

**MODELING OF SYNGAS REACTIONS AND HYDROGEN
GENERATION OVER SULFIDES**

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MODELING OF SYNGAS REACTIONS AND HYDROGEN GENERATION OVER SULFIDES

Abstract

The objective of the research is to analyze pathways of reactions of hydrogen with oxides of carbon over sulfides, and to predict which characteristics of the sulfide catalyst (nature of metal, defect structure) give rise to the lowest barriers toward oxygenated hydrocarbon product. Reversal of these pathways entails the generation of hydrogen, which is also proposed for study.

In this first year of study, adsorption reactions of H atoms and H₂ molecules with MoS₂, both in molecular and solid form, have been modeled using high-level density functional theory. The geometries and strengths of the adsorption sites are described and the methods used in the study are described.

An exposed MO^{IV} species modeled as a bent MoS₂ molecule is capable of homopolar dissociative chemisorption of H₂ into a dihydride S₂MoH₂. Among the periodic edge structures of hexagonal MoS₂, the (1 $\bar{2}$ 11) edge is most stable but still capable of dissociating H₂, while the basal plane (0001) is not. A challenging task of theoretically accounting for weak bonding of MoS₂ sheets across the Van der Waals gap has been addressed, resulting in a weak attraction of 0.028 eV/MoS₂ unit, compared to the experimental value of 0.013 eV/MoS₂ unit.

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Executive Summary

Modeling of hydrogen activation and bonding on molybdenum disulfide was carried out using computational approaches ranging from semi-empirical to high-level all-electron periodic density functional theory (DFT) methods. Because the structure of the trigonal prismatic MoS₂ is highly anisotropic, a large number of surface orientations, features and structural motifs were examined for hydrogen site preferences. The simplest structure, a single MoS₂ molecule, has a stable bent geometry and the exposed Mo atom is a site for a di-hydride formation. Among the extended structures, sites on and between the sulfur and molybdenum atoms display a range of binding power for hydrogen. *Atomic* hydrogen binds weakly (with adsorption energy of -12 to -15 kcal/mol of H) onto *basal plane* sites that include sulfur three-rings and single surface sulfur atoms, but is repelled by subsurface molybdenum. The adsorption energy of two H atoms, -24 to -30 kcal/mol, is insufficient to overcome the dissociation energy of the hydrogen molecule, 104.204 kcal/mol, and therefore dissociative chemisorption of *molecular* hydrogen on the MoS₂ basal plane (0001) is thermodynamically disallowed. A substantially stronger adsorption of H atoms occurs on the *edge* surfaces. Four edge structures, “vertically cut” (10 $\bar{1}$ 0) and (1 $\bar{2}$ 10) planes, and “inclined” (10 $\bar{1}$ 1) and (1 $\bar{2}$ 11) were examined by partial optimization which involved relaxation of the edge surface S and Mo atoms. These structures show distinct differences in surface energies, yielding relative stabilities in the order (1 $\bar{2}$ 11) > (10 $\bar{1}$ 1) > (1 $\bar{2}$ 10) > (10 $\bar{1}$ 0). The most stable (1 $\bar{2}$ 11) edge surface has a penta-coordinated Mo species with the Mo atom exposed through one sulfur vacancy, and binds atomic hydrogen on several sites with adsorption energy exceeding half of the dissociation energy of molecular hydrogen. The strongest sites can break the hydrogen molecule and release 1.06 eV of heat per H₂ molecule. Hence even the most thermodynamically stable edges are capable of activating molecular hydrogen by dissociative chemisorption.

The presently used methodology is far more advanced, and far more accurate, than our early attempts to model the dissociative activation of hydrogen on various sulfides using the Extended Hückel Theory (EHT) for periodic systems [1]. The price paid is the very large demand on computational resources and the concomitant need to adjust the size of the model to a realistic performance time. The results reported here were obtained using the following DFT methods:

- A. Periodic generalized gradient approximation (GGA) LCAO method with the DNP basis set and the Perdew-Wang '91 (PW) functional [2] as embedded in the DMol³ package [3];
- B. Periodic generalized gradient approximation (GGA) FP-LAPW method with a dual planewave/spherical harmonics basis set and the Perdew-Burke-Ernzerhof '96 (PBE) functional [4] as embedded in the Wien2k code [5];
- C. Generalized gradient approximation (GGA) LCAO method with the DN** basis set and the Becke-Perdew functional [6] as embedded in the Spartan package [7];

D. Semiempirical methods for preoptimization of geometry.

Benchmarking and comparison of the various methods were also performed. We find the semiempirical pm3(tm) code [8] particularly deficient by arriving at totally wrong geometries, presumably due to a bad parametrization for molybdenum, a key element in our systems. All other properties obtained with this method are of course also in doubt. In contrast, our experience with methods A-C above [9–14] permits the conclusion that results based on these methodologies are valid and reliable, albeit always amenable to refinement.

One particular challenge is to account for weak interactions such as those between adjacent MoS₂ sheets across the Van der Waals gap. A successful calculation by the periodic full-potential linearized augmented plane wave (FP-LAPW) DFT method is reported herein to yield the weak attraction (0.028 eV/MoS₂ unit), albeit the calculated attractive energy still differs from the experimental value of 0.013 eV/MoS₂ unit and the calculated size of the Van der Waals gap is larger than the experimental value.

Experimental

In this theoretical modeling effort in which all methodology is described in the other sections of this report. In particular, items A-D in the Executive Summary above describe the calculation methods.

Results and Discussion

Objective and Background of the Research

Overall objective. The objective of this research is to analyze pathways of reactions of hydrogen with oxides of carbon over sulfides, and predict which characteristics of the sulfide catalyst give rise to the lowest barriers toward oxygenated hydrocarbon product. The present research aims at providing complementary and predictive theoretical background for an economical optimization of these processes.

Methodology. Molecular conversions at interfaces occur via a flow of electrons during movement of atomic nuclei from reactant to product configurations over energy barriers the magnitude of which determine the reaction rate. Reactants (R) and products (P) are at local minima of a multidimensional energy-coordinate space, and the barrier is at a saddlepoint of that space called the Transition State (TS). The points R, TS and P are the stationary points of the reaction pathway, and search for these points is carried out by optimization methods of quantum mechanics. Specific methods used in this work are listed as A-D on p. 6 of this report. Development of codes for TS searches in periodic systems is also planned. An important aspect of the modeling is evaluation of reliability and accuracy of the methods used.

Dihydride complexes on the MoS₂ molecule

Hydrogenations over MoS₂ catalysts are known to be activated. The commonly suggested mechanisms for this activation are (a) the heteropolar splitting over a surface Mo-S pair into a molybdenum “hydride” Mo-H^{δ-} and sulfhydryl S-H^{δ+} and (b) homopolar splitting over a pair of surface sulfur atoms resulting in two S-H surface species. The mechanism (b) has been suggested for pyritic disulfides, and is discarded for the MoS₂ basal plane by the calculations in Part II. The mechanistic proposal of heteropolar splitting (a), however, lacks solid experimental evidence, and requires theoretical scrutiny.

Since the Mo atoms are only exposed on edges, we have chosen to examine the energetics of hydrogen binding on small clusters. A calculation of an adduct of dihydrogen with a single MoS₂ molecule yielded a stable dihydride in which the hydrogen molecule is dissociated and both hydrogen fragments are bonded to the exposed Mo atom, as seen in Figure 1. This result provides an incentive for examining a mechanism (c), the homopolar splitting of the hydrogen molecule on a single Mo center.

The theory predicts frequencies of the symmetric and antisymmetric vibrational modes of the dihydride H-Mo-H surface species that would be easily detected and identified by infrared spectroscopy of vibrational transitions near 2000 cm⁻¹. The salient features of calculations relevant to mechanism (c) are summarized herein.

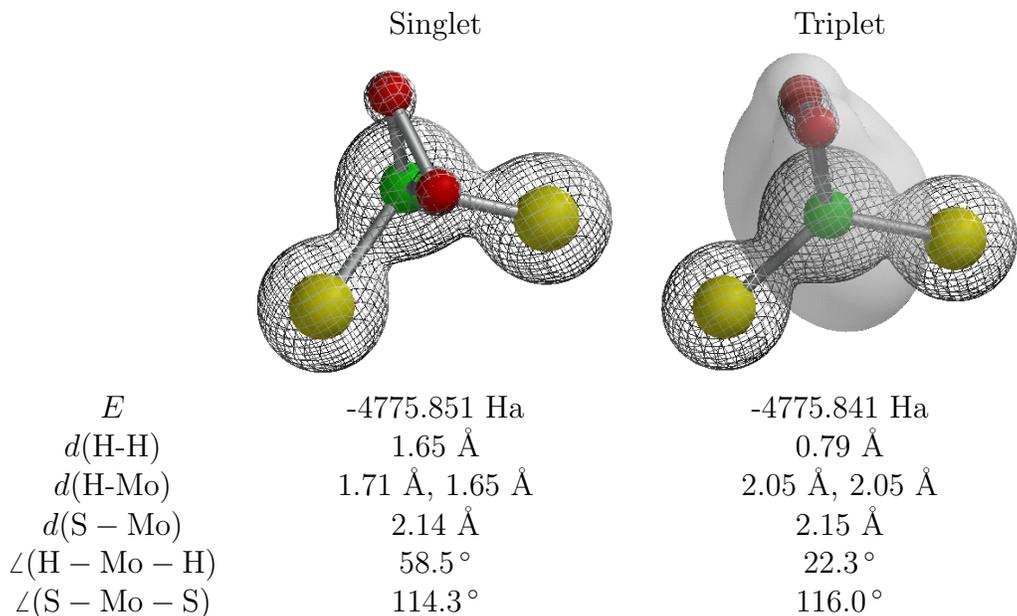


Figure 1: MoS₂-H₂ Complex. Mesh: electron density; Transparent surface: net spin density. The Ground state MoS₂ singlet dissociates the H₂ molecule into a dihydride on the Mo center.

Calculations were performed dealing with H₂ attachment to a single MoS₂ molecule. In these calculations, the DFT method was used with the BP [6] exchange-correlation functional and a DN** LCAO basis. The method is essentially the same as that used for the H atomic adsorption described below.

The minimum energy for the ground state was found when the hydrogen atoms were located on the reflection plane which bisects the S-Mo-S angle of the molecule, as depicted in the figure. In this geometry, the hydrogen atoms dissociate, as evidenced by the lack of charge density between them, the 1.65 Å distance, and the low vibrational frequency. They form a dihydride complex on the Mo atom. In addition, an excited triplet state of the H₂-MoS₂ complex was modeled. This system is less stable, and the H₂ molecule does not dissociate. The vibrational frequency of the H-H bond was not reduced, indicating the character of the H₂ is maintained.

Calculations with models of increasing MoS₂ cluster size and periodic edges, particularly the relaxed (1 $\bar{2}$ 11) structure, are scheduled for the next stage of the study of mechanism (c).

Adsorption of hydrogen on periodic MoS₂ structures

We have studied the adsorption of hydrogen atoms onto MoS₂, both on the basal planes and on edges of planes using high-level DFT calculations. MoS₂ has a graphite-like sheet structure, with tightly bound planes attracted to each other by weak Van der Waals forces. The planes are found to be chemically inactive, while the edges are active, with respect to

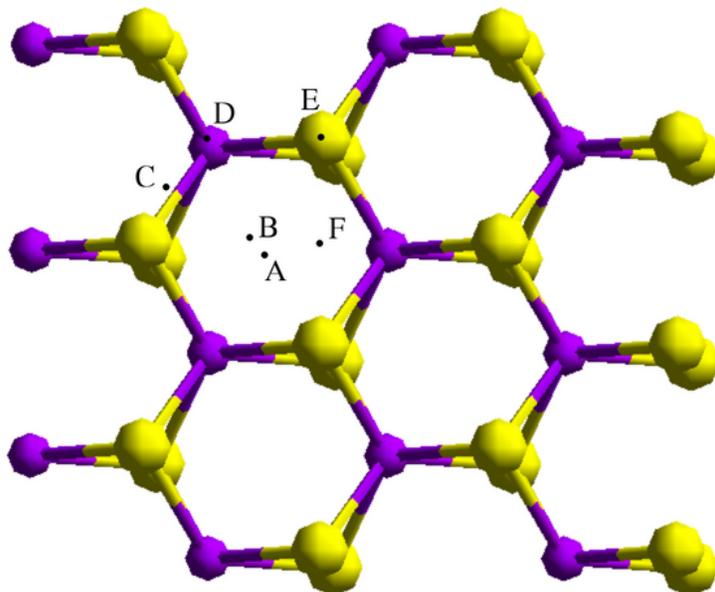


Figure 2: An MoS₂ basal plane, showing the positions where hydrogen was adsorbed. The top and bottom of the figure correspond to the (1 $\bar{2}$ 10) edge, while the left and right correspond to the (10 $\bar{1}$ 0) edge.

adsorption of atomic hydrogen.

These new calculations of H adsorption used a DNP numerical linear combination of atomic orbitals (LCAO) basis set expansion of the electron density in a three-dimensional periodic model with the Perdew-Wang '91 GGA functional [2]. The calculations were performed using the DMol³ [3] DFT electronic structure program. The DNP basis includes approximately two atomic orbitals for every occupied orbital, plus polarization functions on all atoms. The periodicity allows for modeling of bulk solids, surfaces, and edges.

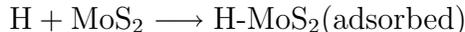
Surfaces and edges are modeled by increasing the cell size to create a large (~ 20 - 40 Å) vacuum gap between cells to prevent interactions. This is where it is advantageous to use an LCAO basis set expansion instead of a plane-wave expansion for the electron density. A plane-wave basis set, like that used in the FP-LAPW method, must fill the entire gap between the isolated cells, greatly increasing the computational cost of using of a large unit cell. With the atomic basis set, there is no additional penalty for increasing the cell size, making the modeling of surfaces and edges in a three-dimensional framework much easier.

For H adsorption onto the basal planes, individual planes of MoS₂ were used. These sheets were spaced 40 Å apart. The use of individual planes reduces the computational demands by about a factor of 4 because there are 2 sheets per unit cell in bulk MoS₂. The lack of neighboring layers across the Van der Waals gap is not expected to affect the hydrogen adsorption.

Label	Position	Adsorption E	
		(Hartrees)	(eV)
A	hollow-inplane	-0.0217	-0.592
B	hollow-above	-0.0118	-0.321
C	over-bond	-0.0214	-0.582
D	over-mo	0.0048	0.132
E	over-s	-0.0199	-0.541
F	s-bridge	-0.0196	-0.533

Table 1: Energies of hydrogen atoms adsorbed onto the MoS₂ surface. The labels correspond to those in Figure 2. The adsorption energies are $E(\text{H-MoS}_2) - (E(\text{H}) + E(\text{MoS}_2))$, and more negative numbers represent more tightly bound states. For reference, the calculated binding energy of H₂ is -2.282 eV/atom.

The low adsorption energies of hydrogen onto the MoS₂ surface reflect the stability of the MoS₂ basal planes, shown in Figure 2. The energies shown in Table 1 are for the reaction:



Large negative energies correspond to tightly bound systems. None of these positions binds H tightly enough to overcome the binding energy of H₂ to allow dissociative adsorption.

Calculations of the MoS₂ edges, however, tell a different story. The first notable observation is that inclined slices of the MoS₂ planes are more stable than vertical slices. These inclined edges are referred to as the (10 $\bar{1}$ 1) and (1 $\bar{2}$ 11) edges. Their geometry roughly corresponds to the (10 $\bar{1}$ 0) and (1 $\bar{2}$ 10) edges pictured in Figure 2, with some atoms removed to form the inclined edge. The energies of the various edges are given in Table 2.

For the calculations of MoS₂ edges, thin “ribbons” of MoS₂ sheets were constructed, as depicted in Figure 3. These ribbons were grown up to 10 atoms (17 Å) wide before interactions between the edges were diminished. The cell size was 40 Å, giving 23 Å of empty space between isolated edges for the widest ribbons.

Table 2: Energies of MoS₂ systems representing the edges. In each system, the unit cell contains a 5×2 array of MoS₂ units. The relative energy is given with respect to the most stable, (1 $\bar{2}$ 11) edge.

Edge	Energy	
	(Hartrees)	(eV/unit cell)
(10 $\bar{1}$ 0)	-8649.646	2.92
(1 $\bar{2}$ 10)	-8649.799	0.83
(10 $\bar{1}$ 1)	-8649.834	0.36
(1 $\bar{2}$ 11)	-8649.860	0.0

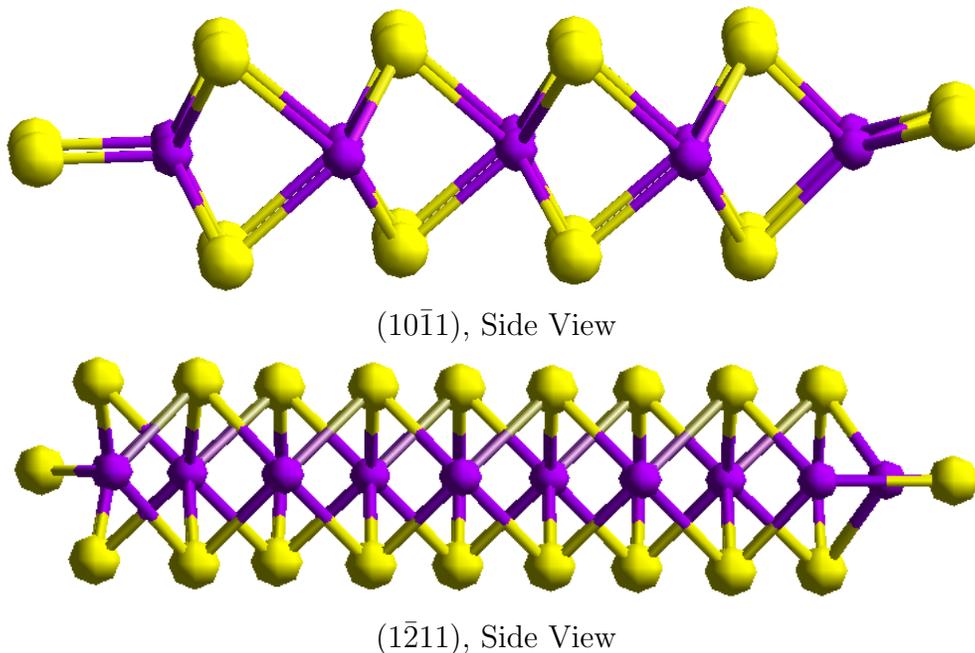


Figure 3: Geometries of the most stable edges of MoS₂. The view is looking down the length of the “ribbon”, and the left and right sides of the figure correspond to the actual edges. The structure repeats in the direction perpendicular to the page. The slices were initially inclined, but during the optimization, the S atoms on the edges migrated into the Mo plane.

Hydrogen atom adsorption was studied in various locations on the two most stable edges, (10 $\bar{1}$ 1) and (1 $\bar{2}$ 11). As the position of the H atom was optimized, the nearby Mo and S atoms were allowed to relax as well, to accurately reflect the reaction of an actual MoS₂ edge to the hydrogen. One such optimized geometry is shown in Figure 4, while the energies of all tested positions are given in Table 3.

These calculations found a maximum adsorption energy of -0.1035 Hartrees (-2.82 eV) on the (1 $\bar{2}$ 11) plane, and -0.0949 Hartrees (-2.58 eV) on the (10 $\bar{1}$ 1) plane. The binding energy of H₂ at the same level of theory, discounting the zero-point energy, is -0.16775 Hartrees (-0.0839 Hartrees/atom, -2.282 eV/atom). So either of the diagonally-cut planes can dissociate H₂ into individual atoms, opening the way for reactions with those atoms.

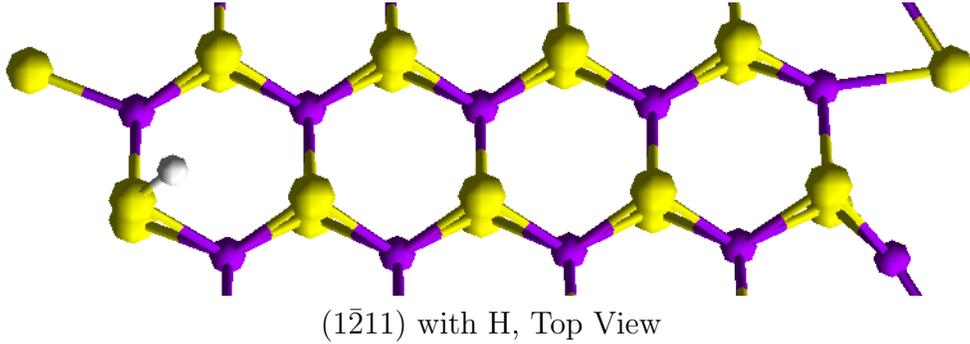


Figure 4: An example geometry for the adsorption of H on the $(\bar{1}211)$ edge of MoS_2 . The “ribbon” repeats in the $[10\bar{1}0]$ direction, and is 17 Å wide. This position is called “mo4_top” because the hydrogen atom started above the left-most Mo atom, though it has migrated to be nearer one of the S atoms.

Edge	Position	Adsorption E	
		(Hartrees)	(eV)
(1011)	mo4-ontop	-0.056	-1.53
	s1-bridge	-0.089	-2.42
	s1-ontop	-0.083	-2.26
	s2-bridge	-0.049	-1.34
	s2-ontop	-0.095	-2.58
(1211)	mo3-side	-0.078	-2.12
	s2-side	-0.059	-1.60
	mo3-top	-0.056	-1.52
	mo3-br	-0.063	-1.71
	mo4-side	-0.063	-1.72
	mo4-top	-0.103	-2.81
	s1-side	-0.079	-2.14
	s1-pocket	-0.101	-2.75

Table 3: Energies for H atomic adsorption on MoS_2 edges. The adsorption energies are $E(\text{H-MoS}_2) - (E(\text{H}) + E(\text{MoS}_2))$, and more negative numbers represent more tightly bound states. The calculated binding energy of the H_2 molecule is -2.282 eV/atom, so several of these adsorption locations are capable of dissociating H_2 .

between the Molybdenum and Sulfur planes, or equivalently, the S-Mo-S bond angle. The cell parameters a and c must also be optimized. To find the Van der Waals gap, the MoS₂ structure was optimized for several cell sizes corresponding to different gap sizes.

Because of the use of plane waves in the regions far from atomic centers, the number of basis functions and hence the difficulty of the calculation increase with large unit cells, such as those used with supercell, surface, and edge calculations. The modeling of MoS₂ edges at the FP-LAPW level requires a large unit cell in two directions and very large resources. Several approaches have so far been employed:

- (a) Low-level periodic structure calculations (EH).
- (b) High-level periodic LCAO calculations as embedded in DMol³, using DFT with a DNP basis.
- (c) Cluster calculations from EH level to DFT/BP/DN** level.

The effort with FP-LAPW continues in selected cases, because this method yields the most accurate data and is capable of reliably predicting valance band electronic structure and core-level chemical shifts verifiable by high-resolution photoelectron spectroscopy.

Conclusion

By high-level LCAO DFT calculations, MoS₂ has been shown to be capable of dissociative adsorption of hydrogen on its edges. This is an important step in the catalytic synthesis of hydrocarbons from natural gas, a process which can reduce our dependence on petroleum-based products. Using the FP-LAPW DFT method, the weak Van der Waals attraction of MoS₂ sheets has been accounted for. Vital to this study is the determination of transition states in periodic systems, which is an ongoing effort.

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