ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

Technical Progress Report for the Period
March 1992-May 1992

Kamil Klier
and
Richard G. Herman
with
Michelle Richards-Babb

Zettlemoyer Center for Surface Studies
and Department of Chemistry
Lehigh University
Bethlehem, PA 18015

June 1992

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY-Pittsburgh Energy Technology Center

Under Contract No. DE-FG22-91PC91301

U.S.-DOE Patent Clearance is not required prior to publication of this document.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL
SULFIDE CATALYSTS

Disclaimer

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.
ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

TECHNICAL PROGRESS

During this quarter, the high pressure (up to 100 atm), high temperature (up to 350°C) catalyst testing system was rebuilt with clean tubing, etc. A new preparation of MoS₂ catalyst was carried out, and this catalyst will be doped with alkali and tested during the next quarter of research.

To provide insight into the desired MoS₂ morphology that will enhance the activation of hydrogen over these catalysts, theoretical calculations have been carried out with respect to the adsorption of hydrogen atoms and molecules on the MoS₂ basal plane and on edge sites. The molecular orbital calculations show that in both cases, with the 1-D model with \( \frac{H}{MoS_2} = \frac{1}{5} \) and the 2-D model with \( \frac{H}{MoS_2} = \frac{1}{1} \), the most stable sites for hydrogen adsorption are the sulfur atoms rather than the molybdenum atoms. However, in the 1-D model calculations, among the molybdenum atom sites the most favorable for hydrogen adsorption would be the four-coordinate edge Mo site (Mo-0101 Edge (1)). The calculations show that the edge S sites are energetically favored sites for the activation of hydrogen. However, the most energetically favored site derived from these calculations is the 1-D MoS₂ S-0301 basal site that is near the MoS₂ edges. Therefore, small crystallite size MoS₂, having a high surface area and a high proportion of edge sites to basal plane sites, is the preferred morphology for these alcohol synthesis catalysts.
ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

TECHNICAL PROGRESS

Alkali doped molybdenum disulfide, A/ MoS\(_2\), has been studied for the production of C\(_1\)-C\(_4\) alcohols from synthesis gas, CO/H\(_2\). In this system, the alkali doped MoS\(_2\) is referred to as a bifunctional catalyst such that the alkali component activates the C-O bond and the MoS\(_2\) surface activates hydrogen. Activation of hydrogen has been proposed to occur via dissociative chemisorption on the MoS\(_2\) surface. However, the exact mechanism and location of hydrogen dissociation is not known. There is no conclusive experimental evidence for either heterolytic or homolytic dissociation of hydrogen. In addition, the location of hydrogen dissociation could be centered on the saturated basal plane atoms or on the coordinately unsaturated edge plane atoms. The focus of this work has been directed at understanding the electronic structure of bare and hydrogen-covered MoS\(_2\) surface both experimentally and theoretically. A simple theory, solid state extended Hückel theory, was used to theoretically calculate binding enthalpies of hydrogen atoms and molecules to basal and edge atoms of MoS\(_2\). A computer program developed by Whangbo et al entitled Extended Hückel Molecular and Crystal Properties Package was used to perform the calculations [1].

Prior to the start of theoretical calculations, it was necessary to obtain a model of basal plane and edge plane surfaces of MoS\(_2\) that retained the original stoichiometry and geometry of single crystal MoS\(_2\). Molybdenum disulfide, MoS\(_2\) forms a layer structure similar to graphite but with two crystal modifications. These modifications are the hexagonal structure denoted 2H-MoS\(_2\) and the rhombohedral structure denoted 3R-MoS\(_2\).
The number in front of the letter in this designation specifies the number of MoS$_2$ molecules per unit cell, two for the hexagonal modification and three for the rhombohedral modification. The focus of this research has been on the hexagonal modification since this is the structure of the synthesized polycrystalline samples, as well as of the naturally grown single crystals of MoS$_2$. Thus, the rest of this discussion will focus on the bulk structure of 2H-MoS$_2$. Background information on the transition metal disulfide structures is obtained from Wilson and Yoffe [2].

In 2H-MoS$_2$, the molybdenum atoms are coordinated to six sulfur atoms in a trigonal prismatic environment. The sulfur atoms are each coordinated to three molybdenum atoms. Formal charges of molybdenum and sulfur are generally given as +4 and -2, respectively. However, MoS$_2$ is actually a fairly covalent compound that shares its electrons between molybdenum and sulfur atoms substantially more than indicated by the formal charges. Calculated charges on molybdenum and sulfur are much smaller than the formal charges indicated.

A layer structure is formed by 2H-MoS$_2$ with two molecules of 2H-MoS$_2$ per unit cell. Three atomic layers consisting of first an atomic layer of sulfur, a second atomic layer of molybdenum, and a third atomic layer of sulfur that together make up one unit of MoS$_2$. One MoS$_2$ unit translated in two-dimensions within the layer by a linear integral combination of primitive translations $a = |a|/2(\bar{x} - 3^{1/2}\bar{y})$ and $b = |a|/2(\bar{x} + 3^{1/2}\bar{y})$ forms the infinite single sheet structure. Three-dimensional crystals are produced by stacking of the layers. The three-dimensional crystal is held together by weak Van der Waals forces between the sulfur atoms on adjacent sandwiches. In the three dimensional crystal, the real lattice vector, $c$, is perpendicular to the real lattice vectors, $a$ and $b$, and to the direction of propagation of the layers. The second MoS$_2$ molecule in 2H-MoS$_2$ resides in a second MoS$_2$. 


layer. This second layer is offset from the first such that molybdenum atoms in the second
are beneath (or above) sulfur atoms in the first layer, while sulfur atoms in the second are
beneath (or above) molybdenum atoms in the first layer. The length of the real lattice
vectors a and b is the same and equal to 3.16 Å. An angle between the vectors a and b is
120°. The length of c is 12.30 Å. The parameter u, equal to 0.128252, is defined as the
elevation of the sulfur atoms above and below the plane of molybdenum atoms in terms of
c. Thus, the two atomic layers of sulfurs in one MoS₂ sandwich are located 1.5775 Å and
-1.5775 Å above and below the atomic layer of molybdenums. The distance between the
layers of sulfur belonging to two different MoS₂ layers, the Van der Waals gap, is defined
as h and is equal to 0.243496 or in actual units, 2.995 Å. The structure of 2H-MoS₂ is
shown in Figure 1.

A two-dimensional infinite sheet of MoS₂ was used to model one layer of a 2H-MoS₂
single crystal. This structure excluded effects due to Van der Waals interactions between
layers. One molecule of MoS₂ translated in both the a and b directions produces the
two-dimensional layer. A schematic picture of the 2-D MoS₂ structure is shown in Figure
2.

The 2-D infinite layer of MoS₂ was terminated at different edge planes to
theoretically study the changes in electronic structure produced by the addition of edges.
Structures with two different edges, consisting of (10\overline{1}0) and (10\overline{1}1), were studied. A
structure with (10\overline{1}0) edges was produced by theoretically terminating the 2-D infinite sheet
with edges perpendicular to the basal plane (0002). A structure with (10\overline{1}1) edges was
produced by theoretically terminating the 2-D infinite sheet with inclined edges. The result
in both cases was a unit cell of five MoS₂ units that when propagated in one-direction, the
x direction, produced a sheet infinite in the x direction but of finite width in the y direction.
Schematic pictures of the 1-D (MoS$_2$)$_3$ structures terminating at the (10\overline{1}0) and (10\overline{1}1) edges are shown in Figures 3 and 4, respectively.

The structures discussed above expose molybdenum and sulfur atoms with different degrees of coordination on edge planes. In 2H-MoS$_2$, the molybdenum atoms are coordinated to six sulfur atoms while the sulfur atoms are coordinated to three molybdenum atoms. Addition of edges into these structures exposes atoms that are not fully coordinated. Addition of (10\overline{1}0) edges exposes two different edges. The first edge consists of two-coordinate molybdenum atoms; the second edge consists of one-coordinate sulfur atoms (in the first and third atomic layers). Addition of (10\overline{1}1) edges also exposes two different edges. The first edge consists of two-coordinate sulfur atoms and four-coordinate molybdenum atoms. The second edge consists of one-coordinate sulfur atoms (first atomic layer only) and five-coordinate molybdenum atoms. Thus, Mo atoms residing on (10\overline{1}1) edges have a higher degree of coordination than atoms residing on (10\overline{1}0) edges.

The energy of formation, $\Delta U^\circ$, of the 1-D (MoS$_2$)$_3$ systems containing edges must be compared to the energy of formation of the 2-D MoS$_2$ system containing no edges. This is a correct comparison since these structures each contain one MoS$_2$ layer such that Van der Waals interactions are not present. The energy of formation of 1-D (MoS$_2$)$_3$ structures terminating at the (10\overline{1}0) and (10\overline{1}1) edges are $-435.75$ kcal/mole and $-447.28$ kcal/mole, respectively, while that of 2-D MoS$_2$ is $-463.58$ kcal/mole. Thus, addition of (10\overline{1}0) and (10\overline{1}1) edges destabilizes the structure since both of the structures with edges were found to be less stable when compared to the 2-D MoS$_2$ system possessing no edges. Theoretically, the energy of formation of the 1-D (MoS$_2$)$_3$ structure was found to be more stable by 11.5 kcal/mole when it terminated at the (10\overline{1}1) edges rather than at the (10\overline{1}0) edges. Addition of these edges also leads to edge states that widen the S 3s valence band.
specifically at the K point. Unoccupied surface states also appear at the top of the valence band leading to overlap of the conduction and valence bands. Since the 1-D (MoS$_2$)$_3$ system terminating in (1011) edges was found to be the more stable structure, this structure was later studied in greater detail in terms of hydrogen adsorption.

Hydrogen adsorption on 2-D MoS$_2$ was first studied by theoretically placing a hydrogen atom at different sites on the basal plane. Since the 2-D MoS$_2$ structure contained no edges, only two hydrogen sites were calculated. In the first structure, a hydrogen atom was placed directly above a basal plane sulfur atom such that the S-H distance was 1.35 Å. The S-H distance in hydrogen sulfide, H$_2$S is 1.3455 Å [3]. In the second structure, a hydrogen atom was placed directly above a molybdenum atom such that the Mo-H distance was 1.7 Å. Due to the trigonal prismatic coordination of molybdenum, hydrogen atoms in the second structure were also located 1.83 Å away from three equivalent sulfur atoms. These structures are highly saturated with hydrogen because there is one hydrogen atom per unit of MoS$_2$. A schematic representation of the sulfur and molybdenum sites is given in Figure 5. Theoretical binding enthalpies can be obtained from the enthalpies of formation of the bare and hydrogen covered 2-D MoS$_2$ surface. The first reaction under consideration is the reaction of hydrogen atoms, $\text{H}^0$, with the basal plane of an MoS$_2$ surface, Equation 1a. As indicated in Table 1, when the MoS$_2$ is theoretically exposed to hydrogen atoms, formed via Equation 1b, hydrogen preferentially adsorbs on exposed sulfur atoms. Molybdenum atoms are not a thermodynamically favored site for hydrogen adsorption in this study, since a positive enthalpy is calculated for reaction 1a. The next reaction under consideration is the reaction of hydrogen molecules, H$_2$, with the basal plane of an MoS$_2$ surface, Equation 1c. This reaction was studied because most of the experimental results for hydrogen adsorption on MoS$_2$ were performed using hydrogen gas not hydrogen atoms.
Again as indicated in Table 1, thermodynamically the most stable sites for hydrogen adsorption are the sulfur atoms.

\[
\begin{align*}
\text{H}^0 (g) + \text{MoS}_2 (s) & \rightarrow \text{H-MoS}_2 (s) \quad \Delta H_1^\circ = \text{see Table 1} \quad (1a) \\
\frac{1}{2} \text{H}_2 (g) & \rightarrow \text{H}^0 (g) \quad \Delta H_2^\circ = 52.10 \text{ kcal/mol} \quad (1b) \\
\frac{1}{2} \text{H}_2 (g) + \text{MoS}_2 (s) & \rightarrow \text{H-MoS}_2 (s) \quad \Delta H_3^\circ = \text{see Table 1} \quad (1c)
\end{align*}
\]

Table 1.

Binding enthalpies of hydrogen atoms, \(\Delta H_1^\circ\), and molecules, \(\Delta H_3^\circ\), on the surface of 2-D MoS\(_2\). The two sites studied were hydrogen on sulfur and hydrogen on molybdenum. (Units are in kcal/mole.)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Atom</th>
<th>Site</th>
<th>Coordination</th>
<th>(\Delta H_1^\circ)</th>
<th>(\Delta H_3^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-D H-MoS(_2)</td>
<td>Mo</td>
<td>Basal</td>
<td>6</td>
<td>+10.24</td>
<td>+62.34</td>
</tr>
<tr>
<td>2-D H-MoS(_2)</td>
<td>S</td>
<td>Basal</td>
<td>3</td>
<td>-68.95</td>
<td>-16.85</td>
</tr>
</tbody>
</table>

Hydrogen adsorption on the 1-D (MoS\(_2\))\(_5\) model terminating in (10\,\overline{1}1) edges was studied theoretically by placing hydrogen atoms at various sites on the edge and basal plane atoms. The structure terminating in (10\,\overline{1}1) edges was chosen since this structure was found to be energetically more stable than the structure terminating in (10\,\overline{1}0) edges. Insight into possible sites for hydrogen adsorption was obtained from a study of the electronic structure of the bare 1-D (MoS\(_2\))\(_5\) surface. For instance, on the edge with 2-coordinate sulfur atoms exposed, dangling sulfur \(p_z\)-type orbitals are present at the top of the valence band. Thus, theoretically placing a hydrogen atom 1.35 Å away from this sulfur atom, in the +y direction, seems like a good site for hydrogen to adsorb. These structures are not as highly saturated
with hydrogen as in the previous case of 2-D MoS$_2$ because there is one hydrogen atom per five units of MoS$_2$. Schematic representations of hydrogen adsorbed edge and basal plane sites are given in Figure 6.

The calculated binding enthalpies of hydrogen atoms, $\Delta H_4^\circ$, on the 1-D (MoS$_2$)$_5$ structure terminating in (10\overline{1}1) edges are given in Table 2. Theoretically on this surface, the most stable sites for hydrogen atoms are on the edge and basal plane sulfur atoms. Reaction 2c shows the reaction of hydrogen molecules with the 1-D (MoS$_2$)$_5$ surface. The enthalpies for this reaction, $\Delta H_5^\circ$, are shown in Table 2. Again, the enthalpies indicate that edge and basal plane sulfur sites are the most thermodynamically favored for hydrogen adsorption. However, the four-coordinate edge molybdenum site is also thermodynamically favored for hydrogen adsorption. Five-coordinate edge and basal plane molybdenum atoms are not thermodynamically favorable sites for hydrogen adsorption. One of the reasons for the unfavorable binding enthalpy for hydrogen adsorption onto molybdenum basal plane sites could be the proximity of basal plane sulfur atoms. The basal plane of 2H-MoS$_2$ is generally thought to consist of sulfur atoms. Since, molybdenum atoms are coordinated to six sulfur atoms in a trigonal prismatic geometry, molybdenum atoms are buried beneath a surface of exposed atoms. Thus, when hydrogen adsorbs on a molybdenum atom it also resides close to three equivalent sulfur atoms. This may be the reason for the destabilization of the molybdenum basal plane sites compared to edge sites with smaller number of coordinating sulfur atoms.

\[
(MoS_2)_5 (s) + H^0 (g) \rightarrow H-(MoS_2)_5 (s) \quad \Delta H_4^\circ = \text{see Table 2} \quad (2a)
\]
\[
1/2 H_2 (g) \rightarrow H^0 (g) \quad \Delta H_2^\circ = 52.10 \text{ kcal/mol} \quad (2b)
\]
\[
(MoS_2)_5 (s) + 1/2 H_2(g) \rightarrow H-(MoS_2)_5 (s) \quad \Delta H_5^\circ = \text{see Table 2} \quad (2c)
\]
Table 2.

Binding enthalpies of hydrogen atoms, $\Delta H_1^\circ$, and molecules, $\Delta H_2^\circ$, on the surface of 1-D (MoS$_2$)$_5$ with (1011) edges. Four different edge sites and two basal plane sites were studied. (Units are in kcal/mole.)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Atom</th>
<th>Site</th>
<th>Coordination</th>
<th>$\Delta H_1^\circ$</th>
<th>$\Delta H_2^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-D (MoS$_2$)$_5$</td>
<td>S-0601</td>
<td>Edge(1)</td>
<td>2</td>
<td>-90.30</td>
<td>-38.20</td>
</tr>
<tr>
<td></td>
<td>Mo-0101</td>
<td>Edge(1)</td>
<td>4</td>
<td>-83.84</td>
<td>-31.74</td>
</tr>
<tr>
<td></td>
<td>S-0501</td>
<td>Edge(2)</td>
<td>1</td>
<td>-92.14</td>
<td>-40.05</td>
</tr>
<tr>
<td></td>
<td>Mo-0301</td>
<td>Edge(2)</td>
<td>5</td>
<td>-37.26</td>
<td>+14.84</td>
</tr>
<tr>
<td></td>
<td>S-0301</td>
<td>Basal</td>
<td>3</td>
<td>-101.60</td>
<td>-49.50</td>
</tr>
<tr>
<td></td>
<td>Mo-0201</td>
<td>Basal</td>
<td>6</td>
<td>-22.73</td>
<td>+29.37</td>
</tr>
</tbody>
</table>

REFERENCES


FIGURE CAPTIONS


2. Schematic representation of the 2-D MoS$_2$ model propagating infinitely in two dimensions but finite in the third direction.

3. A) Side view (parallel to the $x$-axis) of the 1-D (MoS$_2$)$_5$ structure terminating at the (10$\overline{1}$0) edges.
   B) Top view (parallel to the $z$-axis) of the 1-D (MoS$_2$)$_5$ structure terminating at the (10$\overline{1}$0) edges.

4. A) Side view (parallel to the $x$-axis) of the 1-D (MoS$_2$)$_5$ structure terminating at the (10$\overline{1}$1) edges.
   B) Top view (parallel to the $z$-axis) of the 1-D (MoS$_2$)$_5$ structure terminating at the (10$\overline{1}$1) edges.

5. Hydrogen adsorbed on basal plane sulfur and molybdenum in 2-D MoS$_2$.

6. Hydrogen adsorbed on the following adsorption sites on the 1-D (MoS$_2$)$_5$ surface that is terminated at the (10$\overline{1}$1) edges:
   A) edge 1 S-0601 (2-coordinate)
   B) edge 1 Mo-0101 (4-coordinate)
   C) edge 2 S-0501 (1-coordinate)
   D) edge 2 Mo-0301 (5-coordinate)
   E) basal plane S-0301 (3-coordinate)
   F) basal plane Mo-0201 (6-coordinate).
FIGURE 2

Model of 2-D MoS$_2$
FIGURE 3B

1-coordinate S-0501, S-0601 (Edge 2)
2-coordinate Mo-0101 (Edge 1)

(Direction of propagation)
FIGURE 4A

Edge 2

1-coordinate S (S-0501)

5-coordinate Mo (Mo-0301)

4-coordinate Mo (Mo-0101)

2-coordinate S (S-0601)

Edge 1
FIGURE 6B
FIGURE 6C
FIGURE 6E

H on S-0301
(Basal plane, +z)
FIGURE 6F

H on Mo-0201
(Basal plane, +z)

Edge 1

Edge 2
END

DATE FILMED

9/10/4/1992