QUARTERLY

TECHNICAL PROGRESS REPORT

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

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Project Director

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This report describes the work done during the past several months. Due to the initial set up problems and the negative results described in the previous report, we had to make elaborate changes in our approach to the problem. Consequently this report became unduly behind schedule, as explained in my letter to Mr. John Augustine dated July 5, 1990.

INTRODUCTION

The primary objective of the project is to investigate the magnetic nature of the higher alcohol synthesis catalyst-Cu/Co supported on specific supports: chromia and titania with and without an alkali metal promoter, and examine the relations between catalytic and magnetic properties. The preliminary attempts made¹ with cobalt/copper ratio 5:8, and high metal loading in the 30-50% range showed neither copper NQR signals nor cobalt NMR signals. This leads us to believe that in the samples examined, both cobalt and copper were in the oxidic form (CoO, Co₃O₄, CuO) or copper was completely reduced while cobalt remained as an oxide. The third possibility was the formation of different spinels AB₂O₄ of copper and cobalt with titanium. The final question was the appropriateness and effectiveness of the closed system reduction procedure¹.

WORK DONE

To resolve these doubts we began to establish a catalyst preparation and flow through reduction system at our laboratory,

while the consultant, Dr. Akundi Murty (Xavier University, Tulane) undertook the preparation of a series of catalysts varying Co/Cu ratio from 5:1 to 5:5 with and without the support TiO_2 . The metal loading on the support was also reduced to 10%. The following catalysts were carefully prepared following pan Cao, Griffin procedure² and reduced in the same closed system¹ and NQR, NMR and Hysteresis studies were made.

RESULTS AND DISCUSSION

Table I shows the composition of the catalysts as prepared and their hysteresis character after reduction at 350°C .

TABLE I

Sample	J_s $\frac{\text{emu}}{\text{g}}$	J_r $\frac{\text{emu}}{\text{g}}$	$H_C(\text{oe})$	% Reduction
4 Cu/Ti 1:1				
5 Co/Ti 1:3	18	5.3	500	45
6 Co/Cu 5:1	105	35	700	78
7 Co/Cu 5:2	88.5	30.4	660	77
8 Co/Cu 5:3	86.7	22.7	610	87
9 Co/Cu 5:4	70.6	13.8	540	79
10 Co/Cu 5:5	67.4	24.3	690	84
6A 10% L on $\text{TiO}_2\text{Co:Cu}=5:1$	7.8	3.1	750	58
7A 10% L on $\text{TiO}_2\text{Co:Cu}=5:2$	7.2	2.8	700	63
8A 10% L on $\text{TiO}_2\text{Co:Cu}=5:3$	6.8	0.16	525	68
9A 10% L on $\text{TiO}_2\text{Co:Cu}=5:4$	6.1	2.37	675	69
10A 10% L on $\text{TiO}_2\text{Co:Cu}=5:5$	5.5	2.3		69

Though the over-all reduction seems to be low in all these samples, the relative trends lend to some interesting observations. While Mouaddib and Perrichon³ have observed 100% reduction of Cu/Co on titania, the MIT group⁴ reported that presence of water vapor in ZnO/TiO_2 systems inhibits the reduction pro-

cess and produces Zn TiO_2 and $\text{Zn}_2 \text{TiO}_4$. Similar process might be responsible for the poor reduction in the samples examined in this study. The percent reduction is consistently lower in the presence of titania and the efficiency of reduction seems to decrease with the amount of cobalt. These features seems to be an artifact of the experimental system used for reduction.

NQR - NMR STUDIES

The fact that copper exhibits two strong signals for Cu^{63} (69%) and Cu^{65} (31%) in Cu^+ form (Cu_2O) at 26 and 24 MHz was a motivating factor in undertaking an extensive search for the NQR signals of copper in these catalysts our earlier studies⁵ on the NQR of copper in superconducting structures provided further support for pursuing this line of thought. But to our dismay, we could observe no Cu - NQR signals in any of the catalysts as prepared and after reduction. Since copper was found to be easily reducible³ (between 367-415°K) the absence of NQR signals might be due to complete reduction of copper to metallic state. Then, in the pre cursor, copper is likely to be essentially in the CuO form. We plan to experiment the reduction at 100° to examine the transition $\text{CuO}-\text{Cu}_2\text{O} - \text{Cu}$. This may be of academic interest only since under reaction conditions (250°C) this phase is unlikely to exist.

Table II shows the frequencies of the observed NMR signals in the series of catalysts examine (See page 4).

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This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

TABLE II

sample	fcc	faults	faults	hcp	NOT EXPLICABLE / NEED FURTHER INVESTIGATION	
Co powder(lit.values)	213	215.5	217	218.4	221	
Co(pptd.Red.)	210.7	212.8	215.2	218	220.9	224
5CoTi1:3	210.5	212.8	215.3	218	220.9	226.6
6CoCu5:1	oscillator becomes over loaded - sample reduction				78%	
6ACoCu51 10% on TiO2	"	"	"	"	93.6%	
7CoCu5:2	210.7	213	216.1	218.5	221.3	226
7ACoCu52 10% on TiO2	213.6(broad and weak)					
8CoCu5:3	212.9	216.4	218.1	220.1	222.6	224.5
8ACoCu53 10% on TiO2	218.5				221.3	
9CoCu5:4	210.8	212.6	215	217.9	220.2	226.2
9ACoCu54 10% on TiO2	213.8(broad and weak)				220.5	
10CoCu5:5	217.6				220.4	225
10ACoCu55 10% on TiO2	NO SIGNAL				222.8	

But for the lines observed in certain catalysts (samples 7,8) above 221 MHz (normal HCP phase), the spectra observed in general follow the predicted pattern⁶. The appearance of the low frequency line (210.8 MHz-below FCC line) is consistent with our earlier observations⁷ in similar catalysts. We believe, if the electronic charge density on cobalt increases, tending to nickel configuration due to electronic exchanges between cobalt and support or cobalt and cocatalyst copper in this case, the FCC line could be shifted down. Our measurements are generally accurate within 0.3 MHz. The significant differences for ex: the 216 MHz lines in Co/Cu 5/2 and 5/3 samples (7 & 8) and all the high frequency lines above the HCP line pose a serious challenge. At this point we have no clue regarding their origin, nor can we disregard them as spurious. It is interesting to note that the high frequency lines occur only in the unsupported catalysts. Whether they are real or an artifact of the spectrometer performance due to the presence of higher concentration of metal in the oscillator coil is not clear. Further tests are needed to rule out the ambiguities. It becomes imperative to prepare all samples again in triplicate and run the NMR experiments before any meaningful conclusions could be drawn.

PROJECT STATUS AND PROJECTIONS

During the first year of operation, the project proved more complex and challenging. It has been reported earlier that the catalytic results are sensitive to the catalyst preparation and reduction procedures⁸. The magnetic characteristics also seem to be very sensitive to the preparation techniques. We feel that in

addition to the proposed NQR-NMR and hysteresis studies, it is necessary to perform XRD and TMA studies also on the samples to establish meaningful correlations. We plan to procure the professional services of Advanced Materials Corporation to provide this data.

At Grambling State University, we have established the necessary vacuum manifold, heating unit and gas flow systems for H₂, Co and He. The necessary alarms need to be in place before we can prepare and reduce the catalysts here in a flow through system. The Xavier-Tulane system with which we started does not lend itself for continuous flow reduction, and we are left in doubt regarding the appropriateness of the closed system method and reproducibility of the samples and spectra. These concerns have largely contributed to the sluggish progress of the project and left us way behind schedule. We need more time to accomplish the proposed objectives of the project. Originally the grant is scheduled to expire by 09-14-91. We plan to request a no cost extension for an additional year, ie till the end of 09-14-92 to carry out the proposed studies. Soon after revising the budgets to accommodate the services of AMC. we will be sending our letter of request for no cost extension.

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