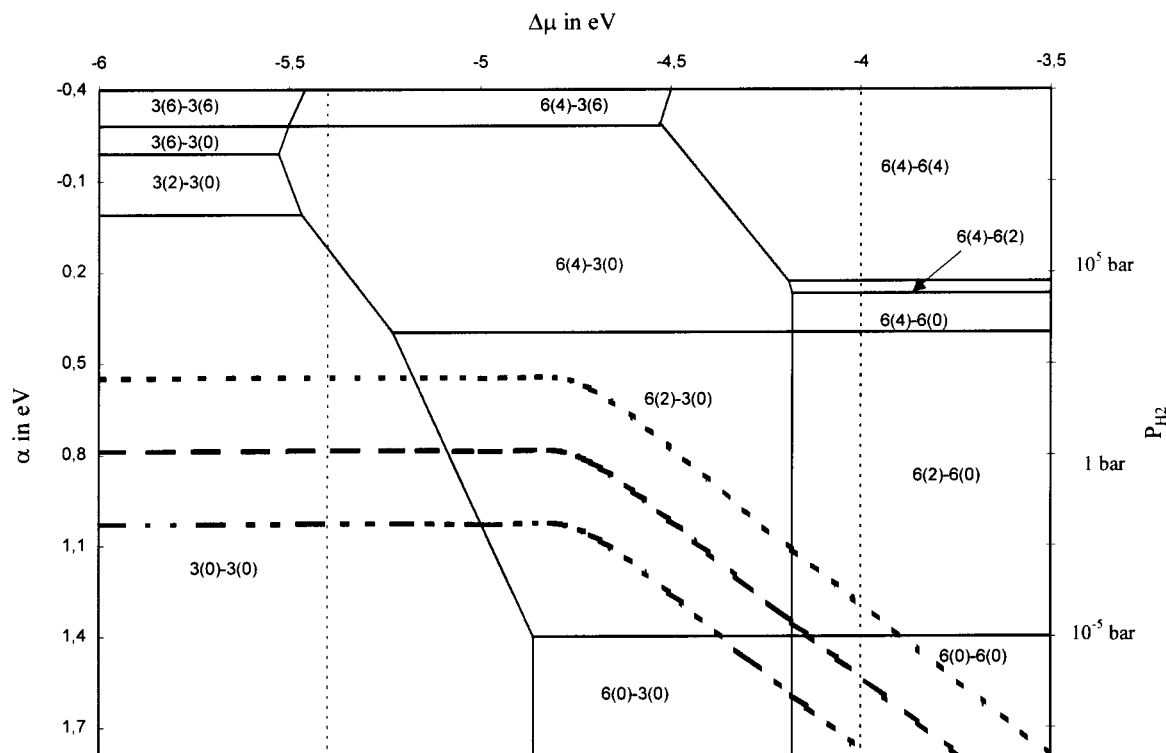
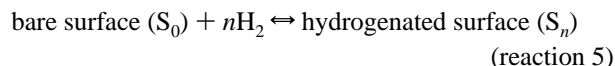


Figure 12. Most stable surfaces diagram depending on α (representing the P_{H_2} parameter) and $\Delta\mu$ (representing the P_{H_2S}/P_{H_2} partial pressure ratio). The y axis of the diagram has been inverted in order to have large H_2 partial pressure on the top of the figure.

adsorption reactions. The method, which is similar to the one used to determine the stability of surface without hydrogen, consists of calculating the free enthalpy ΔrG of the reaction 5.



The Gibbs free energy of the reaction are computed according to the following equations.

$$\Delta rG = \Delta rG^\circ - nRT \ln P_{H_2}/P^\circ$$

where

$$\Delta rG^\circ = \mu^\circ(S_n) - \mu^\circ(S_0) - n\mu^\circ(H_2)$$

Considering that we can approximate the chemical potential difference between the solids by the electronic energy difference, we can write

$$\Delta rG = \Delta E_{el} + n\alpha(T, P)$$

with

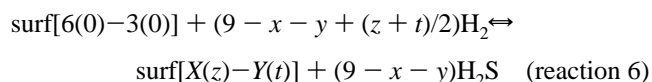
$$\alpha(T, P) = RT \ln(q(H_2)) - RT \ln \frac{P_{H_2}}{P^\circ}$$

where $q(H_2)$ is the H_2 partition function in the gas phase

In this study, the zero point energy correction is directly included in the ΔE_{el} part of the equation. Due to the large translation entropy loss occurring during the hydrogen adsorption, the α parameter is positive when $P_{H_2} = 1$ bar. For example, at a temperature of 623 K, the value of $\alpha(623 \text{ K}, 1 \text{ bar})$ is 0.79 eV. For these experimental conditions, adsorbed hydrogen molecules are thermodynamically stable only if the adsorption energy is greater than 0.8 eV. To increase the stability of hydrogen atoms on the surface, the hydrogen pressure could

therefore be risen. However, the effect of the pressure is weak. Indeed, the decrease of the α parameter is only 0.12 eV when the pressure is increased by a factor of 10. As a consequence, even for $P_{H_2} = 1000$ bar at 623 K, only configurations with adsorption energies larger than 0.4 eV will be stable.

To compare the stability of hydrogenated surface with different sulfur coverages, we have to compute the ΔrG of the following reaction 6:



where the notation “surf[$X(z)-Y(t)$]” is used to label a surface $[X-Y]$ with “ z ” hydrogen atoms on the sulfur edge and “ t ” on the metallic edge. Because the sulfur coverage is defined by the H_2/H_2S ratio, we have to study the effect of the H_2 partial pressure on the hydrogenation of each surface. This is included in the reaction 6 which could be considered as a linear combination of the chemical eqs 2 and 5. To calculate the ΔrG of this reaction, we will have to take into account simultaneously the two independent parameters α and $\Delta\mu$. For a couple of values, it will be possible to estimate the total pressure as α is related to P_{H_2} and $\Delta\mu$ to P_{H_2S}/P_{H_2} . These calculations have all been performed at 623 K, a usual temperature for hydrotreating reactions.

Then a stability diagram (Figure 12) can be drawn, which gives the nature of the most stable surface (surf[$X(z)-Y(t)$]) according to the hydrogen partial pressure given by the α values (y axis), and the H_2S/H_2 ratio given by the $\Delta\mu$ values (x axis). In this figure, bold dashed lines are also drawn corresponding to a total pressure of 10^{-2} , 1, and 10^2 bar starting from the bottom of the diagram. The y axis of the diagram has been inverted in order to have large H_2 partial pressure on the top of the figure. The two vertical dash lines correspond to the thermodynamic stability limits of bulk MoS₂ on the left and to the formation of S_α on the right part of the diagram.

The left part of the diagram corresponds to low H_2S/H_2 ratio: it shows that at low total pressure, hydrogen atoms are not stable on the surface, in agreement with the stoichiometry of the reaction. It also appears that at low values of $\Delta\mu$, which corresponds to a reductive gas phase, a large increase of the P_{H_2} partial pressure does not change the nature of the surface and no stable hydrogen atoms are adsorbed on the edges of the [100] MoS_2 surface.

Within the intermediate partial pressure range, as soon as the value of α becomes lower than 1.4 eV (i.e., $P_{H_2} > 1$ Pa), the S–H groups become stable on the sulfur edge. It should therefore be possible to create one proton per Mo atom on the edge. For α values below 0.4 eV, a second H_2 molecule is adsorbed per unit cell on the sulfur edge. However, this low value of α corresponds to a very high H_2 partial pressure at 623 K ($P_{H_2} > 2 \times 10^3$ bar). Further hydrogenation is therefore impossible whatever the considered edge, as negative values of α are quite impossible to obtain.

The right-hand side of the diagram corresponds to an oxidative atmosphere ($\Delta\mu > -4.20$ eV). Information can then be deduced on the H_2 adsorption on the [6–6] surface, the sulfur edge of the latter is the same as the sulfur edge of the [6–3] surface. So the variation of the hydrogen coverage on the sulfur edge will arise at the same values of α (1.4 and 0.4 eV). Therefore, we will now focus the discussion on the metallic edge. Adsorbed hydrogen molecules are stable on this edge for α values lower than 0.26 eV. This adsorption mode corresponds to the breaking of one S–S bond and to the formation of two S–H groups. For slightly smaller values ($\alpha < 0.24$ eV), the adsorption of a second hydrogen molecule becomes possible creating two H_2S groups on the surface. The accuracy of the calculation does not allow us to confirm the existence of the [6(4)–6(2)] surface. The direct adsorption of two H_2 molecules on the metallic edge cannot therefore be excluded. However, taking into account the large H_2 partial pressure needed for the stable adsorption of hydrogen molecule and the important P_{H_2S}/P_{H_2} ratio that correspond to this part of the diagram, we can consider that the adsorption of H_2 on the [6–6] metallic edge is very unlikely.

As a conclusion, the stable H_2 adsorption on MoS_2 surface is only experimentally possible on the sulfur edge of the [6–3] surface. The hydrogen coverage of the surface will be around one-third because one hydrogen molecule is adsorbed per six Mo atoms (three Mo on the metallic edge and three on the sulfur one). Hydrogen adsorption inducing a large entropy loss, one possibility to increase the number of hydrogen on the surface could be the lowering of the temperature. However, even at a temperature of 100 °K, the value of α (100 K, 1 bar) is still 0.30 eV, a value which is only slightly decreased by an increase of the hydrogen partial pressure (0.04 eV for a factor of 10). Therefore, a temperature variation would only induce a stabilization of the [6(4)–3(0)] surface on which two H_2 molecules are adsorbed per three Mo atoms of the sulfur edge. The H_2 adsorption on the other edges will remain unstable. For very low total pressures, a temperature variation will only slightly shifts the stability limits of the non hydrogenated surfaces. These variations will remain weak as gas-phase molecules are involved on both sides of reaction 1.

VI. Discussion and Conclusion

To confirm our assessments, we have to compare the theoretical prediction with the experimental results. Spectroscopic studies have given indirect evidence of the existence of S–H groups.^{7,8} Brønsted acidity has also been evidenced by

chemisorption of probe molecules⁹ (pyridine and lutidine) characterized by FTIR. It has also been shown that this Brønsted acidity decreases upon reduction at high temperature. Direct evidence of the S–H groups has been given by Moyes et al.¹¹ in INS studies of pure MoS_2 powders. Indeed, they assigned a 600 cm^{-1} line to the Mo–S–H deformation mode of a basal Mo–S–H group. They observed a strong decrease of this line for supported MoS_2 crystallites. Previously,¹⁰ chemical titration of MoS_2 with silver nitrate have also concluded to the presence of some sulfhydryde groups on MoS_2 surfaces. However, the number of S–H groups determined by this method is almost 1 order of magnitude greater than in spectroscopic studies. Most of these characterizations have been performed after reduction at high temperature and/or after vacuum evacuation. In contrast to the observations²¹ on RuS_2 , there is no evidence of the existence of the Mo–H groups.

Considering the experimental conditions in which the experiments have been carried, the most stable surface is always the [3(0)–3(0)] one (bottom left part of the diagram) and corresponds to a surface on which the number of adsorbed hydrogen molecules should be very small. Their characterization by physical techniques will therefore be difficult. Using the thermodynamic diagram, it is possible to determine the experimental conditions that will allow a direct observation of the S–H groups. These species are only stable on the [6–X] surface, so the P_{H_2S}/P_{H_2} partial pressure ratio should be fix around 1 and P_{H_2} may be chosen also around 1 bar within the stability region of the [6(2)–3(0)] surface. The S–H group signal should decrease if the same sample is exposed to pure H_2 or to a high vacuum treatment.

Form the catalytic point of view, the industrial condition of reactors (Total pressure below 100 bar and P_{H_2S}/P_{H_2} ration lower than 0,01) corresponds to domains without stable adsorbed hydrogen atoms and also without stable vacancies that could allow the adsorption of the organic molecules. Furthermore, variation of the working conditions (P, T) will not induced modification of the most stable surface [3(0)–3(0)]. In agreement with the Sabatier principle, the hydrogen atoms that are involved in the reaction are only weakly adsorbed on the surface. To obtain insight on the catalytic mechanism, it is therefore necessary to study the vacancy formation mechanism and the subsequent adsorption of molecules such as 4,6-DMDBT.

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References and Notes

- (1) Knudsen, K. G.; Cooper, B. H.; Topsøe, H. *Appl. Catal. A* **1999**, 189, 205.
- (2) Whitehurst, D. D.; Isoda, I.; Mochida, I. *Adv. Catal.* **1998**, 42, 343.
- (3) Cristol, S.; Paul, J.-F.; Payen, E.; Bougeard, D.; Clemendot, S.; Hutschka, F. *J. Phys. Chem. B* **2000**, 104, 11220.
- (4) Raybaud, P.; Hafner, J.; Kresse, G.; Kasztelan, S.; Toulhoat, H. *J. Catal.* **2000**, 189, 129.
- (5) Byskov, L. S.; Nørskov, J. K.; Clausen, B. S.; Topsøe, H. *Catal. Lett.* **2000**, 64, 95.
- (6) Meille, V.; Schulz, E.; Lemaire, M.; Vrinat, M. *Appl. Catal. A: Gen.* **1999**, 187, 179. Grigis, M. J.; Gates, B. C. *Ind. Eng. Chem. Res.* **1991**, 30, 2021. Topsøe, H.; Clausen, B. S.; Massoth, F. E. In *Hydrotreating Catalysis. Science and Technology*; Andersen, J. R., Boudart, M., Eds.;

Springer: Berlin, 1996; Vol. 11. Chianelli, R. R. Daage, M.; Ledoux, M. *J. Adv. Catal.* **1994**, *40*, 117. Bataille, F.; Lemberon, J. L.; Michaud, P.; Pérot, G.; Vrinat, M.; Lemaire, M.; Schulz, E.; Breysse, M.; Kasztelan, S. *J. Catal.* **2000**, *191*, 409.

(7) Topsøe, N.-Y.; Topsøe, H.; Massoth, F. E. *J. Catal.* **1989**, *119*, 252.
(8) Topsøe, N.-Y.; Topsøe, H. *J. Catal.* **1993**, *139*, 641.

(9) Berhault, G.; Lacroix, M.; Breysse, M.; Maugé, F.; Lavalley, J. C.; Nie, H.; Qu, L. *J. Catal.* **1998**, *178*, 555.

(10) Maternova, J. *Appl. Catal.* **1982**, *1*, 3. Maternova, J. *Appl. Catal.* **1983**, *6*, 61.

(11) Sundberg, P.; Moyes, R. B.; Tomkinson, J. *Bull., Soc. Chim. Belg.* **1991**, *100*, 967.

(12) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558; *Phys. Rev. B* **1994**, *49*, 14251. Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15. Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.

(13) Mermin, N. D. *Phys. Rev. A* **1965**, *137*, 1141.

(14) Vanderbilt, D. *Phys. Rev. B* **1980**, *41*, 7892. Kresse, G.; Hafner, J. *J. Phys.: Condens. Matter* **1994**, *6*, 8245.

(15) Raybaud, P.; Hafner, J.; Kresse, G.; Toulhoat, H. *Surf. Sci.* **1998**, *407*, 237. Raybaud, P. Ph.D. Thesis, Université Paris VI, Paris, 1998.

(16) Traver, A.; Nakamura, H.; Van Santen, R.; Cristol, S.; Paul, J.-F.; Payen, E. *J. Am. Chem. Soc.* In press.

(17) Methfessel, M.; Paxton, A. T. *Phys. Rev. B* **1989**, *40*, 3616.

(18) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048.

(19) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pedersen, M. R.; Singh, D. J.; Frolais, C. *Phys. Rev. B* **1992**, *46*, 6671.

(20) Byskov, L. S.; Bollinger, M.; Nørskov, J. K.; Clausen, B. S.; Topsøe, H. *J. Mol. Catal. A* **2000**, *163*, 117.

(21) Jobic, H.; Clunet, G.; Lacroix, M.; Yuan, S.; Mirodatos, C.; Breysse, M. *J. Am. Chem. Soc.* **1993**, *115*, 3654.