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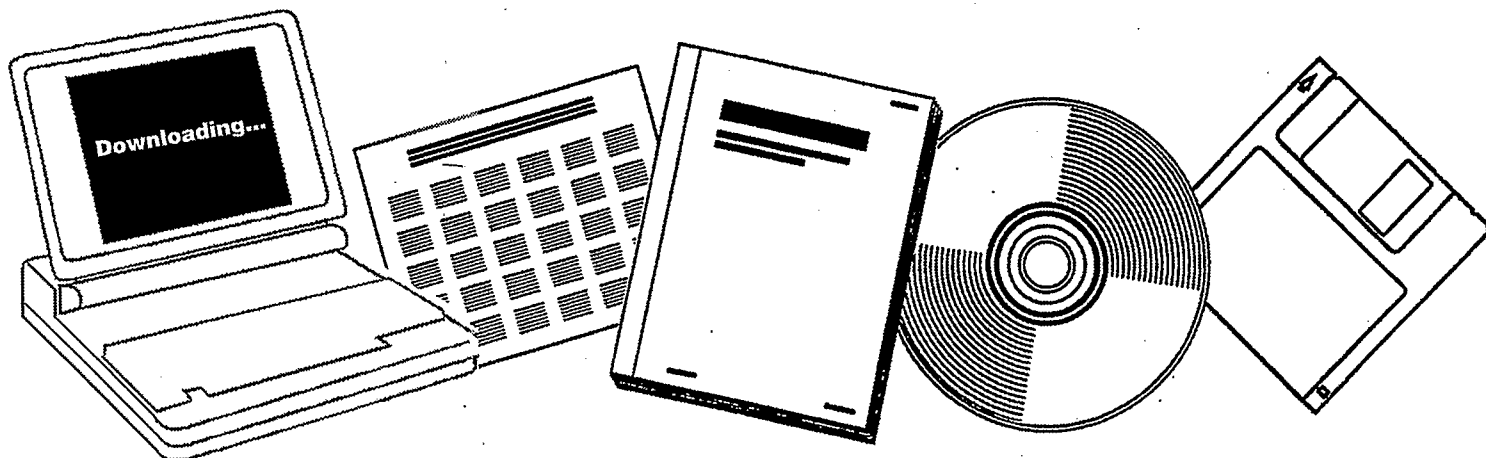
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**PROBE MOLECULE STUDIES: ACTIVE SPECIES IN
ALCOHOL SYNTHESIS. QUARTERLY REPORT NO. 6,
JANUARY 1992--MARCH 1992**

**PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING**

APR 1992



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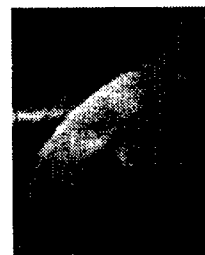
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DOE/PC/90305-T7

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DOE QUARTERLY REPORT, No.6, January 1992 - March 1992

DE92 016682

**PROBE MOLECULE STUDIES:
ACTIVE SPECIES IN ALCOHOL SYNTHESIS**

6th Quarterly Report
January 1992 - March 1992

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April 1992

Prepared for the U.S. Department of Energy
under Grant No. DE-FG22-90PC-90305

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1. OBJECTIVE AND SCOPE OF WORK

The goal of this research is to develop a better understanding of the mechanisms of formation of alcohols and other oxygenates from syngas over supported catalysts. Probe molecules will be added in situ during the reaction to help delineate reaction pathways and identify reaction intermediate species. The key of our study is to investigate how the species generated by these probe molecules interact with surface species present during oxygenate formation.

A reaction and analysis system capable of carrying out the experiments for this study was set up, modified, and tested[1].

CO hydrogenation reactions are being carried out in both the presence and the absence of the probe molecule under conditions which favor the formation of oxygenated products. Nitromethane, acetylenic compounds, alcohols are possible choices as probe molecules for this study. The effectiveness of these probe molecules for the study of mechanisms of alcohol synthesis has to be determined experimentally based on different catalyst systems and reaction conditions.

One of the catalysts chosen for this investigation is Co/Cu/ZnO/Al₂O₃. Detailed motivations for studying this system as well as using CH₃NO₂ as the probe molecule were given in the previous report[2].

Received by OCS
JUL 8 1992

2. SUMMARY OF PROGRESS

(A) A Co(1 wt%)/Cu/ZnO/Al₂O₃ catalyst has been prepared by incipient wetness impregnation of the commercial Cu/ZnO/Al₂O₃ with cobalt nitrate.

(B) Activity and selectivity of this catalyst for CO hydrogenation were tested under different reaction conditions. Conditions under which reasonable amount of ethanol can be produced with relatively low hydrocarbon formation were chosen for the study of probe molecule addition.

(C) The effect of CH₃NO₂ addition to H₂/CO (2:1) over Co/Cu/ZnO/Al₂O₃ was investigated.

3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

(A) Catalyst Preparation

5 g Cu/ZnO/Al₂O₃^[1] was impregnated with 4.3 ml of 2.8709 g Co(NO₃)₂·6H₂O dissolved in 50 ml H₂O by incipient wetness technique to obtain a Co(1 wt%)/Cu/ZnO/Al₂O₃ catalyst. The impregnated sample was dried at 90 °C overnight in air. Then, it was reduced in flowing H₂ (80 cc/min) at 300 °C for 8 hr. The temperature was ramped from 25 °C to 300 °C at 0.5 °C/min. The catalyst was then passivated at 35 °C with 2% O₂ in He for ~2 hr.

(B) Activity and Selectivity Tests

About 1 g of the Co/Cu/ZnO/Al₂O₃ catalyst was loaded in

the reactor for activity and selectivity tests. Before reaction, a re-reduction was performed in the reactor with about 5 % H₂ in He (~80 cc/min) at 1 atm and 300 °C for 8 hr before cooling to the reaction temperature, 250 °C.

The CO hydrogenation reaction was first carried out at 300 psi with H₂/CO/CO₂ (80+40+6 cc/min) reactant mixture at 250, 270, 290, 310, 330, and 350 °C. The product distribution in terms of C (CO+CO₂) conversion (%) is shown in Figure 1. Significant amount of ethanol was produced in this temperature range. As temperature increased, more propanol and dimethylether were formed but C₁-C₆ linear hydrocarbons increased significantly. To study the effects of CH₃NO₂ addition on oxygenates formation the following conditions were chosen:

400 psi, 290 °C, H₂/CO ratio of 2 with or without CO₂.

(C) Effects of CH₃NO₂ Addition

The effects of CH₃NO₂ addition to the steady state of CO hydrogenation reaction were investigated at 290 °C and 400 psi with, first, H₂/CO/CO₂ (80+40+6 cc/min), then, H₂/CO/He (80+40+6 cc/min). The effect of CH₃NO₂ addition on the distribution of the major products, e.g. CH₃OH, C₂H₅OH, (CH₃)₂O, CH₄ and C₂H₆, is shown in Figure 2. CH₃OH and (CH₃)₂O were significantly suppressed upon CH₃NO₂ addition but not C₂H₅OH. CH₄ increased with the addition of CH₃NO₂ but not C₂+ hydrocarbons. As shown in Figure 3, CH₃NO₂ added to the reaction was completely converted to (CH₃)₃N over Co/Cu/ZnO/Al₂O₃. Results from repeating the same reaction showed that

addition of CH_3NO_2 does not poison the catalyst under the selected conditions. $(\text{CH}_3)_3\text{N}$ leaves the surface completely in about an hour (see Figure 4).

The selective interaction of CH_3NO_2 with the CO hydrogenation products raises intriguing questions about the dynamic surface, for example,

- How is CH_3NO_2 converted into $(\text{CH}_3)_3\text{N}$? Which intermediate or surface species in the CO hydrogenation is involved in the $(\text{CH}_3)_3\text{N}$ formation?

- Why does the conversion of CH_3NO_2 to $(\text{CH}_3)_3\text{N}$ only suppress CH_3OH and $(\text{CH}_3)_2\text{O}$ significantly but not C_2+ alcohols? Does $\text{C}_2\text{H}_5\text{OH}$ as well as $\text{C}_3\text{H}_7\text{OH}$ formation involve the same intermediate as CH_3OH and $(\text{CH}_3)_2\text{O}$ formation?

- Why does conversion to CH_4 increase upon CH_3NO_2 addition? Is it caused by breaking of the C-N bond in CH_3NO_2 ?

Answers to these questions could be very helpful in distinguishing which intermediate(s) is (are) involved in the various reaction pathways.

4. PLANS FOR THE NEXT REPORTING PERIOD

Further experiments with both $\text{Co/Cu/ZnO/Al}_2\text{O}_3$ and $\text{Cu/ZnO/Al}_2\text{O}_3$ catalysts have been designed for the next reporting period in order to answer some of the questions raised in the previous section.

REFERENCES

- [1] DOE Quarterly Report, No.1&3, 1991, undr Grant No. DE-FG22-90PC-90305.
- [2] DOE Quarterly Report, No.5, 1991, undr Grant No. DE-FG22-90PC-90305.
- [3] DOE Quarterly Report, No.4, 1991, undr Grant No. DE-FG22-90PC-90305.

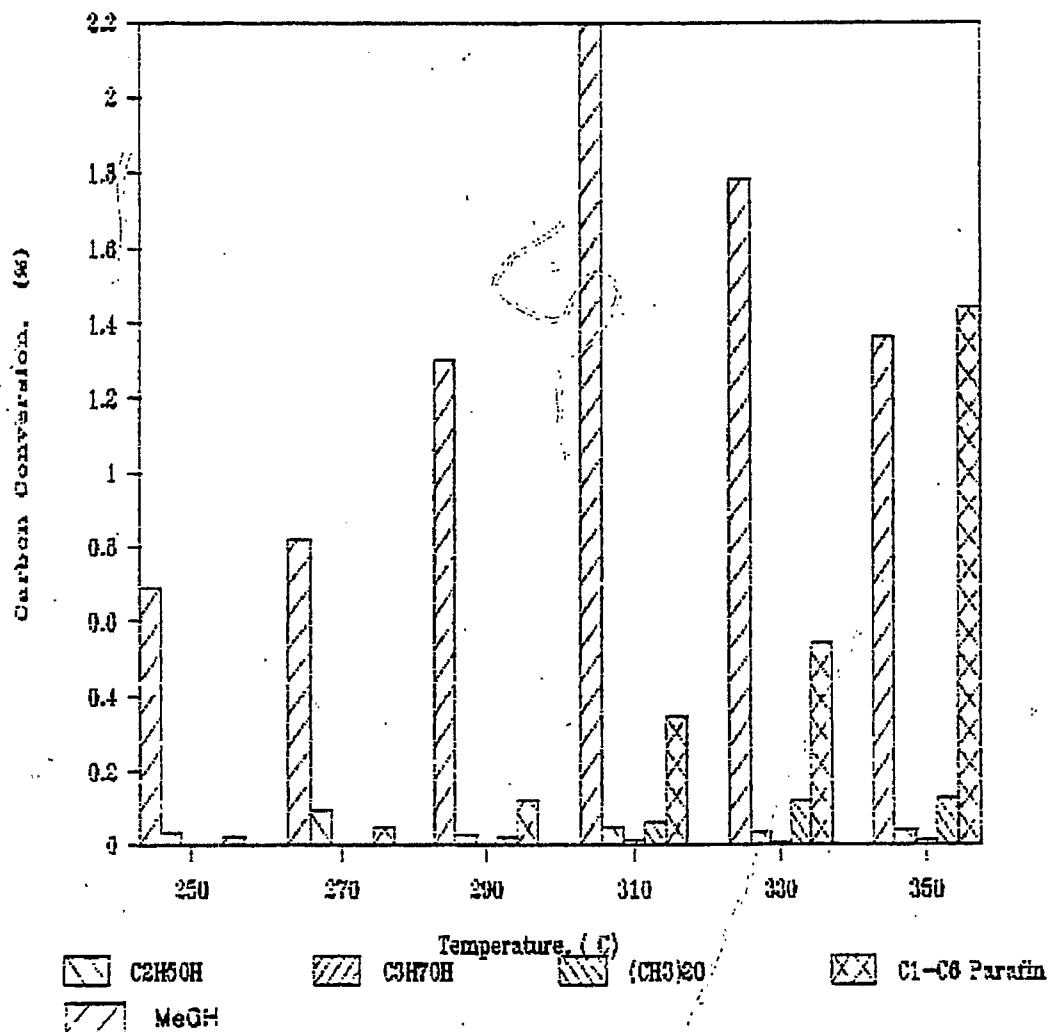


Figure 1. Carbon conversion from H₂/CO/CO₂ (80+40+6 cc/min) to CH₃OH, C₂H₅OH, 1-C₃H₇OH, (CH₃)₂O, and C₁-C₆ linear paraffins over 1 g Co/Cu/ZnO/Al₂O₃ under 400 psi at temperatures ranging from 250-350 °C.

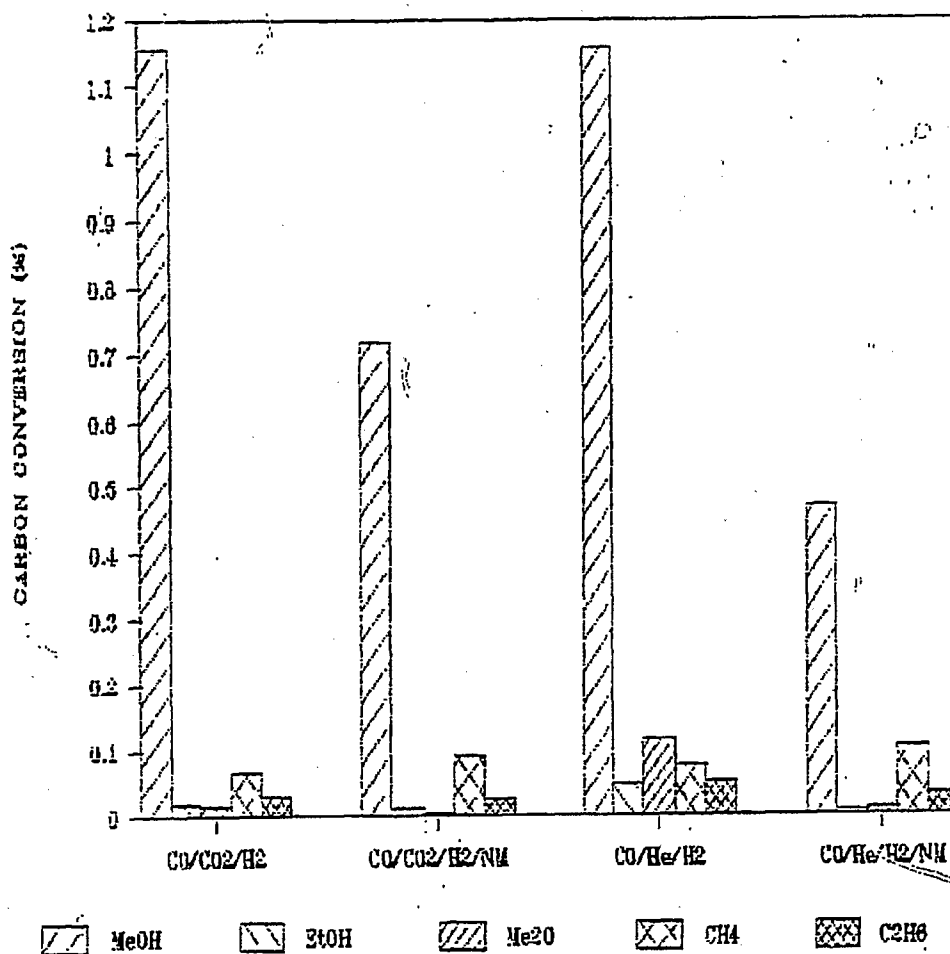


Figure 2. Effect of CH₃NO₂ addition on carbon conversion to CH₃OH, C₂H₅OH, (CH₃)₂O, CH₄ and C₂H₆ over 1 g Co/Cu/ZnO/Al₂O₃ at 400 psi, 290 °C, from H₂/CO/CO₂ (80+40+6 cc/min) and H₂/CO/He (80+40+6 cc/min) mixtures.

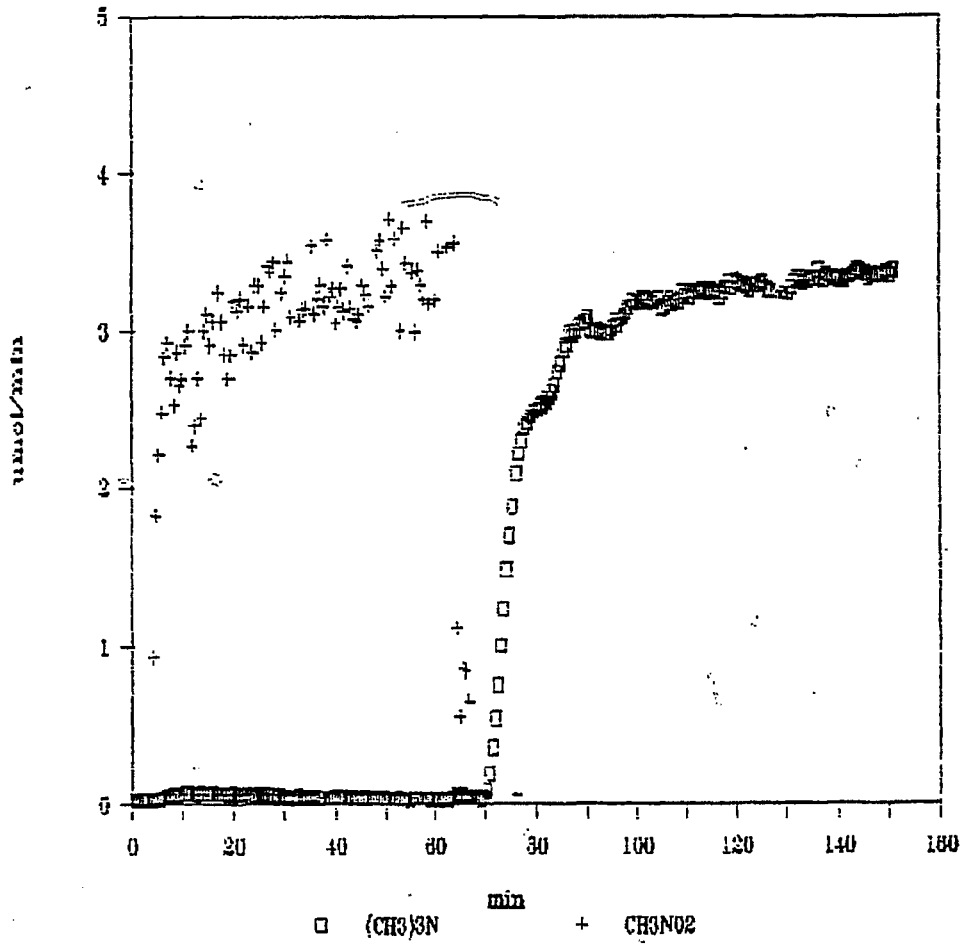


Figure 3. Nitrogen balance in the conversion of CH_3NO_2 into $(\text{CH}_3)_3\text{N}$ over 1 g $\text{Co/Cu/ZnO/Al}_2\text{O}_3$ at 400 psi, 290 °C, and $F(\text{H}_2+\text{CO}) = 80+40$ cc/min.

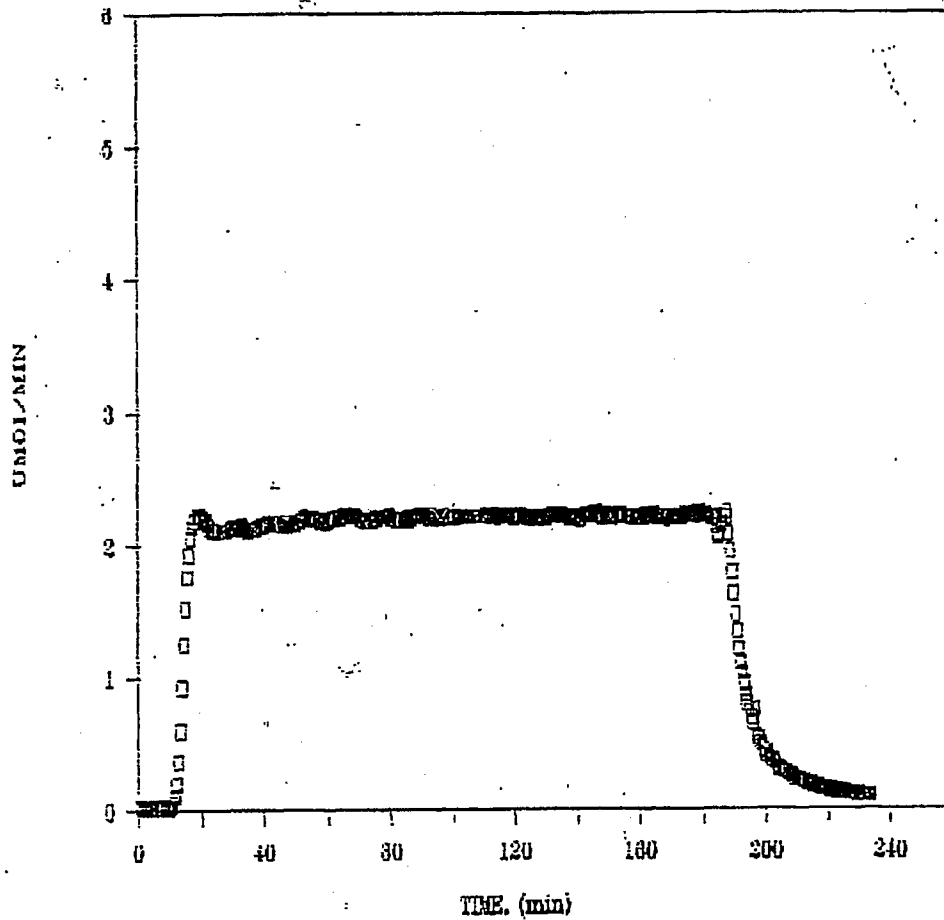


Figure 4. Transient Response of $(\text{CH}_3)_3\text{N}$ formation (by recording $m/z=59$ on an on-line Dycor Mass Spectrometer) upon CH_3NO_2 addition to H_2/CO (80+40 cc/min) over $\text{Co}/\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ at 290°C , 400. psi.

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