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DOE/PC/89761-T4

DOE/PC/89761--T4

QUARTERLY

DE92 015781

TECHNICAL PROGRESS REPORT

Submitted to U. S. Department of Energy

GRANT TITLE: NQR-NMR Studies of Higher Alcohol
Synthesis Cu-Co Catalysts

GRANT NO: DE-FG22 89PC89761 (GSU: 5-5374)

STARTING DATE: 09-15-89

ENDING DATE: 09-14-91

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

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4-4-1991
Date

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QUARTERLY TECHNICAL REPORT

(Dec. 14th 1990 - March 14th 1991)

The primary concern of the study during this period has been to examine the origin and basis of the several nonconforming NMR lines reported in our earlier study (1). Previous studies by earlier investigators (2, 3) indicate that (a) the product distribution in the conversion of synthesis gas to liquid fuels is dependant on the copper/cobalt ratio and (b) that the catalytic results reported by different groups of investigators using the IFP prescription (4) are widely divergent. These observations prompted us to make a critical examination of the effect of metal ratio and the method of preparation on the magnetic character of catalysts.

Results and Discussion:

To begin with we prepared a series of catalysts with Cu/Co ratio varying from 0.2 to 2. These are designated as batch I catalysts and the NMR Data is presented in Table I. This being our initial attempt, no special efforts were made by either Grambling group (code - GSU), or Xavier group (code - XU) to control the method of preparation. Aqueous solutions of the nitrates of copper and cobalt were mixed in the desired ratio and precipitated by adding either Sodium Carbonate or hydroxide. The precipitate is thoroughly washed, dried, calcined, and reduced at 350 - 400°C. Only significant difference between the GSU and XU catalysts of the 1st batch (Table - I) is in the reduction process. GSU catalysts were reduced in a steady flowing stream of hydrogen at 350°C, while XU catalysts were soaked in hydrogen atmosphere in a Micromeretics

TABLE I

Effect of Metal Ratio: NMR frequencies of Cu/Co Catalysts (1st batch)

<u>Sample</u>	<u>Code</u>	<u>FCC</u>	<u>F A U L T L I N E S</u>			<u>HCP</u>	(Reference)
Co		213	215.5	217	218.4	221	
Cu/Co = 0.2 GSU2G	211.2	213.0	215.3		218.2	220.8	
Cu/Co = 0.4 XU7	210.7	213.1		216	218.5	221.3	
Cu/Co = 0.5 GSUS1	211.5	213	214.6		218.7		
Cu/Co = 0.6 XU8				216.3	218.1	220.1	225.9
							222.6
Cu/Co = 0.8 GSU4G	211	213.1	215.4		218.3	220.6	223.6
Cu/Co = 1.0 GSUS2	211.3	213.4	214.5				225
Cu/Co = 1.4 GSU5G	210.8	213.1	215.7		218	220.5	
Cu/Co = 1.5 GSUS3	211.2		213.9	215.3	217.6	220.2	223.5
Cu/Co = 2.0 GSU7G	210.7	212.7	215.1		218	220.2	223.6

chemisorption system for about an hour, evacuated, resoaked and the procedure was repeated until there occurs no hydrogen uptake.

The NMR results for the batch I catalysts (Table - I) do not show any systematic significant changes, that can be attributed to perturbations in the electronic charge density of cobalt atoms due to increase in the copper content of the catalyst. Our Line frequency measurements have an accuracy better than 0.3MHZ. Though there appears no systematic shift in the spectra new lines appear randomly in many catalysts. One consistant factor is the occurrence of HCP line about 0.7MHZ below the expected frequency as the copper content increases above 35%. Simultaneously we also observe lines randomly at much higher frequencies than the HCP line (221 MHZ). These features indicate that there occur significant morphological changes only in the HCP crystalline phase particles as the copper concentration increases.

With a view to reconfirm the findings the Xavier group prepared again a set of catalysts with Cu/Co ratio increasing from 0.2 to 1.0 (designated as batch II catalysts). The NMR results are presented in table II. This time the catalysts were reduced in a flowing stream of hydrogen, instead of in the chemisorption system pulsed reduction procedure. Again we do not find any systematic change in the NMR spectra that shows the influence of the metal ratio. The differences in the spectra seem rather random. However one significant feature of the second batch samples is the consistant occurrence of the FCC line about 0.7MHZ above the normal line (213.0 MHZ). In the first batch we found the HCP line 0.7MHZ below the normal line (221.0MHZ) in several catalysts, while in

TABLE II

Effect of Metal Ratio: NMR Line Frequencies of Cu/Co Catalysts (2nd Batch)

<u>Sample</u>	<u>Code</u>	<u>FCC</u>	<u>F A U L T L I N E S</u>			<u>HCP</u>	
Co		213	215.5	217	218.4	221	(Reference)
Cu/Co = 0.2 XU 11A	210.9	213.7			218.4	221.2	
Cu/Co = 0.4 XU 12A	211.4	213.6				222.1	223.8
Cu/Co = 0.6 XU 13A	211.2	213.8				222.3	223.9 225.4
Cu/Co = 0.8 XU 14A	211.5	213.9			217.9	222.8	
Cu/Co = 1.0 XU 15A						220.2	222.2 225.3

this series a line occurs about 1 MHz above the HCP in all the samples. With no supporting evidence from another source one has to resist the temptation to ascribe these shifts to Cu-Co interaction resulting in a modification of Co electronic charge distribution. The results are intriguing and tend to show that there might be occurring both morphological and metallic charge perturbations in the Cu-Co systems. However these changes do not show any significant dependance on the metal ratio but certainly seem to depend on the method of preparation.

Table III shows a comparison of the NMR results between the two batches for different metal ratios. The spectra are clearly dissimilar indicating that the morphology and metallic charge distribution are very sensitive to the method of preparation, reduction and purity of the starting chemicals. Apparently reproduction of identical catalyst samples is not an easy task unless elaborate precautions are taken to standardize and maintain similar conditions. This explains why the catalytic results reported by different groups using IFP prescriptions are divergent. However one interesting observation emerges from this study-*ie-*. Both the catalytic as well as the magnetic properties are sensitively influenced by the preparation procedure of the catalyst. We believe both the pH of the solution, the calcination and reduction temperatures significantly influence the morphology and metallic charge distribution of the catalyst, which in turn seem to determine the catalytic and magnetic properties

TABLE III

Effect of Method of Preparation: NMR Frequencies Cu/Co Metal Catalysts

<u>Sample Code</u>	<u>FCC</u>		<u>F A U L T L I N E S</u>				<u>HCP</u>
Co	213	215.5	217	218.4	221		(REFERENCE)
		Cu/Co = 0.2					
GSU 2G	211.2	213	215.3	218.2	220.8		
XU 11A	210.9	213.7		218.4	221.2		
		Cu/Co = 0.4					
XU7	210.7	213.1	216	218.5	221.3	222.6	
XU12A	211.4	213.6				222.1	223.8
		Cu/Co = 0.6					
XU8			216.3	218.1	220.1	222.6	225.9
XU13A	211.2	213.8				222.3	223.6
		Cu/Co = 0.8					
GSU4G	211	213.1	215.4	218.3	220.6	222.8	223.6
XU14A	211.5	213.9		217.9	220.1		
		Cu/Co = 1.0					
GSUS2G	211.3	213.4	214.5	215.7	220.2	222.2	225
XU15A							225.3

TABLE IV
EFFECT OF METHOD OF PREPARATION
MAGNETIZATION MEASUREMENTS

Sample	Sat. Mag.		% Redctn		Coercive Field	
	Bat.I	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

Table IV shows a comparison of the magnetization data of the two groups of catalysts. There appear no significant differences either in the saturation magnetization values (S_s) or coercive field values (H_c). Similarly increase in the metal ratio also seems to have no observable effect.

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