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QUARTERLY TECHNICAL PROGRESS REPORT

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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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Date

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Quarterly Technical Progress Report
(Period January 1 to March 31)

This report presents the work done on " Investigation of Syngas Interaction in Alcohol Synthesis Catalysts" during the last three months. In this report an analysis of the work done on Cu/Co/Cr catalysts and the effect of the method of preparation on magnetic character of the catalysts is 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 inter atomic 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 magnetic characteristics of the catalysts.

Experimental Studies: Batch I samples are prepared by precipitating the nitrates of copper and cobalt by continuously adding sodium carbonate solution at $80^{\circ}C$ until the pH reaches a value of 7.5 ± 0.5. Continuous stirring was provided through out the process. While Batch II catalysts were prepared by adding the two nitrate solutions and a dilute solution of sodium hydroxide, all simultaneously while keeping the pH between 7 and 8 and the temperature at $80^{\circ}C$. In both cases the precipitates are washed thoroughly, air dried at $100^{\circ}C$, calcined at $350^{\circ}C$. The calcined sample is reduced at $350^{\circ}C$ with flowing hydrogen for 18 hours. The samples were sealed and sent to Grambling for magnetic characteristic studies. The details of the experimental arrangement for NMR and magnetic susceptibilities studies were given in the earlier reports. We refined the second method and prepared the samples by co-precipitation and by sequential precipitation methods (described in earlier reports).

Results and Discussion: Figure 1 shows the NMR spectra of the samples prepared by both methods. There are distinct differences between the spectra of the two batches and noticeable deviations relative to the pure Co powder spectrum. But for the high frequency lines above the HCP line, the first batch samples closely resemble the Co powder spectrum, while the FCC line is consistently shifted by 0.7 MHz in the second batch catalysts. To examine these differences in the two methods of preparation, we have investigated the pH value of the onset of precipitation of both nitrates (Table I). As can be seen copper nitrate precipitates first. This indicates that in the first group copper and cobalt got separated in the preparation process, each mostly retaining its own identity. Such catalysts are found to have poor selectivity to higher alcohols. On the other hand in the second batch of samples, it seems that there occur noticeable inter metallic interactions between copper and cobalt due to their proximity, and significant modifications in the metallic charge distribution producing shifts in the NMR line frequencies. The magnetization characteristics of the two batches of catalysts after reduction are compared in Table 2. Neither the saturation magnetization value nor the coercive field value reveal any significant differences between the two groups. The subtle differences noticed in the NMR data are not reflected in the magnetization data, perhaps because we are observing the average bulk properties of the composites.

NMR spectra of the catalysts prepared by the co and sequential precipitation methods are shown in figure 2. Magnetization data is presented in Table 3. In general we did not find significant differences in the magnetic characteristics due to the subtle differences in the preparative techniques. However this fact <u>does not</u> assure that catalytic properties also would be similar. The reason being both NMR and magnetization indicate the bulk magnetic characteristics of the sample and not sensitive to the surface character, while catalytic properties are completely governed by the surface character.

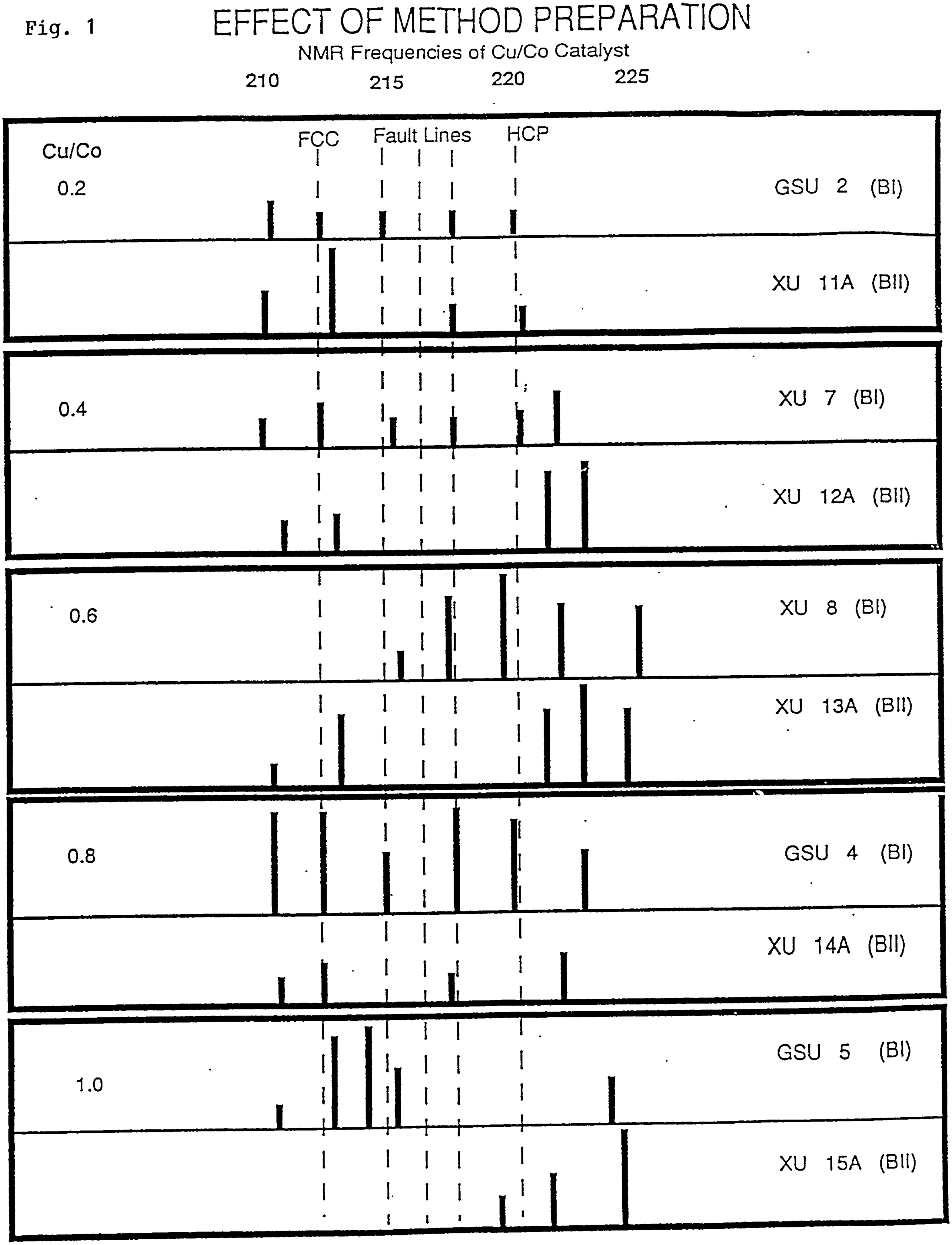
Modifications in the metallic charge distribution are clearly revealed by our magnetic studies as shown in figure 3. Magnetization results are presented in Table 3. The NMR spectra show distinct differences as the selectivity changes from Hydrocarbons-Alcohols-Methanols. In HC selective catalysts cobalt retains its normal chemical as well as magnetic character. The NMR spectral lines span the region from 210 MHz-225 MHz, characteristic of cobalt lines. As copper content increases to Alcohol selective region, high frequency cobalt lines are noticeably absent. Cobalt seems to lie preferentially in the FCC phase particles. The proximity of Cu-Co atoms may lead to this phase and be conducive for alcohol selectivity. Further increase in copper content leads to methanol region, and no NMR spectra are observable indicating that cobalt might be in solid solution with copper.

Future Plans: Cu/Fe/Zn samples are prepared. Magnetization studies will be conducted on these samples. FTIR spectrometer is in the final stage of being purchased. Work on Co adsorbtion studies will be conducted during the summer.

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. In the future I plan to take these students to Grambling State University to train them in NMR and Magnetization experimental techniques .

Fig. 1



EFFECT OF METHOD PREPARATION

NMR Frequencies of Cu/Co Catalyst

Table I

ONSET AND COMPLETION OF PRECIPITATION OF Cu - Co NITRATES

	PH of Nitrate	pH at onset	pH at completion
$Cu(NO_3)_2$	3.5	4.5	4.8
$Co(NO_3)_2$	5.5	7.3	7.5

Table II

Effect Of Method of Preparation : Magnetization Results

Sample	Sat. Mag. (σ_s)		% Reduction		Coercive Field (H_c)	
Cu/Co	BatI	Bat.II	Bat.I	Bat.II	Bat.I	Bat.II
0.2	109	109	82	82	593	563
0.4	96	85	84	74	547	331
0.6	75	84	75	84	477	506
0.8	64	70	72	79	440	594
1.0	63	69	78	86	679	693

Fig. 2

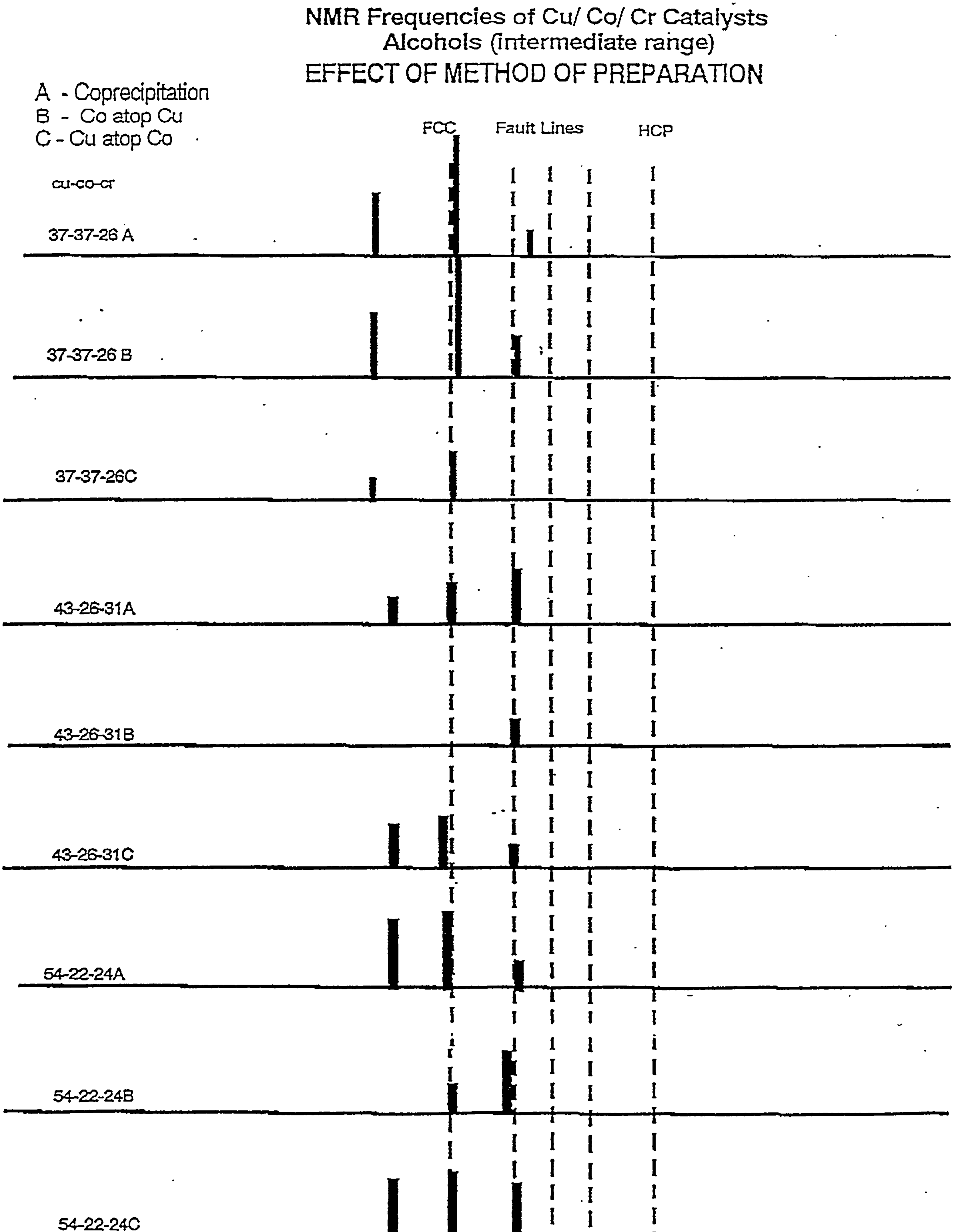

NMR Frequencies of Cu/ Co/ Cr Catalysts
Alcohols (intermediate range)
EFFECT OF METHOD OF PREPARATION
A - Coprecipitation
B - Co atop Cu
C - Cu atop Co
FCC
Fault Lines
HCP
cu-co-cr
37-37-26 A
37-37-26 B
37-37-26C
43-26-31A
43-26-31B
43-26-31C
54-22-24A
54-22-24B
54-22-24C

Table III

Magnetization Results

of Cu-Co-Cr Composites

Coprecipitation

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	6.3	402	17	10%	1250 A
43-26-31	1.65	12.2	519	47	29%	780 A
54-22-24	2.45	14.3	424	65	40%	1101 A
71-11-18	6.45	10.8	323	98	61%	1700 A

Average Particle Size: 125 + 45 nm

Sequential Precipitation - Co atop Cu

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 + 25 nm

Sequential Precipitation - Cu atop Co

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 + 15 nm

Particle size determined using laboski curve.

Fig. 3

NMR Spectra of Syngas Conversion Catalysts