ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

Technical Progress Report for the Period

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Kamil Klier
and
Richard G. Herman
with
Michael Deemer

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

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SUMMARY OF TECHNICAL PROGRESS

During this quarter, the surface areas of various catalysts were determined. The surface area of the catalyst tested last quarter was determined for the undoped catalyst, the doped catalyst before testing, and the doped catalyst after testing. These surface areas were then compared with ones reported earlier [1]. After testing under high temperature and high pressure conditions for 551 hours, there was a loss of surface area. This might be due possibly to agglomeration of cesium formate on the surface.

Higher surface area catalysts were also produced. Two samples of MoS$_2$ were synthesized with surface areas of 96 m$^2$/g and 91 m$^2$/g. These were obtained by varying the heating rate of MoS$_3$ and the calcination temperature.
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TECHNICAL PROGRESS

Surface Area Measurements:

The surface areas were measured on a Gemini 2360 instrument using the BET multipoint method. Nitrogen was used as the adsorbate, and no free space correction was applied. For the undoped catalyst, 10 data points were taken from \( \frac{p}{p_0} = 0.05 \) to \( \frac{p}{p_0} = 0.30 \) (see Figure 1). For the rest of the samples, seven data points were obtained from \( \frac{p}{p_0} = 0.05 \) to \( \frac{p}{p_0} = 0.30 \) (see Figures 2-5).

The samples were weighed in air. They were then degassed by heating to 300°C in a flow of nitrogen for two hr. The samples were cooled to room temperature under nitrogen. The samples were then reweighed and the surface areas were measured at liquid nitrogen temperature.

Surface Areas of the Tested Catalyst:

The surface areas of the catalyst tested last quarter were determined for the undoped catalyst, the doped catalyst before testing, and the doped catalyst after testing. These surfaces areas are compared with previous catalysts in Table 1. The surface areas were determined to probe why the catalyst was losing activity over time. The surface area of the undoped catalyst was found to be 60 m²/g. This is comparable to the previously reported surface area of a different preparation of the undoped catalyst of 63 m²/g. This present sample of MoS₂ was obtained by heating MoS₃ to 500°C for 1 hr, using a heating rate of 10°C/min.

The surface area of the 20% Cs/MoS₂ before catalytic testing, but after drying to
300°C, was found to be 14 m²/g. This is also consistent with 13 m²/g reported. The surface area of the cesium doped catalyst after testing decreased to 6 m²/g. This decrease in surface area occurred over 551 hr of high temperature and high pressure conditions. Although a slight decrease in surface area during catalyst testing was previously reported (see Figure 6) [1], the loss of surface area for the present catalyst is quite significant. One possible reason for this loss of surface area is the cesium formate could have agglomerated on the surface during testing. These agglomerations, in turn, could have blocked the pores of the catalyst, thus giving a lower surface area. This agglomeration may have been more pronounced in this catalyst, because a different doping method was used. Previously, the doping was carried out in vacuum [2]. For the current catalyst, doping was done at atmospheric pressure in air. This latter procedure might not allow the cesium to disperse into the pores. In this case of lower dispersion, under reaction conditions the cesium component could have more easily agglomerated.

### TABLE 1. Comparison of surface areas of the undoped MoS₂, untested 20wt% Cs/MoS₂, and test 20wt% Cs/MoS₂.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface areas of last quarter catalyst (m²/g)</th>
<th>Surface areas of earlier catalysts (m²/g) [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped MoS₂</td>
<td>60</td>
<td>63</td>
</tr>
<tr>
<td>Untested Cs/MoS₂</td>
<td>14</td>
<td>13</td>
</tr>
<tr>
<td>Tested Cs/MoS₂</td>
<td>6</td>
<td>--</td>
</tr>
</tbody>
</table>

**Higher Surface Area Catalysts:**

Two higher surface area catalysts were produced, one with a surface area of 96 m²/g and another with 91 m²/g. The synthesized MoS₃ used to produce these catalysts was the same as for the previous catalyst. For the 96 m²/g MoS₂, approximately 2 g of MoS₃ was added with glass beads into a quartz tube. The sample was flushed with nitrogen and then
heated under nitrogen up to 210°C. This temperature was held for 10 min, and then the sample was heated up to 450°C at a rate of 13°C/min. This temperature was maintained for 1.5 hr. The sample was allowed to cool to room temperature under nitrogen, and then the sample was transferred from the quartz tube in air.

For the MoS$_2$ with a surface area of 91 m$^2$/g, approximately 2 g of MoS$_3$ was added with glass beads to the quartz tube. Under nitrogen flow, the sample was heated to 250°C and held there for 15 minutes. The sample was then heated at a rate of 15°C/min up to 460°C, and this temperature was maintained for 2 hr. The sample was allowed to cool to room temperature under nitrogen. The sample was transferred from the quartz tube in air.

REFERENCES:


FIGURE 1. BET Plot
For Undoped MoS$_2$
FIGURE 2. BET Plot For Untested 20 wt% Cs/MoS2
FIGURE 3. BET Plot for Tested 20wt% Cs/MoS$_2$
FIGURE 4. BET Plot for
For 96 m$^2$/g MoS$_2$

Relative Pressure

$\frac{z}{(1-z)V}$
FIGURE 5. BET Plot
For 91 m$^2$/g MoS$_2$
FIGURE 6. Relationship Between the Surface Areas of the Cs/MoS$_2$ Catalysts
END

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