

# Experimental and Theoretical Properties of MoS<sub>2+x</sub> Nanoplatelets

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## ABSTRACT

The synthesis and the catalysis in the HDS of DBT reaction of nanostructured self-supported catalyst containing MoS<sub>2+x</sub> nanoplatelets have been investigated. Enhancement of higher activity observed in sulfide catalyst sample (d) with respect to the *ex situ* and *in situ* references is more closely related to the morphology change of particles (nanoplatelets). In this work, we suggest that certain structures present in model catalysts maybe related to low dimensional structures and present a theoretical study of two MoS<sub>2</sub> clusters (one made of 34 atoms/cluster and the second one made of 41 atoms/cluster), to these clusters seven sulfur atoms were randomly located at the surface of the sulfur layer, in order to simulate certain structures resembling arrow shaped nanoplatelets that were found in a High Resolution TEM analysis performed in some MoS<sub>2</sub> samples. Additionally, one of the goals is to enquire about the electronic properties presented in such structures when the clusters terminated as Mo- or S-edge and if it could be correlated to the catalyst behavior of these compounds. To the 34 atoms/cluster Mo-edge yielded metallic behavior while the second cluster the 41 atoms/cluster S-edge yielded a semiconductor behavior with a forbidden energy gap E<sub>g</sub> of the order of  $\cong 3.6$  eV between the Valence and Conductions bands respectively. Moreover, to the same clusters enunciated formerly, when the sulfur atoms were located at the surface of the S-layer, for the first cluster (34 atoms/cluster) yielded a more metallic behavior, while the second one (41 atoms/cluster) yielded an isolator behavior. Our results agree with the experimental and theoretical results presented by several groups in different laboratories arriving to the conclusion that the S-Mo-S Mo-edge arrow heads structures could be responsible to the enhancement of the catalytic activity on the MoS<sub>2</sub> studied samples.

**Keywords:** Hydrodesulfurization; Tight-Binding; Catalyst; Tem; Clusters

## 1. Introduction

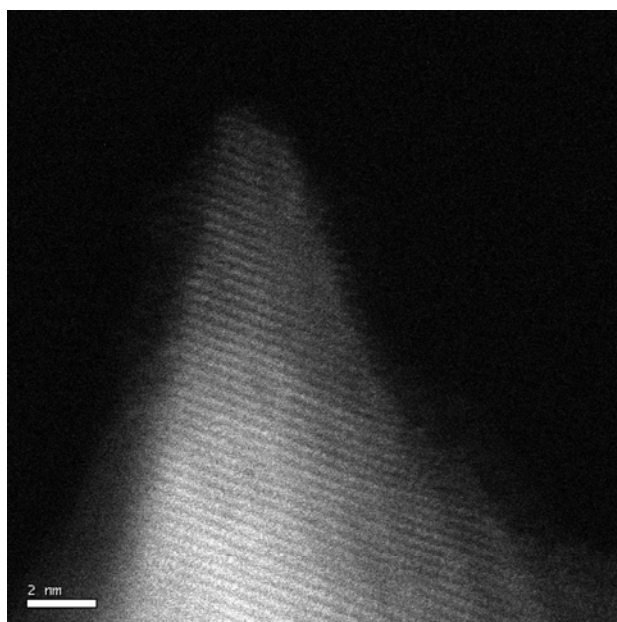
The most commonly used industrial hydro treating catalysts for sulfur removal from heavy oils are based on cobalt or nickel promoted MoS<sub>2</sub> [1].

Atom-resolved scanning tunneling microscopy (STM) studies of catalyst model systems have recently given the first direct insight into the atomic-scale structure of model MoS<sub>2</sub> nanoclusters and the promoted CoMoS structures [2,3]. These model systems consisted of a few nanometer wide, gold-supported MoS<sub>2</sub> and CoMoS nanoclusters, and with the STM, it was possible to characterize their geometrical and electronic structure in great detail. On this basis, new important insight was obtained on the nanocluster morphology, on the atomic-scale structure of

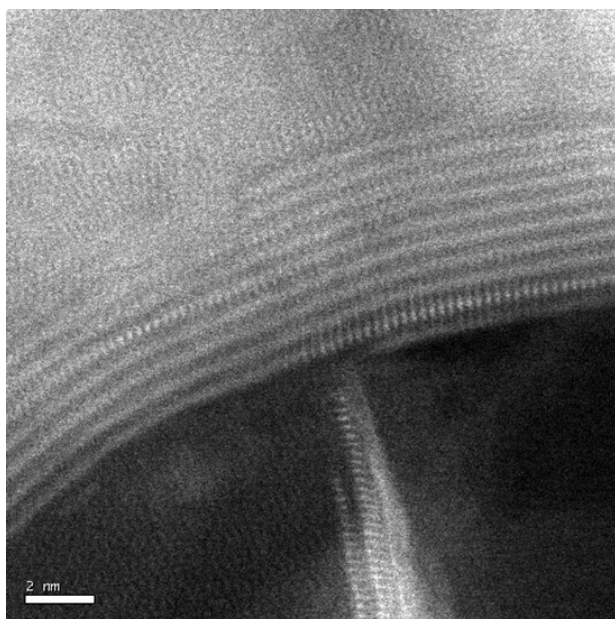
the catalytically important edges, and on the formation of sulfur vacancies. It was also shown that the nanocluster morphology and exact edge structures were sensitive to reaction conditions [4-8].

Those catalysts consist of small MoS<sub>2+x</sub> particles of finite size supported on alumina. A more deep analysis of these wires shows a remarkable structure which resembles to the theoretical models used by several groups [1-11].

**Figures 1(a)** and **(b)** show how a typical catalyst can be formed by these nanoplatelets of MoS<sub>2</sub> that also show an enhanced selectivity toward hydrogenation [12]. Two types of structures can be seen: triangular platelets and cone shaped platelets. These structures contain metallic edge sites (brims).



(a)



(b)

**Figure 1.** Shows that the model catalyst of  $\text{MoS}_2$  presents crystalline structures with an arrow shaped nanoplatelets by High Resolution Electron Microscopy (HREM).

The contrast observed at the tip was measured and corresponds to  $2\text{H-MoS}_2$  basal plane, thus the structure grows along a direction perpendicular to either  $\{10.0\}$  or to  $\{11.0\}$ .

It has been assumed that the platelet-like structure observed in **Figure 1(b)** corresponds to a transversal section of large  $\text{MoS}_2$  crystallites. It has been shown by the group of Haldor Topsøe Laboratory and the University of Aarhus the existence of metallic one dimensional state on

$\text{MoS}_2$  clusters and establishes a new view of the catalytic active sites. Traditionally, it was believed that the hydrodesulfurization (HDS) reactions occur at sulfur vacancies and the metallic edges (the so-called brim sites) on the  $\text{MoS}_2$ , but *in situ* STM observations of the interaction between  $\text{MoS}_2$  clusters and thiophene indicate activity at the metallic edges, which seem to be terminated by sulfur dimers. The catalytic behavior changes strongly depend on the type of surfaces present in the material [13]. It is extremely important to determine the relevance of these findings for real systems.

Recently, a model  $\text{MoS}_{2+x}$  ( $x \cong 0.5$ ) catalysts has been reported [13]; this material showed an increased activity for HDS and selectivity toward hydrogenation, contained one-dimensional structures like the one shown in **Figure 1**. This behavior may be attributed to metallic states at the edges of the nano wires. In the present paper, the synthesis and the catalysis in the HDS of DBT reaction of nanostructured self-supported catalyst containing  $\text{MoS}_{2+x}$  nanoplatelets have been investigated. Moreover, we demonstrate a new way to simulate the platelet arrow head structures that appear in some  $\text{MoS}_2$  samples and furthermore to investigate if the platelet-like structures show a special type of behavior (metallic, semiconductor or insulator) depending on how the cluster terminates Mo- or S-edge.

## 2. Experimental and Calculations

A film of  $\alpha\text{-MoO}_3$  nanoribbons was prepared by a hydrothermal process. The procedure consisted of adding drop wise a 4 M solution of HCl to a saturated solution of sodium molybdate. The mixture is placed in a Teflon-lined autoclave and left at 423 K for 8 h (precursor of sample d). Once the reaction time was completed, the product was filtered and dried. Sections of these films were reacted with a stream of  $\text{H}_2\text{S}$  gas mixed with 90% inert gas  $\text{N}_2$  and 10%  $\text{H}_2$  in a 9/1 volume ratio at 723 K for 1.5 h, in order to produce the corresponding sulfide of molybdenum (catalyst d). The unreacted excess of  $\text{H}_2\text{S}$  was neutralized with a saturated solution of NaOH.

Specific surface areas of catalysts were determined with a Nova 1000 series from Quantachrome by nitrogen adsorption at 77 K, with the BET method. Samples were degassed under vacuum at 523 K before nitrogen adsorption. Reference catalysts were prepared by decomposition of ammonium thiomolybdate (ATM). One of them was sulfided *ex situ* in a tubular reactor with 15% volume  $\text{H}_2\text{S}/\text{H}_2$  flow at 673 K for 4 h (heating rate 4 K/min) before catalytic testing; the other one was left to be sulfided *in situ* during the reaction. The decomposition of ATM precursor is a well-known reaction that occurs very fast, generating  $\text{MoS}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{S}$  [14].

The hydrodesulfurization (HDS) of dibenzothiophene (DBT) has been studied as a model reaction of HDS of

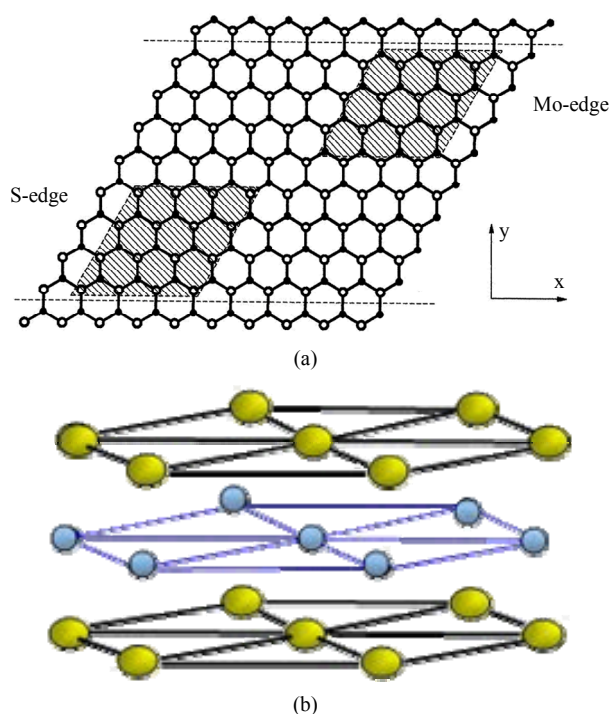
petroleum feedstock. For this work the HDS was carried out in a Parr Model 4522 high-pressure batch reactor. The catalysts were placed in the reactor with a gram of each one respectively (*ex situ* catalysts (1 g) or *in situ* catalysts, the appropriate amount of ATM to yield 1 g of  $\text{MoS}_2$ ) along with the reaction mixture (5% weight of DBT in decalin), then pressurized with hydrogen and heated to 623 K at a rate of 10 K/min under a constant agitation of 600 rpm.

When the working temperature was reached, sampling for chromatographic analysis was performed to determine conversion versus time dependence; the reaction was run for 5 h. Reaction products were analyzed with an AutoSystem XL gas chromatograph (Perkin Elmer Instruments) with a 9-ft, 1/8-inch-diameter packed column containing OV-17, on Chromosorb WAW 80/100 as the separating phase.

Samples of commercial spent catalysts were pulverized and dispersed in isopropanol. A droplet of this suspension was deposited on lacey carbon copper grids for transmission electron analysis (TEM). The catalyst samples were analyzed with the aid of a JEOL 2010 F microscope equipped with a Schottky-type field emission gun, ultra-high resolution pole piece, and a Scanning-Transmission (STEM) unit with a high angle annular dark field detector (HAADF) operating at 200 kV, a Gatan CCD camera was used for image acquisition.

The calculations reported in this work, have been carried out by means of the tight-binding method [15] within the Extended Huckel [16] framework using YAeH-MOP (Yet Another extended Huckel Molecular Orbital Program) computer package with f-orbitals [17,18]. The Extended Huckel method is a semi empirical approach for solving Schrödinger equation for a system of electrons, based on the variational theorem. In this approach, explicit electron correlation is not considered except for the intrinsic contributions included in the parameter set. More details about the mathematical formulation of this method have been described elsewhere [19] and will be omitted here. The calculations were performed in super-computer Berenice 32 (32 parallel processors) Silicon Graphics Origin 2000 using the input file accordingly to each specific case.

In order to simulate the *arrow like* structures from **Figures 1(a)** and **(b)** we constructed the appropriate Mo or S-MoS<sub>2</sub> systems starting from an infinite hexagonal array like the one depicted in **Figure 2**. Notice **Figure 2** indicates that it has been constructed from Mo dark spheres and S white spheres respectively, then construct a finite x-y and an infinite z-structure in order to simulate the appropriate cluster under consideration. From the selected cluster we simulate a three dimensional S-Mo-S arrangement just considering that the selected cluster ought to terminate as Mo or S-edge respectively, as depicted in **Figures 2(a)** and **(b)**. On the same figure, on



**Figure 2. (a) Infinite hexagonal array of Mo and S atoms; (b) Three layers of S-Mo-S to create the appropriate structure.**

the right hand top side it is possible to find a small hatched rectangle terminating on Mo atoms all the way around, consequently it is called Mo-edge, while on the same figure we can locate similar hatched rectangle on the lower left corner terminating of S atoms, hence is called S-edge. For the Mo-edge MoS<sub>2</sub> cluster it was necessary to use 16 Mo plus 18 S in order to construct a 34 atoms/cluster as the one depicted in **Figure 2** right hand side of the figure. Alternatively in order to construct the S-edge MoS<sub>2</sub> left hand side of **Figure 2**, it was necessary to use 9 Mo plus 32 S atoms in order to build 41/atoms/cluster respectively. Moreover, in order to perform a more realistic experimental image, seven sulfur atoms were randomly located at the top the sulfur layer, hence for the S-Mo-S Mo-edge plus seven S-atoms, a new cluster made of 41 atoms/cluster were selected, mean while, for the S-Mo-S S-edge a 48 atom cluster were selected. It is good to point out that in order to generate the appropriate clusters they aroused from crystalline MoS<sub>2</sub> using the primitive vectors:  $a = 3.1604 \text{ \AA}$ ,  $c = 12.295 \text{ \AA}$  and space group P6<sub>3</sub>/mmc (194) [20].

Atomic parameters for Mo and S atoms used throughout the calculations were obtained from Alvarez *et al.* and provided in **Table 1** [21]. It is necessary to stress that experimental lattice parameters instead of optimized values were used searching for a best match between our results with the available experimental information provided in the literature.

### 3. Results and Discussion

We sulfidized sections of a film of  $\alpha$ -MoO<sub>3</sub> nanoribbons, keeping the H<sub>2</sub>S/H<sub>2</sub> ratio constant at 90/10 and the inert carrier gas was N<sub>2</sub>. The sulfidation process produces metallic grey powders whose morphology differs from that one of the parent oxide.

In case of catalyst d, X-ray diffraction showed the presence of two crystalline phases, molybdenum dioxide (Tugarinovite, JCPDS 78-1073) and molybdenum disulfide (Molybdenite-2H, JCPDS 65-0160) (**Figure 3**). We also perform the quantitative phase analysis by X-ray powder diffraction dates by the internal-standard method [22]. The amounts of the MoO<sub>2</sub> phase and the MoS<sub>2</sub> phase are 82% and 18% in weight respectively.

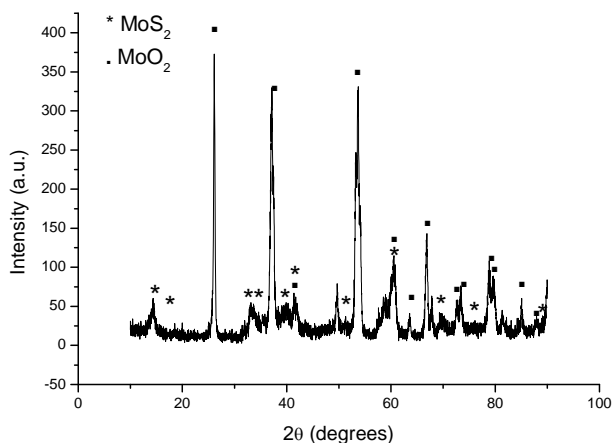
The catalyst d contains MoS<sub>2</sub> nanoplatelets and it was prepared from  $\alpha$ -MoO<sub>3</sub> nanoribbons like precursor. It reacted with H<sub>2</sub>S/H<sub>2</sub> under reaction conditions. MoS<sub>2</sub> nanoplatelets and the MoO<sub>2</sub> were obtained.

The catalytic activity of catalyst d for HDS was of  $12.8 \times 10^{-7} \text{ mol}\cdot\text{s}^{-1}\cdot\text{g}^{-1}$  and the selectivity for hydrogenation was of 1.7. The d catalyst is more efficient in activity and selectivity than both *ex situ* and than *in situ* references has can be seen from **Table 2**.

The material tested for catalytic activity presented a surface area of 14 m<sup>2</sup>/g. Compared with the surface of reference catalysts, sample d presents a typical value for this kind of catalyst, intermediate between the *in situ* and *ex situ* references (see **Table 2**).

The HDS of DBT was studied under conditions of 623 K and 3.4 MPa, which are close to those used in industrial applications. DBT was chosen because it is considered an appropriate compound for the investigation of activity and reaction mechanisms of proposed HDS catalysts.

The HDS of DBT yields two main products: biphenyl (BP) through the so-called direct desulfurization pathway (DDS) and cyclohexilbenzene (CHB) and tetrahydrodi-



**Figure 3.** X-ray diffraction pattern of the sample d tested for the catalytic properties.

**Table 1.** Atomic parameters used in the Extended Huckel tight-binding calculations,  $H_{ii}$  (eV) and  $\zeta$  (Valence orbital ionization potential and exponent of Slater type orbitals). The d-orbitals for Mo are given as a linear combination of two Slater type orbitals. Each exponent is followed by a weighting coefficient in parentheses. A modified Wolfsberg-Helmholtz formula was used to calculate  $H_{ij}$  [28].

Atom	Orbital	$H_{ii}$	$\zeta_1$	$C_1$	$\zeta_2$	$C_2$
Mo	5s	-8.34	1.96			
	5p	-5.24	1.90	(0.6397)	1.90	(0.6097)
	4d	-10.50	4.54			
S	3s	-20.00	2.12			
	3p	-11.00	1.83			

**Table 2.** Surface area calculated by the BET equation from nitrogen absorption at 77 K, rate constants ( $k$ ), and HYD/DDS ratios for HDS of DBT (3.4 MPa of hydrogen, 623 K).

Sample	Surface area before reaction	Rate constant $k$ ( $\times 10^7$ )	Selectivity HYD/DDS
	( $\pm 0.5$ ) m <sup>2</sup> /g	(mol·s <sup>-1</sup> ·g <sup>-1</sup> )	
D	14	12.8	1.7
<i>Ex situ</i>	9	1.8	0.5
Reference			
<i>In situ</i>	57	7.0	1.4
Reference			

benzothiophene (TH-DBT) through the hydrogenative pathway (HYD) as can be seen in **Figure 4(a)**. Since these two pathways are parallel and competitive, the selectivity (HYD/DDS) is determined by [23]:

$$\text{HYD/DDS} = ([\text{CHB}] + [\text{TH-DBT}]) / [\text{BP}] \quad (1)$$

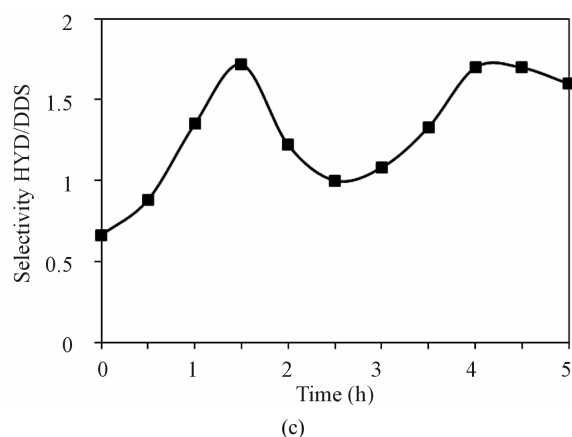
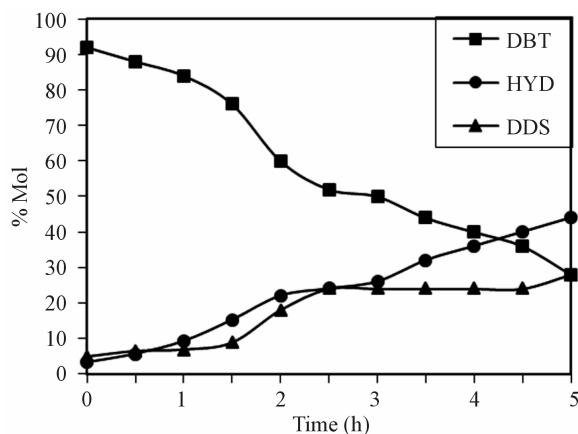
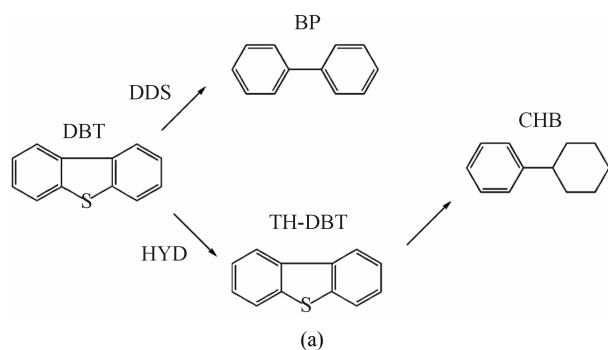
The experimental constant rate (pseudo-zero-order because the DBT concentration decreased linearly with time) is given in moles of DBT transformed by second in 1 g of catalyst, and it was calculated from the experimental slope of the plots of DBT concentration versus time according to the equation:

$$\begin{aligned} & [\text{Slope}(1/\text{Hr})] \times (\text{Hr}/3600 \text{ s}) \\ & \times (1 \text{ mol}/1000 \text{ mmol}) \times 34 \text{ mmol} \times (1/\text{g}_{\text{cat}}) \end{aligned} \quad (2)$$

Where 34 mmol is the initial concentration of DBT.

The pseudo-zero-order rate constant values ( $k$ ) were calculated from the slope of the experimental data.

**Figure 4 (b)** shows the catalytic activity and the distribution of the reaction products of HDS of DBT of catalyst d. The final hydrogenation (HYD) products were cyclohexylbenzene (CHB) and tetrahydrodibenzothiophene (TH-DBT), and biphenyl (BP) of direct desulfuri-

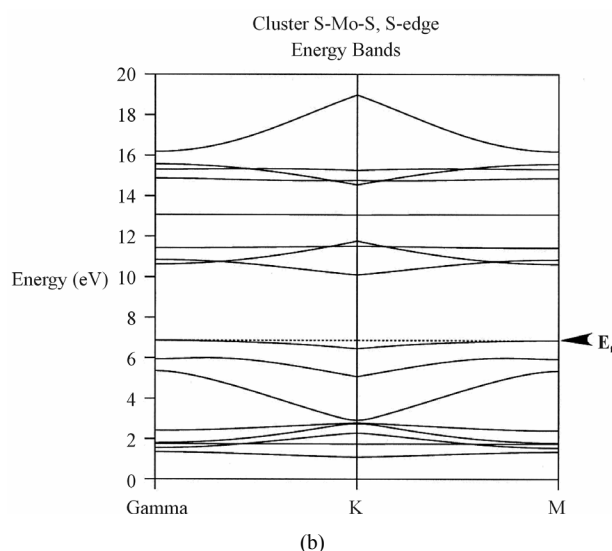
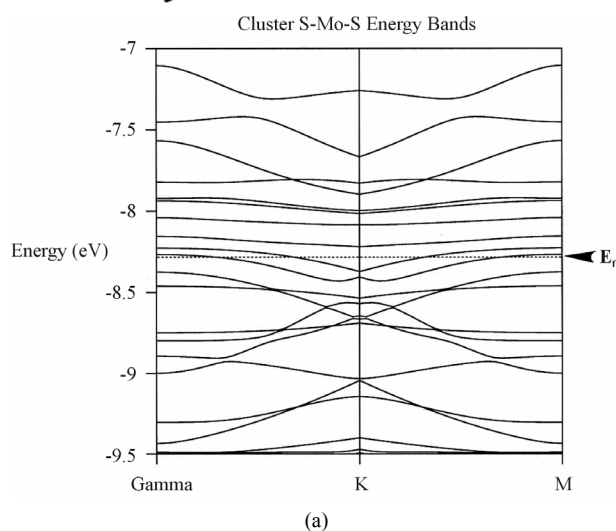
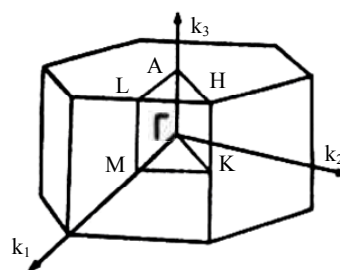


**Figure 4.** (a) Scheme of the HDS of DBT pathways; (b) Catalytic activity plots for the HDS of DBT for sample d, considering pure MoS<sub>2</sub> like the active phase; (c) Molar selectivity HYD/DDS plots of sample d.

zation (DDS).

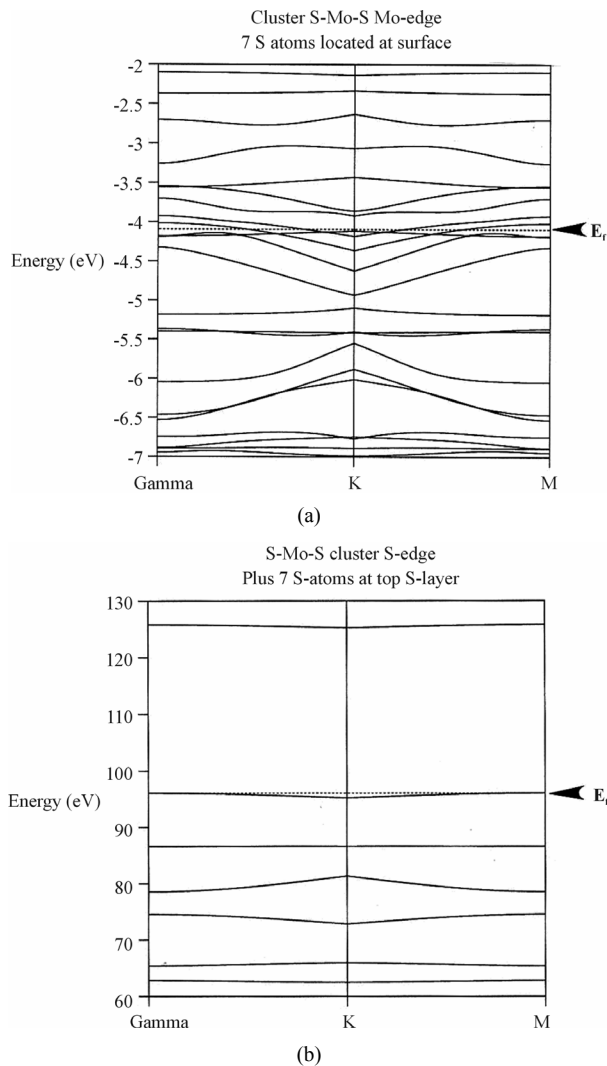
The molar selectivity HYD/DDS for hydrogenation reached a maximum of 1.7 in sulfide catalyst (for catalyst d) has can be seen from **Figure 4(c)**.

Band structure calculations for the 34 atoms/cluster Mo-edge and the 41 atoms/cluster S-edge MoS<sub>2</sub> clusters with and without seven S-atoms at the top the S-layer were calculated using 51 k-points for each case, and sampling the First Brillouin zone (FBZ) as depicted in **Figures 5** and **6(a)** and **(b)**, respectively.



**Figure 5.** (a) and (b) Band structure calculations for S-Mo-S Mo-edge and S-Mo-S S-edge with no sulfur atoms in the surface of S-layer. The inset depicts the Wigner-Seitz cell for a hexagonal configuration.

The inset in **Figure 5** depicts the Wigner-Seitz cell for a hexagonal configuration used in the calculations. The Fermi level is indicated by a horizontal dotted line separating the valence band (VB) from the conduction band (CB) respectively. Energy in eV vs  $k$ -values were plotted for each case, ranging from  $\Gamma$  (0 0 0) to K ( $1/3$   $1/3$  0) to M ( $1/2$  0 0) of  $\pi/a$ .



**Figure 6. (a) and (b) Energy bands for S-Mo-S Mo-edge and S-Mo-S S-edge with seven sulfur atoms decorated randomly at the surface of S-layer.**

It is accepted that 2H-MoS<sub>2</sub> crystalline bands are split into three sub bands separated by a forbidden gap ranging from 1.0 to 1.9 eV [24,25]. It is mandatory to mention that the cluster behavior could be expected to be different than the crystalline MoS<sub>2</sub> but the cluster should preserve some of the properties inherited from the crystal where it came from. Our calculations yielded indication of this event.

Energy bands for the 34 atoms/cluster Mo-edge and for the 41 atoms/cluster S-edge without and with seven sulfur atoms decorated at the surface of the S-layer are depicted in **Figures 5(a) and (b)** and **Figures 6(a) and (b)** respectively.

**Figure 5(a)** yields information regarding S-Mo-S Mo-edge (34 atoms/cluster) without the seven sulfur atoms at the surface of the S layer. Notice that  $E_f$  level is located within two multiple degenerate bands, providing indica-

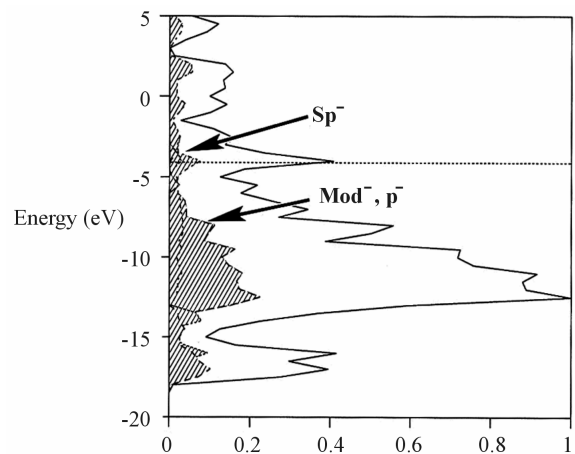
tion that the system is semi metallic. Whereas, **Figure 5(b)** yields information about S-Mo-S S-edge (41/atoms/cluster) without S-atoms located randomly at the surface of the S-layer. Opposite to the case of **Figure 5(a)**, the  $E_f$  is located at the top of a multiple degenerate band yielding a forbidden gap  $E_g \sim 3.6$  eV yielding information of a semiconductor.

In addition, **Figures 6(a) and (b)** yielded information regarding S-Mo-S Mo-edge and S-Mo-S S-edge when seven sulfur atoms were randomly decorated on the surface of the S-layer to form 41 atoms/cluster and 48 atoms/cluster respectively.

**Figure 6(a)** yielded information regarding S-Mo-S Mo-edge with seven S-atoms at the surface of the S layer. The  $E_f$  has been shifted up due to the seven sulfur atoms and it is now located in between three or more multiple degenerate bands, providing information that the new system has become more metallic than the case of **Figure 5(a)**. On the other hand, **Figure 6(b)** yielded information regarding S-Mo-S S-edge plus seven sulfur atoms decorating the sulfur layer. The  $E_f$  has been shifted up promoting a large gap and the system becomes an insulator.

Bollinger *et al.* [1] reported that one-dimensional metallic states formed at the edges of a single layer of MoS<sub>2</sub> clusters, showing that if MoS<sub>2</sub> gets confined to a size where only edges are present, both the geometric and the electronic configurations will be different from the bulk. Hence, it is expected that the nanofibers, undergoes a structural rearrangement preserving a resemblance to the crystal with a subsequent formation of metallic states.

Similarly, Sun *et al.* [26] performed an investigation on the details of the edge surfaces of unprompted and Ni(Co)-promoted WS<sub>2</sub> catalysts using density functional (DFT) under generalized gradient approximation (GGA) considering the effect of reaction conditions. Nickel tends to substitute the tungsten on the W-edge in the Ni-



**Figure 7. Total and projected DOS for S-Mo-S Mo-edge with seven sulfur atoms located randomly at the surface of the S-layer.**

promoted catalyst, while cobalt rather takes the position of tungsten at the S-edge in the Co-promoted catalyst.

The total and projected density of states (PDOS) for the S-Mo-S Mo-edge is depicted in **Figure 7**. Solid line represents total DOS, while the hatched dotted lines are the selected projected DOS for each orbital of the selected atoms. Horizontal dotted line indicates the Fermi level. We have shown only the S-Mo-S Mo-edge, due that catalytic enhancement toward hydrogenation is speculated, to be responsible off. Furthermore, we concentrate on those orbitals from the atoms which contributes most to the total DOS in the vicinity of  $E_f$  because they manifest their metallic behavior.

The overlap (hybridization) is formed by Mo d- and p- with S p-orbitals of the same symmetry. This hybridization could be considered to be responsible of the metallic states presented at the Mo-edge. Moreover, it is necessary to point out that the contributions from the seven sulfur atoms randomly located at the sulfur layer, contribute almost nothing to the total DOS. Instead, they participate as bridges through out the metallic states are promoted. Similar behavior has been reported by Reshak *et al.* [27] in 2H-MoS<sub>2</sub> intercalated with lithium where they reported that Li has a weak hybridization with Mo and S-states.

#### 4. Conclusions

We have shown the synthesis and the catalysis in the HDS of DBT reaction of a nanostructured self-supported catalyst containing MoS<sub>2+x</sub> nanoplatelets. The enhancement of higher activity observed in sulfide catalyst d with respect to the *ex situ* and *in situ* references is more closely related to the morphology change of particles (nanoplatelets).

Cluster calculations made on the S-Mo-S Mo-edge (34 atoms/cluster) cluster and on the S-Mo-S S-edge (41 atoms/cluster) without and with seven sulfur atoms randomly located at the surface the sulfur layer yield the following conclusions.

Our results yielded indication that the fact to form the S-Mo-S Mo-edge, S-Mo-S S-edge without and with seven sulfur atoms on the surface the S-layer, their properties depart from the crystalline MoS<sub>2</sub> but not to a great extent as to preserve resemblance of the microscopic crystal.

From the energy band analysis, the following conclusions were obtained:

1) For the cluster S-Mo-S Mo-edge without the S-atoms located at the surface the S-layer yielded metallic behavior.

2) For the cluster S-Mo-S S-edge without seven sulfur atoms at the surface of the S-layer yielded semi conductor behavior with a reported  $E_g \sim 3.6$  eV between the valence band and the conduction band.

3) For case a) with seven sulfur atoms located at the top of S-layer, the system becomes more metallic. While for case b) with seven sulfur atoms located at the top of S-layer, the system indicates an insulator behavior.

Total and projected DOS provide information that there exists hybridization in the vicinity of the  $E_f$  for the S-Mo-S Mo-edge with seven sulfur atoms at the top the S-layer. The contributions were from Mo d- and p- with S p-orbitals. The S p-orbital contributions from the seven sulfur atoms were negligible, which make us believe that they serve only as a bridge throughout the metallic states promoted.

Our results corroborate experimental findings that the catalytic activity could be correlated to the existence of metallic edges of the MoS<sub>2</sub> clusters decorated with S atoms at the top the sulfur layer and suggest a direct way of tailor catalysts.

#### 5. Acknowledgements

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#### REFERENCES

- [1] M. V. Bollinger, J. V. Lauritsen, K. W. Jacobsen, J. K. Nørstov, S. Helveg and F. Besenbacher, "One-Dimensional Metallic Edge States in MoS<sub>2</sub>," *Physical Review Letters*, Vol. 87, No. 19, 2001, Article ID: 196803. <http://dx.doi.org/10.1103/PhysRevLett.87.196803>
- [2] S. Helveg, J. V. Lauritsen, E. Lægsgaard, I. Stensgaard, J. K. Nørskov, B. S. Clausen, H. Topsøe and F. Besenbacher, "Atomic-Scale Structure of Single Layer MoS<sub>2</sub> Nanoclusters," *Physical Review Letters*, Vol. 84, No. 5, 2000, pp. 951-954. <http://dx.doi.org/10.1103/PhysRevLett.84.951>
- [3] J. V. Lauritsen, S. Helveg, E. Lægsgaard, I. Stensgaard, B. S. Clausen, H. Topsøe and F. Besenbacher, "Atomic-Scale Structure of Co-Mo-S Nanostructures in Hydro treating Catalysis," *Journal Catalysis*, Vol. 197, No. 1, 2001, pp. 1-5.
- [4] J. V. Lauritsen, M. V. Bollinger, E. Laegsgaard, K. W. Jacobsen, J. K. Nørskov, B. S. Clausen, H. Topsøe and F. Besenbacher, "Atomic-Scale Insight into Structure and Morphology Changes of MoS<sub>2</sub>," *Journal of Catalysis*, Vol. 221, No. 2, 2004, pp. 510-522. <http://dx.doi.org/10.1016/j.jcat.2003.09.015>
- [5] J. V. Lauritsen, M. Nyberg, J. K. Nørskov, B. S. Clausen, H. Topsøe, E. Laegsgaard and F. Besenbacher., "Hydrodesulfurization Reaction Pathways on MoS<sub>2</sub> Nanoclusters," *Journal of Catalysis*, Vol. 224, No. 1, 2004, pp. 94-106. <http://dx.doi.org/10.1016/j.jcat.2004.02.009>
- [6] L. S. Byskov, J. K. Nørskov, B. S. Clausen and H. Topsøe, "DFT Calculations of Unpromoted and Promoted MoS<sub>2</sub>-Based Hydrodesulfurization Catalysts," *Journal of Catalysis*, Vol. 187, No. 1, 1999, pp. 109-122. <http://dx.doi.org/10.1006/jcat.1999.2598>

- [7] L. S. Byskov, J. K. Norskov, B. S. Clausen and H. Topsøe, "Edge Termination of MoS<sub>2</sub> and CoMoS Catalyst Particles," *Catalysis Letters*, Vol. 64, No. 2-4, 2000, pp. 95-99. <http://dx.doi.org/10.1023/A:1019063709813>
- [8] H. Schweiger, P. Raybaud, G. Kresse and H. Toulhoat, "Shape and Edge State Modification of MoS<sub>2</sub> Catalytic Nanoparticles Induced by Working Copnditions: A Theoretical Study," *Journal of Catalysis*, Vol. 207, No. 1, 2002, pp. 76-87. <http://dx.doi.org/10.1006/jcat.2002.3508>
- [9] A. Carlsson, M. Brorson and H. Topsøe, "Morphology of WS<sub>2</sub> Nanoclusters in WS<sub>2</sub>/C Hydrodesulfurization Catalysts Revealed by High-Angle Annular Dark-Field Transmission Electron Microscopy (HAADF-STEM) Imaging," *Journal of Catalysis*, Vol. 227, No. 2, 2004, pp. 530-536. <http://dx.doi.org/10.1016/j.jcat.2004.08.031>
- [10] M. Egorova and R. Prins, "Hydrodesulfurization of Dibenzothiophene and 4,6-Dimethyldibenzothiophene over Sulfided NiMo/γ-Al<sub>2</sub>O<sub>3</sub>, CoMo/γ-Al<sub>2</sub>O<sub>3</sub> and Mo/γ-Al<sub>2</sub>O<sub>3</sub> Catalysts," *Journal of Catalysis*, Vol. 225, No. 2, 2004, pp. 417-427. <http://dx.doi.org/10.1016/j.jcat.2004.05.002>
- [11] M. Egorova and R. Prins, "Competitive Hydrodesulfurization of 4, 6 Dimethyldibenzothiophene, Hydrodinitrogenation of 2-Methylpyridine, and Hydrogenation of Naphthalene over Sulfided NiMo/γ-Al<sub>2</sub>O<sub>3</sub>," *Journal of Catalysis*, Vol. 224, No. 2, 2004, pp. 278-287. <http://dx.doi.org/10.1016/j.jcat.2004.03.005>
- [12] F. Dumeignil, K. Sato, M. Imamura, N. Matsubayashi, E. Payen and H. Shimada, "Characterization and Hydrodesulfurization Activity of CoMo Catalyst Supported on Sol-gel Prepared Al<sub>2</sub>O<sub>3</sub>," *Applied Catalysis A: General*, Vol. 287, No. 1, 2005, pp. 135-145.
- [13] G. A. Camacho-Bragado, A. Olivas, S. Fuentes, D. H. Galvan and M. José-Yacamán, "Structure and Catalytic Properties of Nanostructured Molybdenum Sulfides," *Journal of Catalysis*, Vol. 234, No. 1, 2005, pp. 182-190. <http://dx.doi.org/10.1016/j.jcat.2005.06.009>
- [14] T. P. Prasad, E. Diemann and A. Muller, "Thermal Decomposition of (NH<sub>4</sub>)<sub>2</sub>MoO<sub>2</sub>S<sub>2</sub>, (NH<sub>4</sub>)<sub>2</sub>WO<sub>2</sub>S<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub>," *Journal of Inorganic and Nuclear Chemistry*, Vol. 35, No. 6, 1973, pp. 1895-1904. [http://dx.doi.org/10.1016/0022-1902\(73\)80124-1](http://dx.doi.org/10.1016/0022-1902(73)80124-1)
- [15] M.-H. Whangbo and R. Hoffmann, "The Band Structure of the Tetracyanoxilatinate Chain," *Journal of the American Chemical Society*, Vol. 100, No. 19, 1978, pp. 6093-6098. <http://dx.doi.org/10.1021/ja00487a020>
- [16] R. Hoffmann, "An Extended Hückel Theory of Hydrocarbons," *Journal of Chemical Physics*, Vol. 39, No. 6, 1963, pp. 1397-1412. <http://dx.doi.org/10.1063/1.1734456>
- [17] G. A. Landrum, "F Orbitals Are Included in the Calculations as Version 3.0x, Using W. V. Glassey's Routine." <http://overlap.chem.Cornell.edu:8080/yaehmop.html>
- [18] W. V. Glassey, G. A. Papoian, R. Hoffmann, "Total Energy Partitioning within a One-electron Formalism: A Hamiltonian Population Study of Surface-CO Interaction in the C(2x2)-CO/Ni(100) Chemisorption System," *Journal of Chemical Physics*, Vol. 111, No. 3, 1999, pp. 893-910.
- [19] D. H. Galvan, "An Extended Hückel Calculation on Cubic Boron Nitride and Diamond," *Journal of Materials Science Letters*, Vol. 17, No. 10, 1998, pp. 805-810. <http://dx.doi.org/10.1023/A:1006630320896>
- [20] P. D. Fleischauer, J. R. Lince, P. A. Bertrand, R. Baner, "Electronic Structure and Lubrication Properties of MoS<sub>2</sub>: A Qualitative Molecular Orbital Approach," *Langmuir*, Vol. 5, No. 4, 1989, pp. 1009-1015. <http://dx.doi.org/10.1021/la00088a022>
- [21] S. Alvarez, "Tables of Parameters for Extended Huckel Calculations," Universitat de Barcelona, Barcelon, 1993.
- [22] E. Lifshin, "X-Ray Characterization of Materials," Wiley-VCH, Weinheim, Federal Republic of Germany, 1999, p. 74.
- [23] D. D. Witheurst, T. Isoda and I. Mochida, "Present State of the Art and Future Challenges in the Hydrodesulfurization of Polyaromatic Sulfur Compounds," *Advanced Catalysis*, Vol. 42, No. 4, 1998, pp. 345-471. [http://dx.doi.org/10.1016/S0360-0564\(08\)60631-8](http://dx.doi.org/10.1016/S0360-0564(08)60631-8)
- [24] L. F. Mattheiss, "Band Structure of Transition-Metal-Chalcogenides Layer Compounds," *Physical Review*, Vol. 8, No. 8, 1973, pp. 3719-3740.
- [25] A. J. Grand, T. M. Griffiths, G. D. Pitts and A. D. Yoffe, "The Electrical Properties and the Magnitude of the Indirect Gap in the Semiconducting Transition Metal Dichalcogenide Layer Crystals," *Journal of Physics C: Solid State Physics*, Vol. 8, No. 1, 1975, p. L17.
- [26] M. Sun, A. E. Nelson and J. Adjaye, "A DFT Study of WS<sub>2</sub>, NiWS and CoWS Hydrotreating Catalysts," *Journal of Catalysis*, Vol. 226, No. 1, 2004, pp. 41-53. <http://dx.doi.org/10.1016/j.jcat.2004.04.023>
- [27] A. H. Reshak and S. Auluck, "Calculated Optical Properties of 2H-MoS<sub>2</sub> Intercalated with Lithium," *Physical Review*, Vol. 68, No. 12, 2003, Article ID: 125101.
- [28] M. W. Wolfsberg and L. Helmoltz, "The Spectra and Electronic Structure of the Tetrahedral Ions MnO<sub>4</sub><sup>-</sup>, CrO<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>," *Journal of chemical Physics*, Vol. 20, No. 5, 1952, pp. 837-843.