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QUARTERLY TECHNICAL PROGRESS REPORT

Submitted to U.S Department of Energy

GRANT TITLE:	Investigation of Syngas Interaction in alcohol Synthesis Catalysts
GRANT NO:	DE-FG22-93MT93010 (XU: 235-860)
STARTING DATE:	09-01-93
ENDING DATE:	08-31-96
PROJECT DIRECTOR:	MURTY A. AKUNDI PHYSICS/ENGINEERING DEPARTMENT
INSTITUTION:	Xavier University of Louisiana New Orleans, La 70125

*U.S. / DOE Patent Clearance is not required prior to the publication of this document

murty a akundi
Project Director

Feb. 27, 1995
Date

DISCLAIMER

Quarterly Technical Progress Report
(Period August 1 St. to ~~October~~ Dec 31 St.)

This report presents the work done on " Investigation of Syngas Interaction in Alcohol Synthesis Catalysts" during the first quarter of the 2nd year of the project. In this report we plan to compare the particle sizes of the catalysts using the magnetization data.

Experimental Studies: The Saturation magnetization and hysteresis character of nine samples were investigated using a vibrating sample magnetometer (Figure I). The sample is loaded and vibrated between the pole faces of an electromagnet. This vibration induces a voltage in the pick up coils which is proportional to the magnetization of the sample. The larger the magnetization, the larger the voltage. The magnetic field is continuously varied up to 13,500 gauss and the magnetization is measured. This system is completely computer controlled. The nine samples that were selected are alcohol selective catalysts that were prepared by co-precipitation and sequential precipitation methods. The details of the methods of preparation was given in earlier reports.

Results and Discussion: The behavior a paramagnetic sample recorded by the magnetometer is shown in Figure II. As the field increases, the magnetization increases. All our calcined samples exhibit this behavior before reduction. After reduction however, all samples show typical ferromagnetic behavior (Fig III). They reach a saturation point at the high field and retain magnetization even when the field is zero. The field required to bring the magnetization to zero value is called the coercive field. While the saturation field is dependent upon the ferromagnetic character of the composite, the coercive field is dependent on the particle size. The particle size also governs the efficiency of the syngas conversion while the selectivity of the catalyst is governed by the magnetic character. We made rough estimate of the typical particle sizes from the Luborsky curve (Figure IV). Using the H_C values obtained from the magnetization data, we were able to use the Luborsky curve to determine the particle sizes. However, since this is a log-log graph, the estimations are accurate with in an order of magnitude. The particles on the left side of the curve are extremely small and are called super paramagnetic which will never reach saturation. However, since all our particles exhibit saturation, we assume multi-domain particle character as given by the right side of the curve.

Tables I, II and III indicate the H_C values and the particle size estimates for the samples studied sofar. From the data , it appears that there is no significant impact on the particle sizes due to method of preparation . In all our samples studied so far, the Luborsky curve analysis yielded particle sizes in the range of 140 ± 25 nm. One sample was used for

particle size analysis using Scanning Electron Microscope (SEM) available at Tulane University. Making random measurements from the SEM micro graph, the particle size turned out to be around 40 nm which is an order of magnitude less than those obtained from Luborsky curve. It is too early to make any conclusions without investigating more samples .

Future Plans:

During the coming quarter, We plan to complete preparation of Cu/Fe/Zn catalysts and collect the magnetization data on these samples. NMR and magnetization studies will be undertaken on CO adsorbed Cu/Co catalysts. FTIR Spectrometer will be purchased and installed.

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 catalytic preparation techniques by the three different methods. The newly obtained laboratory is currently set up by the students for preparation of samples. In the future I plan to take these students to Grambling State University to train them in NMR and Magnetization experimental techniques .

VG. NO._____

DMS VIBRATING SAMPLE MAGNETOMETER

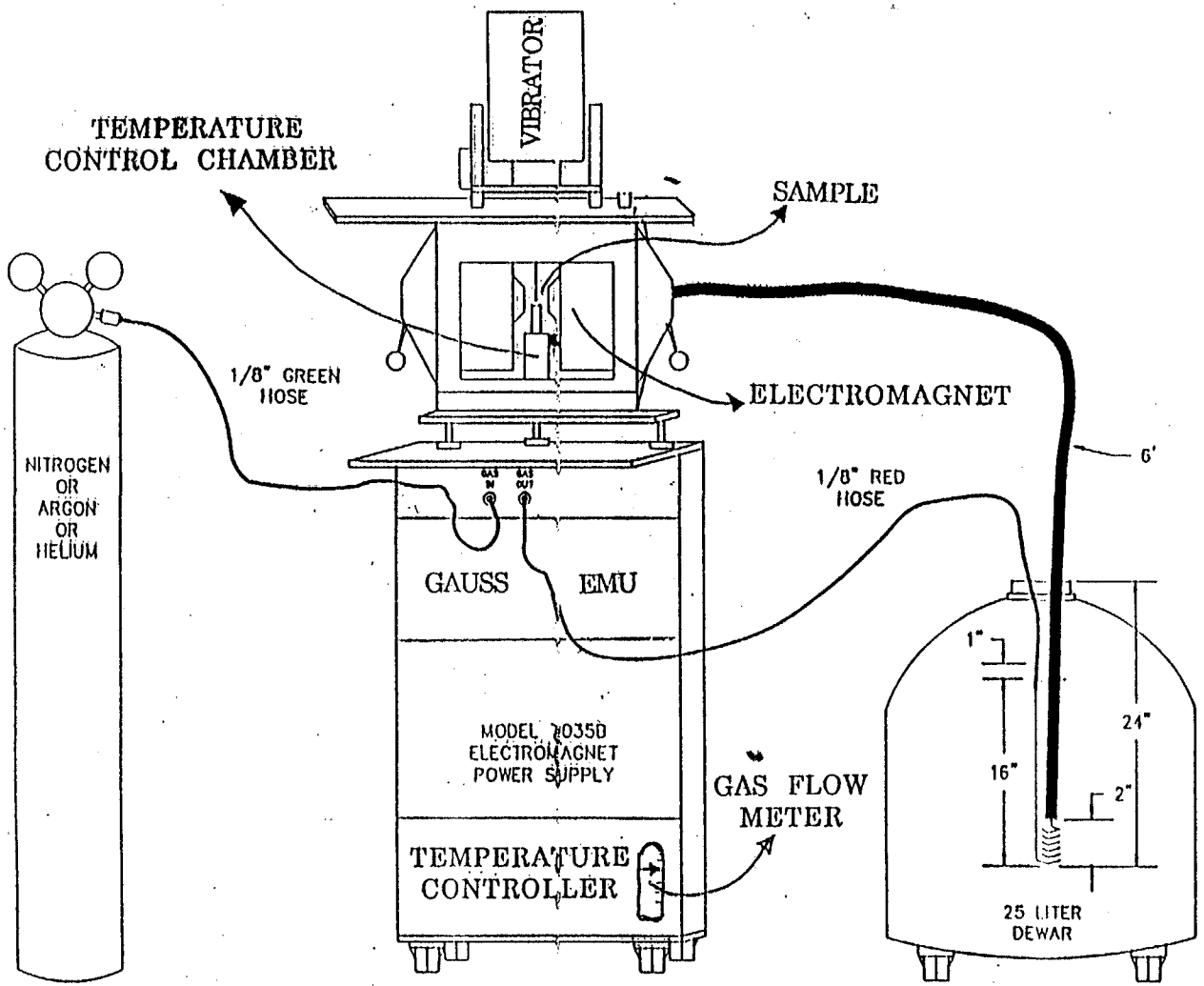
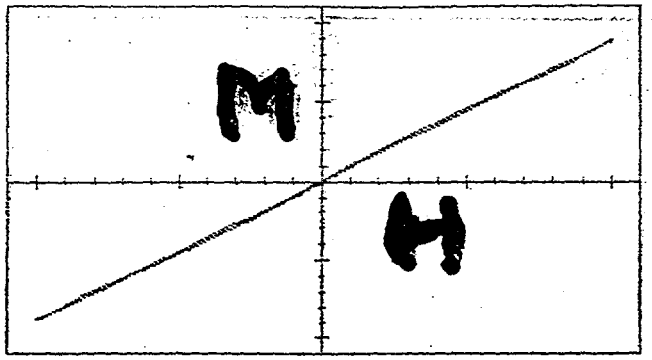


Figure 1

AT&T

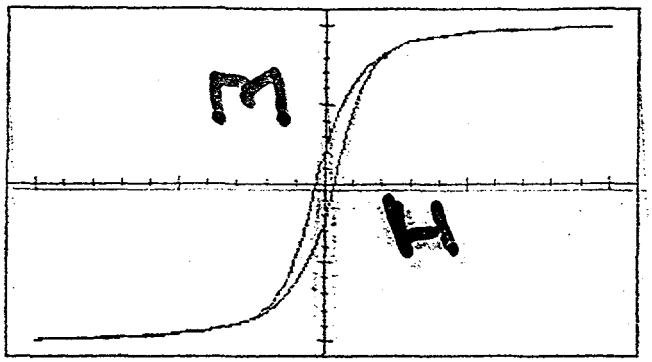


Digital Measurement Systems - Vibrating Sample Magnetometer

Filename: 441343XA		Sample ID:GREGORY441343XAA
Date:	11 Apr 1994	
Test start time:	10:10:29	Test duration : 00:15:26
Temperature:	27.4°C	Rotation angle: 0.0 deg
Volume in cc:	0.000E+00	Mass in grams : 1.961E-01
Hmax	1.350E+04	Oersted
Ss	2.048E-01	EMU/g
Sr	-9.502E-04	EMU/g
SQ	-4.640E-03	Ir/Is
S* hys	2.000E+00	1-(Ir/Hc)(1/Slope at Hc)
Hc	5.544E+01	Oersted
dH in Oersted	2.635E+04	between 50% of peak of dEMU/dH
SFD	4.754E+02	dH/Hc
Hknee 90% of Ir	5.544E+00	Oersted
SIGMA	2.048E-01	Is/gram
Slope at .75*Hc	-7.619E-01	(EMU[at H=0]- EMU[at H=Hc/1.33])/Ir
Area 1st Quad	-8.351E+00	EMU/g * Oersted
Area 2nd Quad	8.190E-02	EMU/g * Oersted
Total Area	-1.654E+01	EMU/g * Oersted
Hk eff - area	1.348E+04	Oersted
Slope at Hc	1.714E-05	EMU/g / Oersted

S_s	Sr	Hc	S_r/S_s	Sample	Cu/Co	S_s Co
.204	.00094,50	55.4	-4.6	44-13-43 XA	3.3	1.5 Co

Figure II



Digital Measurement Systems - Vibrating Sample Magnetometer

Filename: A542224X		Sample ID:GREGORY542224XAA	
Date:	5 Apr 1994		
Test start time:	06:17:21	Test duration :	00:15:29
Temperature:	26.5°C	Rotation angle:	0.0 deg
Volume in cc:	0.000E+00	Mass in grams :	3.379E-02
Hmax	1.350E+04	Oersted	
Ss	2.108E+01	EMU/g	
Sr	4.926E+00	EMU/g	
SQ	2.336E-01	Ir/Is	
S* hys	1.392E-01	1-(Ir/Hc)(1/Slope at Hc)	
Hc	4.345E+02	Oersted	
dH in Oersted	2.126E+03	between 50% of peak of dEMU/dH	
SFD	4.893E+00	dH/Hc	
Hknee 90% of Ir	4.601E+01	Oersted	
SIGMA	2.108E+01	Is/gram	
Slope at .75*Hc	7.207E-01	(EMU[at H=0]- EMU[at H=Hc/1.33])/Ir	
Area 1st Quad	2.887E+02	EMU/g * Oersted	
Area 2nd Quad	3.772E+01	EMU/g * Oersted	
Total Area	6.529E+02	EMU/g * Oersted	
Hk eff - area	3.102E+03	Oersted	
Slope at Hc	1.317E-02	EMU/g / Oersted	

S_s	S_r	H_c	S_{SCD}	S_r/S_s	Sample	CW/CO
21.1	4.93	434	96	.23	54-22-24XA	2.45

Figure III

The Luborsky Curve

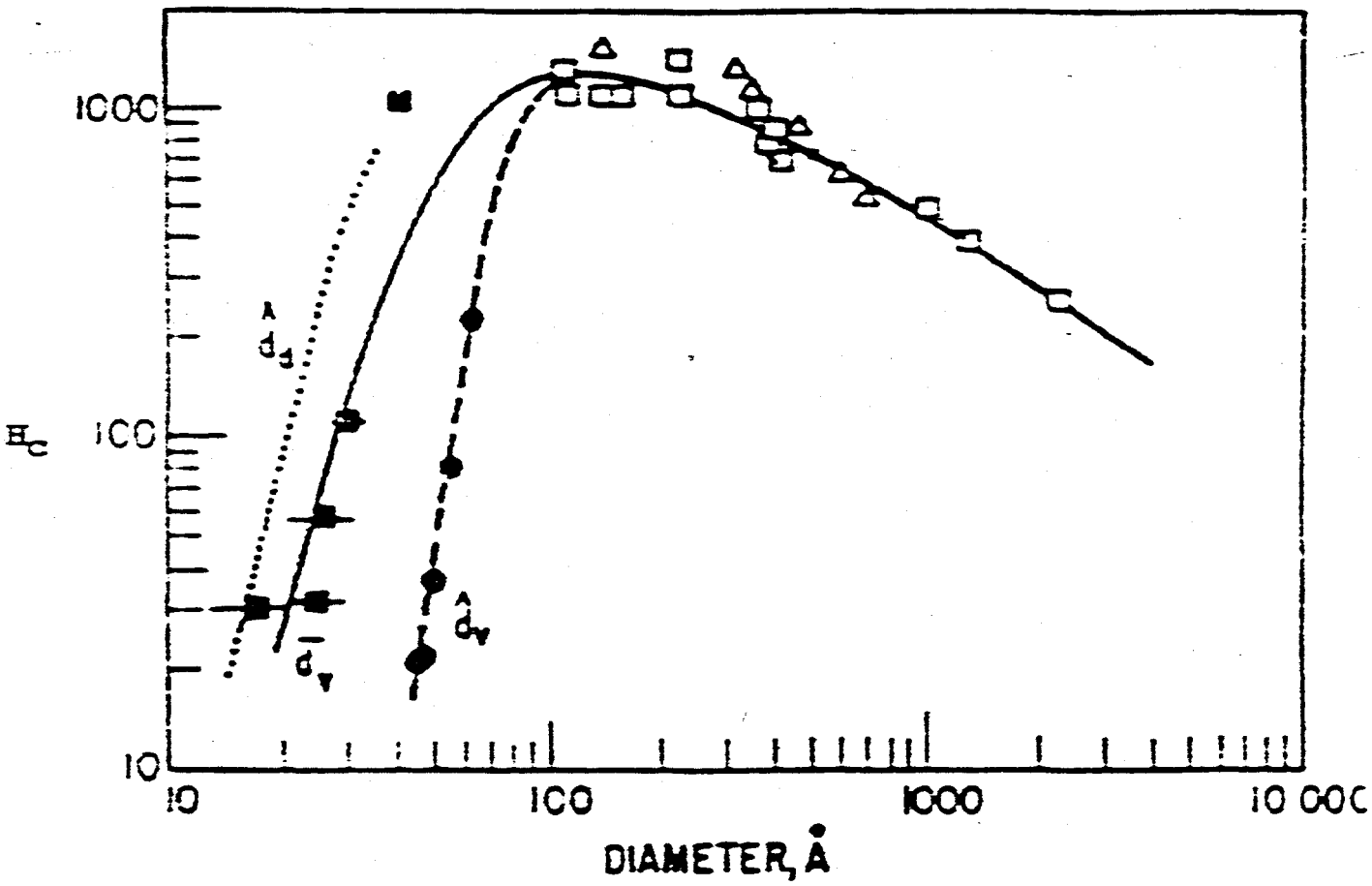


Figure IV

Table

Magnetization Results of Cu-Co-Cr Composites

Mechanical Alloying: Co Concentration

Sample	H_c (Oe)	σ_s (emu/g)	H_c (Oe)	σ_s/Co (emu/g of Co)	% Reduction of σ_s	Particle size
[illegible]	[illegible]	9.3	402	17	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	512	47	[illegible]	[illegible]
[illegible]	[illegible]	14.3	62	65	[illegible]	[illegible]
[illegible]	[illegible]	10.9	87	28	[illegible]	[illegible]

Average Particle Size: [illegible] Å

Table II

Magnetization Results of Cu-Co-Cr Composites

Method of Preparation: Sequential Precipitation - Co atop Cu

Sample	Cu/Co (Ratio)	S_S (emu/g-sample)	H_C (Oe)	S_SCo (emu/g of loaded Co)	%Reduction of Co	Particle size
37-37-26	1	15.3	338	41	25%	1668 A
43-26-31	1.65	15.5	351	60	37%	1500 A
54-22-24	2.45	10.6	431	48	30%	1160 A

Average Particle Size: 140 $\pm$ 25 nm

Table III

Magnetization Results of Cu-Co-Cr Composites

Method of Preparation: Sequential Precipitation - Cu atop Co

Sample	Cu/Co (Ratio)	S_S (emu/g-sample)	H_C (Oe)	S_SCo (emu/g of loaded Co)	%Reduction of Co	Particle size
37-37-26	1	4.86	373	13	8%	1416 A
43-26-31	1.65	12.3	433	47	29%	1167 A
54-22-24	2.45	9.29	423	42	26%	1100 A

Average Particle Size: 125 $\pm$ 15 nm