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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: A. N. Murty
Physics Department

INSTITUTION: Grambling State University
Grambling, Louisiana 71245

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A. Narasimhan
Project Director

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Date

MASTER

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(For period 9-15-91 to 12-15-91)

Introduction

Our studies were essentially concerned with analyzing the magnetic character of the Cu-Co catalysts for Cu/Co ratio ranging from 0.2 to 4 [1,2]. The results clearly indicate that

- a) as the copper content increases beyond 50% significant inter-metallic interactions occur between copper and cobalt.
- b) the magnetic character of the bimetallic clusters formed is sensitively dependant on the method of preparation.

Interestingly, the NMR results proved to be far more sensitive to the chemical character of the catalyst than the magnetization results. The magnetization results predictably show a gradual decrease in the magnetic moment for Cu/Co ratios greater than one [2]. However, the results for Cu/Co ratios less than one are irregular with no discernable pattern.

The NMR spectra, on the other hand, seem to reveal subtle changes in the chemical character of the catalyst. High frequency lines above the HCP line (221 MHz) in the catalysts with Cu/Co ratios < 1 and the substantial shift of the entire spectrum to higher frequencies (Fig. I) as the Cu/Co ratio increased beyond 50% lead us to believe that a distribution of bimetallic clusters might

be forming randomly with varying composition and morphology. As the Cu/Co ratio increases beyond one, actual alloying might take place between copper and cobalt hence giving rise to strong intermetallic interaction/bond formations. These conclusions support the views expressed by Xu Xiaodong et.al [3], the IFP group [4] and others [5] that alcohol formation occurs for Cu/Co ratios, $1 < \text{Cu/Co} < 3$ and that such alloy clusters are the active species for alcohol formation. In the catalysts with $\text{Cu/Co} < 1$ it seems copper and cobalt mostly crystallize separately leading to the production of hydrocarbons. We felt it necessary to verify the NMR results with a fresh batch of samples, and to examine the role and function of chromium in the IFP type catalyst systems [4].

Project Activity

During this quarter our major focus has been

- 1) to prepare all the catalysts again following an identical preparative technique and confirm the NMR results. The Xavier group led by the collaborating consulting Prof. Akundi adopted the following procedure and prepared the precursors which are now being reduced in our laboratory. One molar solutions of the nitrates of copper and cobalt were mixed in the desired ratio. The mixed nitrate aqueous solution was allowed to drop slowly into a beaker containing a 7 pH solution of sodium hydroxide while stirring continuously at a temperature of 80°C . The pH of the solution was continuously monitored and maintained between 7 and 8 by adding the necessary amount of NaOH. The precipitate is thoroughly boiled and washed three

times with distilled water, filtered, air dried at 80°C for 18hrs. and air calcined at 350°C for 18hrs. The samples are reduced in a flowing stream of hydrogen (20-25 cc/min) for 18 hrs at a temperature of 350°C. The NMR spectra of these samples are now being scanned in our lab.

- 2) The second aspect we explored is the role of chromium in the tri-metallic Cu/Co/Cr higher alcohol synthesis catalyst system investigated by the IFP group [4]. The current view of the reaction mechanism and the roles of the different metals is summarized below. [3]

*_H site for H₂ dissociation which is metallic Cu or Co

H* adsorbed surface hydrogen atom

*_a site for associative CO adsorption which is either Cu or Co ion
CO* adsorbed CO molecule

*_d site for CO dissociation which is CO metal

and the final step

thus it is believed that CO insertion represents a termination step rather than propagation. Other reactions that are pertinent to the study indicate the role of copper in methanol synthesis.

The above analysis shows that the role of copper, the major element for MeOH synthesis, is the dissociative chemisorption of hydrogen and the associative adsorption of CO. The role of cobalt, the element frequently encountered in F-T synthesis, is the dissociative CO adsorption (C-C chain growth) and hydrogenation. The specific role of chromium is obscure in the proposed schemes except perhaps as a stabilizing agent.

EXPERIMENTAL STUDIES

Following the preparative procedure outlined above, we examined the role of chromium in the catalyst system Cu-Co-Cr. Three catalysts with Cr/Co = 0.5, 1.0, 2.0 were prepared, and the hysteresis character and NMR spectra were analyzed. The results for Cr/Co catalysts are compared with previously obtained Cu/Co catalyst data; and are presented in tables I and II. The NMR line positions in Cr/Co and Cu/Co catalysts relative to pure Co powder lines are shown in Figure I.

All the precursors exhibit typical paramagnetic character as discussed earlier [2]. No NQR lines of Cu could be detected in any of the catalysts. This indicates that Cu should be either in CuO form or in a spinel structure CuCo_2O_4 ($\text{CuO} + \text{Co}_2\text{O}_3$) and does not occur in Cu^+ (Cu_2O) state. The reduced samples are ferromagnetic, typical of the cobalt metallic behavior (table II). However, the percent reduction is in general lower than what we encountered in supported Co catalysts [6]. In Cu-Co catalysts the percent reduction is 75% while in Cu-Cr catalysts it drops to as low as 5% (Table II). Nearly 90% of the loaded Co remains in an irreducible form in the presence of Cr although all the samples, Cu/Co and Cr/Co, were reduced under identical conditions. The coercive field values are also consistently lower in Cr/Co catalysts than in Cu/Co catalysts. Since NMR line intensities (Fig I) are fairly comparable, the Co particles in Cr/Co catalysts might be relatively larger. Whatever Co occurs in metallic form, it seems to retain its identity unlike in the Cu/Co catalysts where bimetallic cluster formation and strong intermetallic interaction is evident. All the observed lines in Cr/Co catalysts are fairly close to the Co powder spectrum lines while Cu/Co catalysts show strong lines beyond the Co spectral range (Fig II). Chromium may be serving as a retarding agent and may effect a decrease in the hydrocarbon productivity of cobalt. The amount of cobalt that is not in metallic form, if it occurs in an ionic form it could enhance the associative adsorption of CO, and improve alcohol selectivity.

TABLE I
NMR DATA: COMPARISON OF Cu/Co AND Cr/Co CATALYSTS

sample	FCC	FAULT LINES		HCP			
Co powder	213.0	215.5	217.0	218.4	221.0		
Cu/Co=0.6	213.8					222.3	223.9 225.4
Cr/Co=0.5	213.6		216.5	218.9	221.8		
Cu/Co=1.0						220.2	222.2 225.3
Cr/Co=1.0	213.3	215.7		218.1	221.0		
Cr/Co=2.0						222.0	223.9
Cr/Co=2.0	213.4		216.2	218.5			227.6 230.6

TABLE II
MAGNETIZATION DATA: COMPARISON OF Cu/Co and Cr/Co CATALYSTS

sample ratio	Ss	Sr	Hc	% Reduction
Cu/Co=0.6	59.9	20.2	655	60
Cr/Co=0.5	17.4	3.5	395	16
Cu/Co=1.0	61.6	16.8	503	77
Cr/Co=1.0	12.2	0.8	212	15
Cu/Co=2.0	40.7	16.4	746	76
Cr/Co=2.0	2.6	0.2	199	5

FIG. 1. NMR LINE FREQUENCIES OF Cr/Co and Cu/Co CATALYSTS

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