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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Project Director

10/27/95
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Quarterly Technical Progress Report

(Period July 1 St. to September 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 of the work done on the effect of CO adsorbtion on the magnetic character of cobalt in the Cu/Co/Cr catalysts is discussed. The results of this work were presented at the Fourth National Conference on Diversity in the Scientific and Technological Workforce sponsored by the National Science Foundation.

Introduction: Transition metals copper, cobalt, and iron play a significant role in the conversion of syngas(CO & H_2) to liquid fuels. Several catalytic studies indicate that product selectivity is governed by the inter-metallic ratios and the method of preparation. The catalytic as well as the magnetic character of the catalyst are known to be influenced by the modifications in the metal crystallites. With a view to examine the relations between the magnetic and catalytic properties, a series of Cu/Co/Cr catalysts were prepared using the co-precipitation method. The inter-metallic ratios were chosen to cover the three regions of selectivity reported by the IFP: hydrocarbons - mixed alcohols - methanols as the metal ratio (Cu/Co) increases . During this quarter we examined the effect of the adsorbtion of carbon monoxide on the magnetic characteristics of the samples.

Experimental Studies: A total of 10 samples were prepared by co-precipitation method. One Molar solutions of copper, cobalt and chromium nitrates are mixed in the proportions needed to obtain the desired cation ratio in the catalyst. By adding one molar solution of sodium hydroxide, the catalyst was precipitated while maintaining neutral pH conditions at a temperature of 80°C. The precipitate was thoroughly washed in warm water, dried at 80°C and calcined in air for 18 hours at 350°C. The calcined sample was reduced in a flowing stream of hydrogen for 18 hours at 350°C. Hydrogen was outgassed while reducing the temperature to 250°C. At this temperature a steady flow of carbon monoxide was introduced for 30 minutes. Continuing the flow of carbon monoxide, the temperature was reduced to 50°C. The sample tube was sealed under partial vacuum and NMR of Co and magnetization of the catalyst were investigated at Grambling State University.

Results and Discussion: NMR spectra were taken for all the samples. Figure 1 shows the NMR spectra of Cobalt due to one of the catalysts with and without CO. Preliminary examination of the NMR spectra of cobalt indicate a downward shift of about O.5 MHz in the presence of CO. A detailed examination of the NMR spectra of all the samples is in progress to confirm the findings.

The saturation magnetization data of CO adsorbed samples is shown in Table 1. The following inferences can be drawn from an examination of the magnetic moments of the three ferro magnetic materials and their 3d electronic structures: Fe ($3d^6$ - 218 emu/g), Co ($3d^7$ - 161 emu/g), and Ni ($3d^8$ - 54 emu/g). It seems the magnetic moment decreases in the ferro magnetic materials as the 3d electron density increases.

For Cu/Co < 2 the magnetic moment of the adsorbed sample is consistently lower than the sample without CO. This suggests that charge transfer could be occurring from CO - Co. This condition seems to be conducive for the production of hydrocarbons. However as copper content increases, in the alcohol selective region, for Cu/CO > 2, the magnetic moment of the CO adsorbed sample is higher than the catalyst without CO. This shows a reverse charge transfer from cobalt to carbon monoxide. This observation shows a clear link between the selectivity character and the nature of the inter metallic charge distribution.

The last column in Table 1 represents the magnetization data of the CO desorbed samples. Desorption of CO was done by simply outgassing the samples over night in high vacuum at room temperature. All the samples consistently show a significant further drop of magnetic moment. This feature seems to indicate that a sharing of charge between CO and cobalt metal prevail as long as the solid and the gas are in equilibrium. Further decrease in magnetic moment could result if there occurs an enhancement in the metallic charge distribution.

These two features, increase in the magnetic moment of the adsorbed samples as the metal ratio Cu/Co increases, and a drop in the moment as carbon monoxide is desorbed is interesting and intriguing. Further explanation of this phenomena is necessary to understand this unusal behavior.

Future Plans: The present studies indicate a possible charge transfer between cobalt metal and carbon monoxide due to the adsorbtion process. We plan to repeat these experiments to reconfirm the results obtained. We also intend to extend these studies to Cu/Fe/Zn samples.

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. One of the students worked with Dr. A.N. Murty , the Co-PI , and a Grambling State Univesity physics student involved in the project, received training in the operation of ZFNMR spectrometer and Vibration sample mgnetometer during the summer. She acquired the needed skills to collect and analyze the data on the samples investigated.

NMR SPECTRA OF Cu/Co/Cr SAMPLES

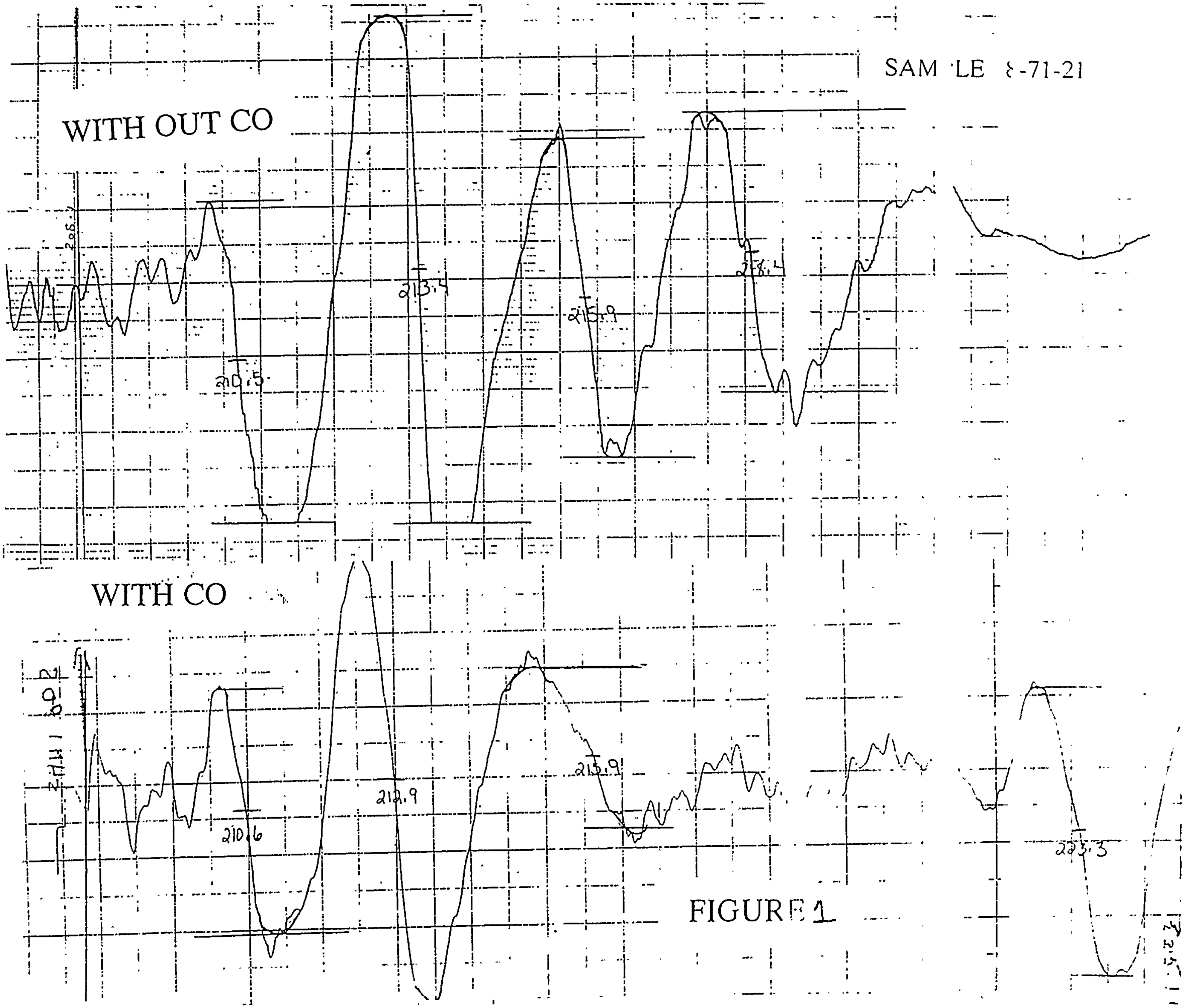
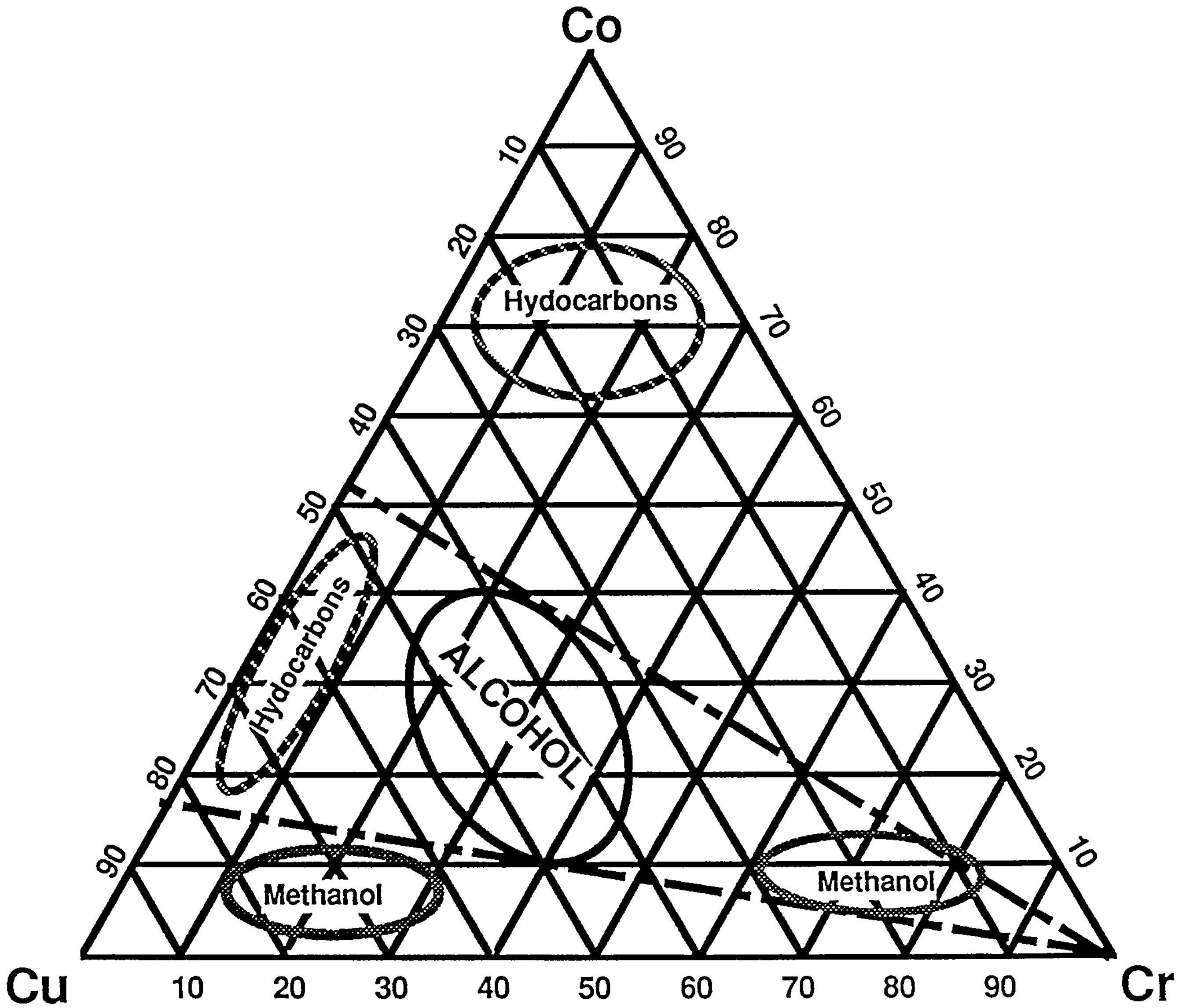


FIGURE 1

TABLE 1

MAGNETIZATION DATA OF CO ADSORBED AND DESORBED SAMPLES

		Magnetic Moment (emu/g)		
			Cu/Co/Cr	Cu/Co/Cr
Sample	**Cu/Co**	**Cu/Co/Cr**	**CO-adsorbed**	**CO-desorbed**
8-71-21	0.11	87.2	69.9	64.1
17-78-5	0.22	117	83.6	37.1
37-37-26	1.00	17.0	14.2	12.2
43-26-31	1.70	47.0	1.52	2.45
22-12-66	1.80	1.50	0.37	0.41
58-29-13	2.00	30.7	33.4	28.9
54-22-24	2.50	6.00	19.6	2.18
16-6-78	2.70	3.80	5.30	3.20
74-21-5	3.50	28.3	71.9	11.19
74-2-24	37.0	5.30	8.30	7.00


Co
Cu
Cr
10
20
30
40
50
60
70
80
90
Hydocarbons
Hydocarbons
ALCOHOL
Methanol
Methanol

nsf

National Conference on
Diversity in the Scientific
and Technological Workforce

RESEARCH ABSTRACTS

FOR

STUDENT PRESENTATIONS

September 21-23, 1995
Washington Hilton and Towers Hotel
Washington, D.C.

NATIONAL SCIENCE FOUNDATION
Directorate for Education and Human Resources

Methodology, Mechanism, and Synthesis of Alpha Substituted Isoxazoline Compounds

Conditions required to successfully introduce substitution at the carbon alpha to the isoxazoline ring of the methyl ester starting material were investigated The saponification reaction on the ester using potassium carbonate in a deuterated aqueous environment has been shown to give deuterium incorporation at the methylene alpha to the carboxyl group in addition to hydrolysis to the free acid. This reaction was repeated under the same conditions while sampling the mixture at timid intervals. Monitoring the reaction for the incorporation of deuterium, percent racemization of starting material ester, product acid, and rate of saponification allowed for the comparison of these reactions. Using this mechanistic study as a model, an attempt was made to develop new methodology for the introduction of other substituents at this alpha carbon position.

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Name of Presenters: Leon Cole and Mario Thomas
Institution: Jackson State University
Classification: Junior
Major Area of Study: Physics
NSF Sponsored Program: RCMS
Faculty Advisor or Mentor: Mr. Carl Drake

The Use of X-Ray Detectors in High Energy Physics

Five x-ray detectors were constructed to detect the amount of radiation given off when accelerated electrons with energies of 60 KeV to 300 KeV strike a stainless steel beampipe consisting of iron atoms. The detectors are composed of a photomultiplier tube with a one inch thick plastic scintilla connected to the end. The detectors were tested by using a Cobalt-60 source and different voltage settings. The signal from these tests were checked on an oscilloscope. Along side testing the x-ray detectors, the expected sensitivities of a 60 KeV and a 300 KeV electron beam was calculated.

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Name of Presenter: Ruby Cruz
Institution: Stevens Institute of Technology
Classification: Sophomore
Major Area of Study: Biology
NSF Sponsored Program: RCMS
Faculty Advisor or Mentor: Prof. A.K. Bose

Synthesis of the Taxol Side Chain

4-Aryl-3-hydroxy beta-lactams can serve as synthons for the synthesis of the C13 side chain of taxol -- a very promising antitumor drug. A series of 1,4-diaryl-3-acetoxy beta-lactams were synthesized by the Staudinger reaction (acetoxyacetyl chloride + diaryl schiff bases) After hydrolysis of the acetyl group, these were resolved by reaction with glucal (Ferrier reaction) Separation of the diastereomeric alpha-glycosides, followed by removal of the sugar residue gave enantiomerically pure beta-lactams with defined stereochemistry at C2/C3 Reaction of these with baccatin can give taxol analogs with variations in the side chain stereochemistry and substituents The factors affecting the stereochemistry of the products obtained will be discussed

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Name of Presenter: Shalarma Davis
Institution: Xavier University of Louisiana
Classification: Sophomore
Major Area of Study: Mechanical Engineering
NSF Sponsored Program: RCMS
Faculty Advisor or Mentor: Dr. Akundi

NMR and Magnetic Character Studies on CO Adsorbed Syngas Catalysts

Transition metals, copper, cobalt, and iron, play a significant role in the conversion of syngas ($Co+H_2$) to liquid fuels. Several catalytic studies indicate that product selectivity is governed by the inter metallic ratios and the method of preparation. The catalytic as well as the magnetic character of the catalyst are known to be influenced by the modifications in the metallic charge distribution and morphological changes in the metal crystallites. With a view to examine the relations between the magnetic and catalytic properties we investigated the Zero - field NMR and magnetization character studies of a series of Cu/Co/Cr and Cu/Fe/Zn catalysts for a wide range of inter metallic ratios covering the three regions of selectivity reported by IFP: hydrocarbons to mixed alcohols to methanols as the metal ratio (Cu/Co or Cu/Fe) increases.

Catalysts were prepared using the co-precipitation method by mixing simultaneously I molar solution of the respective nitrates. The precipitate was washed, air dried at I000°C and calcined at 350° C. The precursor was then reduced with flowing hydrogen at 350°C for 18 hours. Hydrogen was out-gassed while reducing the temperature to 250°C. At this temperature CO was admitted for 30 minutes and then while continuously admitting CO the temperature was reduced to 50°C- The sample tube was sealed under partial vacuum. These samples were used for NMR and Magnetic character studies at Grambling State University. The results of this investigation will be presented.