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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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Date

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This report presents the progress of work so far in the project "NMR-NQR Studies of Cu/Co Higher Alcohol Synthesis Catalysts".

The project involves establishing the necessary experimental and laboratory facilities between Xavier University (Consultant Dr. Akundi A. Murty) and Tulane University (Collaborating scientist: Dr. Vijay T. John) for the preparation of Catalysts and examination of the catalytic properties. This phase of the work has been considerably slowed down due to the involved administrative policies and procedures in procuring the necessary chemicals, glassware and auxiliary supplies.

After examining several methods of preparation¹⁻⁶, we have selected the following techniques as suitable procedures for the preparation of the catalyst samples.

Co-precipitation technique: 1M. aqueous solutions of copper-nitrate and cobalt-nitrate are mixed in the proportions needed to obtain the desired cation ratio in the catalyst along with the appropriate amount of titanium dioxide. By adding 1M solution of sodium hydroxide, the catalyst was precipitated while maintaining neutral pH conditions at a temperature of 80°C. The precipitate is thoroughly washed in hot water, dried at 110°C and calcined in air for 12 hours at 350°C. Before calcination, the precursor is divided into equal portions and 5 wt% of sodium is added as promoter to one part by adding (1.144 X ml) 1

molar Na_2CO_3 solution (where X is the grams of dried powder) to the point of incipient wetness. The calcined catalyst samples were subjected to the reduction process using a micromeretics chemisorption system (shown in Fig 1). The sample was loaded in a sample tube at one of the entry ports and evacuated while raising the temperature to 400°C . Then Hydrogen was introduced into the tube until the pressure is slightly above the atmospheric pressure. Every few hours the pressure dropped due to adsorption and water vapor condensed on the cool end of the sample tube which was evacuated and hydrogen refilled. This procedure was repeated until there was no noticeable drop in the H_2 pressure. The sample tubes were sealed and examined for the NMR spectrum of cobalt and NQR spectrum of copper.

Results and discussion:

Following the procedure described, four calcined samples and one reduced sample were prepared with the following compositions.

- (a) Cu/Co/Ti: Cu/Co = 1.6, Ti/Co = 2
- (b) Cu/Co/Ti: Cu/Co = 1.6, Ti/Co = 2, Na = 5wt%
- (c) Cu/Co/Ti: Cu/Co = 1.6, Ti/Co = 3
- (d) Cu/Co/Ti: Cu/Co = 1.6, Ti/Co = 3, Na = 5wt%

To our disappointment, we could not observe either NMR or NQR signals in any of the samples. We did not expect to see NMR signals of cobalt-metal in the calcined samples since cobalt is likely to be in the oxidic phase and not in the

metallic form. However, in the reduced sample, we expected cobalt to be in the metallic form from our past experience^{7,8} on cobalt-titania catalysts. Not only the NMR signals were fairly strong, both the magnetic and NMR measurements indicated that there occurs strong metal-support interaction between Cobalt and Titania⁷. The absence of Co-metal in the catalyst could be either due to improper reduction procedure or as suggested by Shefer et al³ that cobalt might form a cobalt titanium spinel. We are currently engaged in a thorough investigation of this aspect, by duplicating and revising the preparation and reduction procedures. The reason for examining the calcined samples was, we expected that copper will be in the oxide form before reduction and Cu_2O gives strong NQR signals for both the isotopes (Cu^{63} and Cu^{65}). It is disturbing to note that neither the calcined nor the reduced samples show observable NQR signals. Again, we feel that the results are inconclusive and the preliminary samples that were tried need to be critically examined after standardizing the preparation and reduction procedures. The closed system reduction procedure will be tested using a previously tested Co-ZSM-5 precursor which was reduced in a flow through system⁹. We are presently establishing facilities for the preparation and reduction of the catalyst in our laboratory at GSU. The vacuum manifold has been set up and we are trying oxalate precipitation from homogeneous solution: To an aqueous solution containing nitrate of Co (ii) and Ti

(iii) (in the desired ratios) in 1M HNO_3 , a 10% solution of diethyl oxalate would be added such that its concentration in excess of the stoichiometric requirements would be 0.1 M. The temperature of the solution would be raised to 70 - 80°C so as to precipitate the mixed oxalate of the component metal ions. The precipitate would be allowed to settle for an hour, filtered and dried in a vacuum desiccator. The dried precipitate would be calcined at 300°C to obtain the oxide precursor - NMR/NQR measurements on catalysts produced with different preparation and reduction procedures are expected to establish the chemical character of the two metals copper and cobalt, which are the major players in higher alcohol synthesis.

Figure 5. Schematic Diagram of Manifold, Gas and Sample Attachment and Pressure Measuring System

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