

# HYDRODESULFURIZATION OF THIOPHENIC COMPOUNDS ON MoS<sub>2</sub>: A COMPUTATIONAL STUDY USING ZINDO

Xiaoliang Ma and Harold H. Schobert  
Fuel Science Program, Department of Materials Science and Engineering  
The Pennsylvania State University, 209 Academic Projects Building,  
University Park, PA 16802-2303

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## INTRODUCTION

To meet environmental regulations on reduction of sulfur content in fuels there has been a growing need to develop new catalysts that can carry out deep hydrodesulfurization (HDS). MoS<sub>2</sub> and sulfided Co (or Ni) promoted molybdenum catalysts have been used extensively in HDS, both in basic investigations and in petroleum refineries. However, the nature of the active sites, even on a single slab of MoS<sub>2</sub>, as well as how they interact with sulfur species are still unclear. Considerable effort has been devoted to understanding the active sites of MoS<sub>2</sub> crystal and their HDS mechanisms. Some excellent reviews have been published in this regard (1-3). Since it is still difficult technically to characterize the chemical properties of the MoS<sub>2</sub> surface, some researchers have done chemical simulations or calculations in order to understand the active sites on the surface of MoS<sub>2</sub> catalyst and their interaction with sulfur species. Most of them used smaller clusters as a model, the classical Newtonian physics method (molecular mechanics) or the extended Hückel molecular orbital method which is an empirical approximation (4-9). The nature of the active sites and mechanisms of reaction suggested by the results were very different among these various studies.

In this study, we used a semi-empirical quantum chemical method, ZINDO (Zerner's Intermediate Neglect of Differential Overlap program), and chose a single slab of regular hexagonal Mo<sub>12</sub>S<sub>38</sub> as a basic model to examine possible active sites or active edges by removing the sulfur atoms from the periphery of Mo<sub>12</sub>S<sub>38</sub> cluster on the basis of their bond orders and required energy. Furthermore, the interaction of inferred active sites with the sulfur species was explored by comparison of the total energies of different adsorption states. We attempt to answer 1) which positions at MoS<sub>2</sub> crystal are easier to form the sulfur vacancies, or which edge in a single slab of MoS<sub>2</sub> is easier to form a sulfur poor edge; and 2) how such sulfur vacancies or sulfur poor edge interact with thiophenic compounds.

## MODELING AND COMPUTATION

In order to make the cluster of MoS<sub>2</sub> be a more realistic mimic of highly dispersed MoS<sub>2</sub> particles, we designed a single slab of regular hexagonal Mo<sub>12</sub>S<sub>38</sub> as a basic model cluster, which contains 12 Mo and 38 S atoms as shown in Figure 1. There are two types of edge plane, as noted by I (1010) and II (1010) respectively. Each S atom in the edge I plane bonds with only one Mo atom, and each S atom in the edge II plane bonds with two neighboring Mo atoms. In this cluster, the S/Mo ratio is not stoichiometric. To keep the S/Mo ratio around 2 and to form the sulfur vacancies, the sulfur atoms at the periphery of the cluster should be removed. Reasonable positions of the sulfur vacancies and the sulfur-poor edge were determined by comparison of the charge distribution, bond indexes in the Mo<sub>12</sub>S<sub>38</sub> cluster, and the total energy of the clusters with sulfur vacancies. The adsorption configuration of sulfur species on the formed sulfur vacancies was examined by locating the sulfur atom of a sulfur species at an appointed sulfur vacancy. The adsorption state was explored by comparison in the total energy of compound-cluster system.

The Mo—Mo, Mo—S and S—S bond lengths were determined according to MoS<sub>2</sub> crystal size from the literature (4, 6). The geometries of the sulfur species were optimized by using ZINDO before locating them at the sulfur vacancies. The calculation of charge distribution, bond order and the total energy of the clusters and compound-cluster was done without geometry optimization.

All quantum chemical calculation in this study was done by using ZINDO, which was developed by the University of Florida Quantum Theory Project. ZINDO uses the theoretically based INDO parameterization and therefore can use d orbitals, and then can be used for many transition series metals (10).

## RESULTS AND DISCUSSION

*1) Electronic properties of Mo<sub>12</sub>S<sub>38</sub> cluster.* According to their different positions, the sulfur atoms in Mo<sub>12</sub>S<sub>38</sub> cluster can be classified into five types which are labeled with *a*, *b*, *c*, *d* and *e*, respectively, as shown in Figure 1. Each sulfur atom on the corner (position *b*) and in the edge plane I (position *a*) is bonded to one Mo atom, and each sulfur atom in the edge plane II (position *c*) is bonded to two Mo atoms. All sulfur atoms in the basal plane are connected with three Mo atoms. The Mo atoms sandwiched between the top and bottom basal planes in the cluster can also

be classified into three types on the basis of their positions, which are labeled with  $\alpha$ ,  $\beta$  and  $\gamma$ , respectively.

The calculated results of charge distribution and bond index of  $\text{Mo}_{12}\text{S}_{38}$  cluster are listed in Table 1 and 2, respectively. The results show that the charge distribution is strongly dependent on the atomic position in the cluster. S(b), the sulfur located at the position *b*, has the least negative charge in all of S atoms, being  $-0.486$ . S(a) located in the position *a* has the second least negative charge. As connected with two Mo atoms, S(c) has larger negative charge although it is located in a edge plane. The sulfur atoms in the two basal planes, S(d) and S(e), have the largest negative charge among the five types of the sulfur atoms, due to their bonding with three Mo atoms. Such charge distribution suggests that S(b) and S(a) atoms have less interaction with the cluster whole than that of S(c) atoms.

With the bond indexes listed in Table 2, it was found that all bond indexes between neighboring S and Mo atoms are higher than 0.8, indicating that there is a strong interaction between neighboring S and Mo atoms, and the atoms in  $\text{MoS}_2$  lattice are held together dominantly through such bonding. There is also considerable interaction between two neighboring Mo atoms, their bond indexes being in the range 0.18–0.31. Most pairs of two neighboring S atoms show weak interactions, with the exception of S(a)—S(a') and S(b)—S(b') bonds. In this study, our interest is focused on the sulfur atoms at the periphery of the cluster. The S(c)—Mo( $\beta$ ) bond index is 1.023, lower than those of S(a)—Mo( $\alpha$ ) (1.248) and S(b)—Mo( $\beta$ ) (1.158). However, the S(c) atom is connected simultaneously with two Mo( $\beta$ ) atoms, and the sum of the two bond indexes is as high as 2.046. The results indicate that S(a) and S(b) atoms are the easier to be removed than an S(c) atom during the formation of the sulfur vacancies, which is in agreement with the charge distribution as stated above. The calculation of the total energy of the cluster with a sulfur vacancy at the position *a*, *b* and *c*, respectively, was also done, and the results show that the cluster with S(b) vacancy has the lowest energy, while the cluster with S(c) vacancy has the highest energy in three types of the sulfur atoms. These results further support the point that the sulfur vacancies formed should be on the corner and the edge plane 1.

2) *Adsorption of sulfur species on sulfur vacancies.* In order to examine the interaction of sulfur species with the sulfur vacancies, we chose Mo( $\alpha$ ) in the  $\text{Mo}_{12}\text{S}_{36}$  cluster with six sulfur vacancies at the edge plane 1 as an active adsorption site, and assume that the sulfur atom of sulfur species is adsorbed at the position *a*. Considering atom limit and CPU in the calculation, a smaller cluster  $\text{Mo}_6\text{S}_{24}$  as shown in Figure 2A was designed to replace the  $\text{Mo}_{12}\text{S}_{36}$  cluster used above for the compound-cluster adsorption model. The reasonableness for such replacement is based on the consideration that 1) the edge in  $\text{Mo}_6\text{S}_{24}$  cluster has the same structure as the edge plane 1 in  $\text{Mo}_{12}\text{S}_{36}$  cluster; and 2) the calculated charge distribution in the edge plane of  $\text{Mo}_6\text{S}_{24}$  cluster shows it is similar to that in the edge plane 1 of  $\text{Mo}_{12}\text{S}_{36}$  cluster. The structure of  $\text{Mo}_6\text{S}_{18}$  cluster, which is derived from  $\text{Mo}_6\text{S}_{24}$  cluster by removing six sulfur atoms in an edge plane, and the thiophene- $\text{Mo}_6\text{S}_{18}$  adsorption are shown respectively in Figure 2B and 2C. The change in the total energy of the thiophene- $\text{Mo}_6\text{S}_{18}$  with the angle included between thiophenic plane and the edge plane are listed in Table 3. It was found that the thiophene- $\text{Mo}_6\text{S}_{18}$  has the least energy at  $0^\circ$  angle, meaning that a parallel adsorption as shown in Figure 3A is the most stable. The same results were also observed when replacing the adsorbate on  $\text{Mo}_6\text{S}_{18}$  cluster with dibenzothiophene. Two other adsorption configurations, as shown in Figure 3B and 3C, respectively, were also calculated, and both have higher total energy than that of the parallel adsorption. The calculated results suggest that thiophene and dibenzothiophene are adsorbed on the exposed Mo( $\alpha$ ) atom not only through a S—Mo( $\alpha$ ) bond but also through a bond between  $\pi$  electrons on the thiophenic ring and Mo( $\alpha$ ) atom. The parallel adsorption of such sulfur compounds on the exposed Mo( $\alpha$ ) atom is the most stable in the all adsorption cases addressed in this study.

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**Table 1** Charge distribution in  $\text{Mo}_7\text{S}_{38}$  cluster

Atom	Charge
Sulfur	
a	-0.550
b	-0.486
c	-0.733
d	-0.748
e	-0.808
Molybdenum	
$\alpha$	+2.095
$\beta$	+2.173
$\gamma$	+1.609

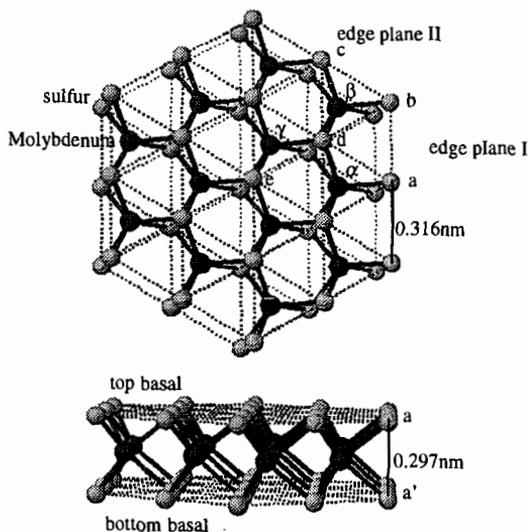
**Table 3** Total energy of compound- $\text{Mo}_6\text{S}_{18}$  at different included angle  $\theta$

Included angle $\theta^\circ$	Total energy (a.u.*)	
	thiophene	dibenzothiophene
0	-275.53	-330.49
45	-273.65	-325.89
90	-273.00	
135	-272.90	

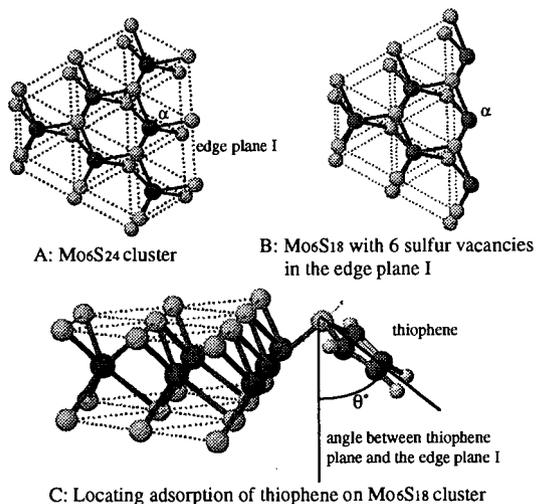
\* atomic units

**Table 2** Bond index in  $\text{Mo}_7\text{S}_{38}$  cluster

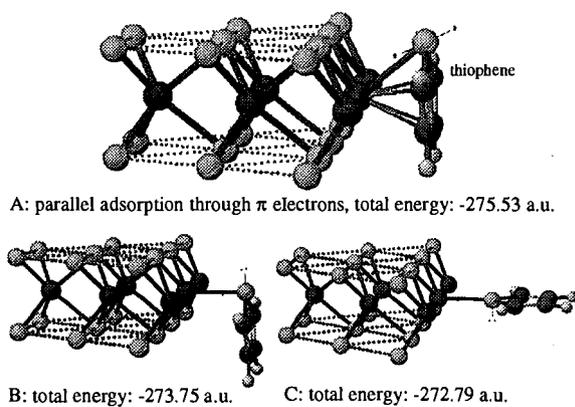
S-Mo bond	bond index	Mo-Mo bond	bond index	S-S bond	bond index
S(a)-Mo( $\alpha$ )	1.248	Mo( $\alpha$ )-Mo( $\beta$ )	0.185	S(a)-S(b)	0.153
S(b)-Mo( $\beta$ )	1.158	Mo( $\alpha$ )-Mo( $\gamma$ )	0.296	S(a)-S(d)	0.060
S(c)-Mo( $\beta$ )	1.023	Mo( $\beta$ )-Mo( $\beta$ )	0.232	S(b)-S(c)	0.068
S(d)-Mo( $\alpha$ )	0.815	Mo( $\beta$ )-Mo( $\gamma$ )	0.302	S(b)-S(d)	0.057
S(d)-Mo( $\beta$ )	0.844	Mo( $\gamma$ )-Mo( $\gamma$ )	0.308	S(a)-S(a')	0.206
S(d)-Mo( $\gamma$ )	0.826			S(b)-S(b')	0.738
S(e)-Mo( $\gamma$ )	0.836			S(c)-S(c')	0.094



**Figure 1** Schematic diagram of  $\text{Mo}_{12}\text{S}_{38}$  cluster



**Figure 2** Schematic diagrams of Mo<sub>6</sub>S<sub>24</sub> and thiophene-Mo<sub>6</sub>S<sub>18</sub>



**Figure 3** Different adsorption states of thiophene on sulfur poor edge of Mo<sub>6</sub>S<sub>18</sub>