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DOE/PC/91301-9

**ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL
SULFIDE CATALYSTS**

**Technical Progress Report for the Period
September 1993-November 1993**

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March 1994

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

Under Contract No. DE-FG22-91PC91301

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ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

SUMMARY OF TECHNICAL PROGRESS

During calcination of the precipitated and dried MoS_3 to form MoS_2 , it was found that small sample sizes were needed to provide thermal control of the highly exothermic decomposition reaction in the 8 mm ID quartz tube used for this purpose. Characterization of MoS_2 and Cs/MoS_2 catalysts have been carried out by X-ray powder diffraction (XRD) after each synthesis step. In addition, the XRD analyses were conducted after prolonged air exposure of the Cs-doped MoS_2 catalyst. It was shown that prolonged exposure to the ambient atmosphere led to segregation and crystallization of the cesium formate dopant. Thus, catalytic testing should be carried out with freshly prepared samples that are protected from the ambient atmosphere. Catalytic testing is underway to determine if there is an inverse correlation of catalytic activity and selectivity with prolonged air exposure of the catalyst.

ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

TECHNICAL PROGRESS

Catalyst Preparation:

In the previous quarterly technical progress report, the preparation procedure utilized to obtain MoS_2 was described in detail. The conversion of the precipitated and dried MoS_3 to MoS_2 by calcination is a highly exothermic reaction. This step is carried out in an 8 mm ID quartz tube about 60 cm long that is heated by a horizontal tube furnace. Our most recent preparations employed sample sizes consisting of 2-3 g of MoS_3 that were mixed with 3 mm Pyrex beads. This mixture was then centered in the tube by using add layers of Pyrex glass wool and additional Pyrex beads. During the calcination, a constant flow of helium, nitrogen, or other gas was maintained (typically 60 ml/min). The thermal program consisted of increasing the temperature up to 200°C quickly using a differential heating devise and holding for 10 min. Then the temperature was increased to 450°C for 1.5 hr, after which cooling in the flowing gas was carried out. As pointed out in the previous report, the sulfur released by the decomposition of the MoS_3 to form MoS_2 was condensed on Pyrex beads at the cool outlet of the tube.

It became evident that temperature control during the exothermic decomposition reaction was difficult when large sample sizes were used. Thus, X-ray powder diffraction (XRD) characterization of the samples prepared during the previous research was carried out. In addition, doping of the samples with Cs, as cesium formate, had been carried out before testing. XRD analysis of the Cs-doped samples was also carried out.

Characterization by X-Ray Powder Diffraction Analysis:

Two large batches of MoS_2 was prepared from two batches of MoS_3 that had been synthesized by coprecipitation from aqueous solution. The calcination of the MoS_3 was carried out using 2-3 g samples and the products of several of these portions were combined to form the two larger batches of MoS_2 . Figures 1 and 2 show the XRD patterns obtained for the two batches, which are designated as 2A and 1B. It is apparent that the patterns are nearly identical. The diffraction peaks exhibit appreciable width, which is indicative of small crystallite size of the MoS_2 .

A portion of the 1B batch of MoS_2 , as described in the previous technical progress report, was added to a measured quantity of an aqueous cesium formate solution, which was then evaporated to dryness under flowing nitrogen while maintaining constant stirring. The XRD pattern of the freshly prepared Cs/ MoS_2 catalyst, containing ≈ 10 wt% CsOOCH , is shown in Figure 3. The only dominant features in this pattern are the same MoS_2 diffraction lines as seen in Figures 1 and 2.

In contrast, a portion of the Cs/ MoS_2 sample prepared from the 2A batch of MoS_2 was allowed to stand in air for over three weeks before XRD analysis was carried out. The resultant XRD pattern is shown in Figure 4. By the presence of the new sharp diffraction line observed in the XRD pattern, it is evident that crystalline cesium formate has formed on the surface of the catalyst. From the sharpness of the lines, the CsOOCH crystallites are larger than 100 nm in diameter. It is proposed that upon standing in an ambient atmosphere, the Cs dopant that had initially been present in a dispersed state has migrated, agglomerated, and crystallized into large particles of cesium formate. Thus, upon use under catalytic conditions for alcohol synthesis from H_2/CO synthesis gas, the cesium dopant would likely exist as a segregated component that would not provide the high conversion of

reactants to alcohols that is desirable.

An additional series of experiments was carried out with a third batch of MoS_2 . After being prepared by calcination of MoS_3 , doping of the MoS_2 was carried out as for the samples described above to provide a doping level of ≈ 10 wt% CsOOCH . This sample was stored in a sealed vial, and the XRD pattern for the freshly prepared sample is shown in Figure 5. This sample was then allowed to stand in ambient atmosphere for a prolonged period of time (> 1 month), and the resultant XRD pattern is shown in Figure 6. Very sharp strong diffraction lines for cesium formate are evident in Figure 6.

Catalytic testing of an analogous sample for alcohol synthesis from $\text{H}_2/\text{CO} \approx 1$ synthesis gas at 8.2 MPa and 295°C was carried out in our continuous flow gas phase reactor system ($\text{GHSV} = 7750 \text{ l/kg cat/hr}$) after reductive pretreatment at 400°C in flowing 2.04 vol% $\text{H}_2/97.96$ vol% N_2 (60 ml/min) for 1 hr. Alcohols (dominant product) and hydrocarbons were formed, as expected from the results presented in the previous quarterly progress report and from earlier published data, but the overall catalytic activity was only about half of that expected for the Cs doping level utilized with this catalyst. The XRD pattern of the tested catalyst is shown in Figure 7, and the presence of a small quantity of cesium formate in this sample is evident. Therefore, the catalyst samples used for catalytic testing should be freshly prepared and not allowed to stand in ambient atmospheres, i.e. those containing oxygen, water vapor, and carbon dioxide.

Sample: 2A File: MD6J02.SM

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

Sample:

File: MD8J03.SM

FIGURE 6

FIGURE 7

Sample: USED File: MD9J03.SM

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