

# QUARTERLY TECHNICAL PROGRESS REPORT

Submitted to U.S Department of Energy

**GRANT TITLE:** Investigation of Syngas Interaction in alcohol Synthesis Catalysts  
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\*U.S. / DOE Patent Clearance is not required prior to the publication of this document

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## Quarterly Technical Progress Report (Period April 1 St. to June 31 St.)

This report presents the work done on " Investigation of Syngas Interaction in Alcohol Synthesis Catalysts" during the last three months. In this report the results on the effect of method of preparation on the catalytic properties will be discussed.

**Introduction:** Several catalyst systems containing copper and cobalt in combination with a number of other elements and supports have been extensively investigated by the IFP ( Institute Francois Du Paris) group . Several investigators report difficulties in reproducing the IFP results. It is generally believed that besides the interatomic ratios, preparation conditions of the precursors, such as pH, temperature of precipitation, drying and calcination temperatures, etc., significantly influence the behavior of the catalysts. In this report we plan to examine the effect of preparative techniques on the catalytic properties of the catalysts.

**Experimental Studies:** Three different Cu/Co metal ratios (.2, 1, and 37) are chosen to represent the three selectivity regions: Hydrocarbons/Alcohols/ Methanols respectively for this study. Each sample at a given metal ratio is prepared by three different methods. Samples labeled A are prepared using co-precipitation method as described earlier while samples labeled B and C are prepared sequentially.

In B samples, one molar solutions of copper and cobalt nitrate solutions are taken in the desired ratio in separate beakers and equal amounts of chromium nitrate solution is added to them. The mixture of copper chromium nitrate solution is precipitated first by adding a dilute solution of sodium hydroxide while keeping the PH between 7 and 8 and the temperature at 80°C. The precipitate is allowed to settle and the supernatant liquid is decanted. On the top of this precipitate cobalt + chromium nitrate solution is precipitated while maintaining the same conditions. The final precipitate is washed air dried at 100°C and calcined at 350°C. The same procedure is adopted for the samples labeled C except that the mixture of copper + chromium nitrate solution is precipitated on the top of cobalt + chromium nitrate precipitate. These samples were sent to Air Products Inc., the industrial collaborator of this project, for catalytic studies. The experimental procedural details for catalytic studies were presented in an earlier report.

**Results and Discussion:** The results of the catalytic data are presented in Table 1.

#### Hydrocarbon range catalysts ( $\text{Cu/Co} < 1$ ):

All three catalysts independent of method of preparation produced on the average about 50% hydrocarbons as expected for cobalt rich catalysts. As can be seen from the data table the percent yield of hydrocarbons is significantly less for Co atop Cu catalysts compared to Cu atop Co catalysts. This might suggest that copper promotes cobalt reduction better when Cu is atop of Co, in cobalt rich catalysts.

#### Alcohol range catalysts ( $1 < \text{Cu/Co} < 3$ ):

In this group, both co-precipitated and Co atop Cu catalyst seems to yield higher alcohol production compared to Cu atop Co catalysts. It is also observed that hydrocarbon yield is significantly higher (about 50%) in Co atop Cu catalysts compared to Cu atop Co catalysts. This indicates that, when cobalt is precipitated on the top of copper, it may be enhancing the production of hydrocarbons. More clear understanding of this behavior may be possible after analyzing the magnetic character of these catalysts with CO adsorption. We are currently conducting investigations in this direction.

#### Methanol range catalysts ( $\text{Cu/Co} > 3.0$ ):

All three catalysts produced methanols as expected. It seems sequential precipitation methods seems to lead to higher yield of methanols compared to co-precipitation methods. However we cannot distinguish the significance of sequence of precipitation.

**Future Plans:** We are currently in the process of investigating the effect of CO on the NMR and Magnetic character of Co. Cu/Fe/Zn samples are prepared. Data on the magnetic character of these catalysts has been collected at Grambling State University on these samples. This data will be analyzed in the coming quarter. FTIR spectrometer has been purchased. It will be installed during the next quarter and FTIR studies on Cu/Co/Cr catalysts will be done.

#### **Student Training:**

One of the objectives of this project is to provide research training for minority undergraduate students at a school with predominant African American enrollment. Out of four new students involved in the project, three are engineering majors and one is a physics major. All these students have learned the catalyst preparation techniques by the three different methods. The newly obtained laboratory is currently set up by the students for preparation of samples. One student spent three weeks this summer at Grambling State University and worked on the NMR and Vibration sample magnetometer.

**Table 1 Catalytic Data**

Sample	Cu/Co	CO2 %	Methanols %	Mixed alcohols %	Hydrocarbons %	Unknowns %
17-78-5A	0.1	41	1	6	50	2
17-78-5B		36	3	18	37	6
17-78-5C		9	1	1	85	5
37-37-26A	1	55	5	10	25	5
37-37-26B		20	3	11	62	5
37-37-26C		61	3	6	30	<1
74-2-24A	37	51	34	2	13	<1
74-2-24B		28	60	4	7	1
74-2-24C		34	52	3	10	1

A Co-precipitation

B Co atop Cu

C Cu atop Co