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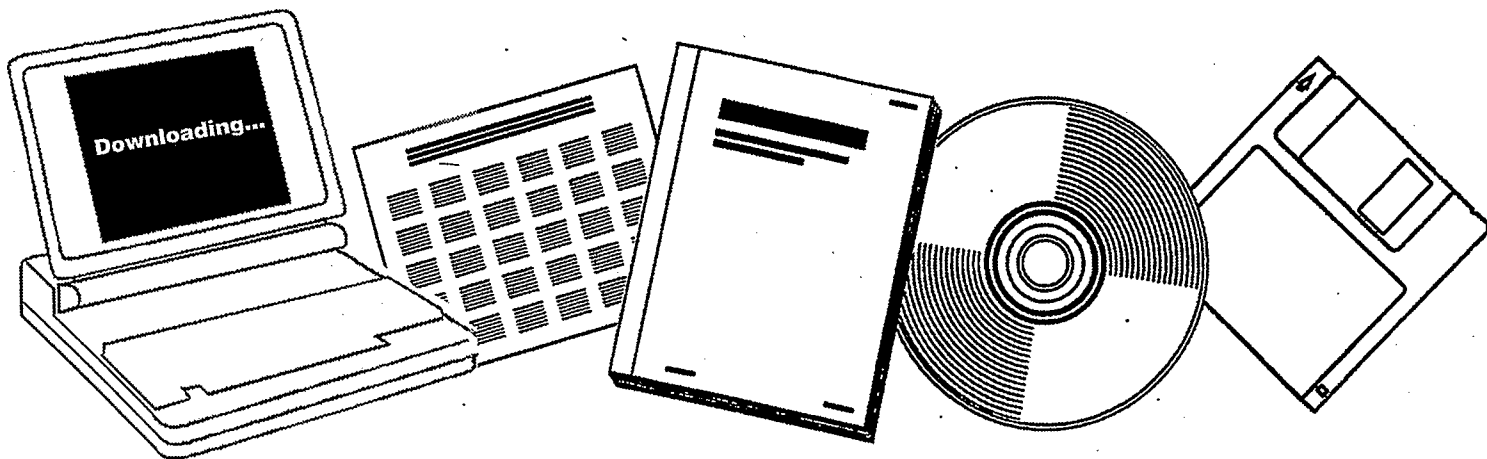
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**PROBE MOLECULE STUDIES: ACTIVE SPECIES IN
ALCOHOL SYNTHESIS. FOURTH QUARTERLY
REPORT, JULY 1991--SEPTEMBER 1991**

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

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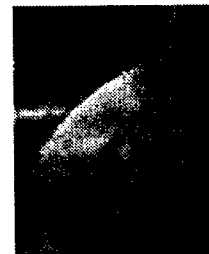
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**PROBE MOLECULE STUDIES:
ACTIVE SPECIES IN ALCOHOL SYNTHESIS**

4th Quarterly Report
July 1991 - September 1991

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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 (see DOE Quarterly Reports No.1, No.3).

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.

Cu/ZnO/Al₂O₃, as well as supported Pd and/or Rh, without and with alkali promoters are catalysts for this study.

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.

2. SUMMARY OF PROGRESS

During this period, the effect of CH_3NO_2 addition to MeOH synthesis from $\text{H}_2/\text{CO}/\text{CO}_2$ over $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ has been studied.

Prior to the reaction studies, blank runs were performed in order to understand the behavior of CH_3NO_2 under the selected experimental conditions.

It was found that over $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ CH_3NO_2 behaves in a more complex manner than that was observed over supported Ru in our previous work (DOE Grant #FG22-8SPC80526). In that work, the probe molecule formed CH_x surface species by cleavage of the C-N bond. It appears that over $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$, the C-N bond of nitromethane is not selectively cleaved.

3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Blank runs with CH_3NO_2 and He and H_2 were carried out at 400 psi, 503 K, with GHSV = 4190 hr^{-1} over both the empty reactor and the $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$. The empty reactor was inert in all cases. The He/ CH_3NO_2 blank over $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ is shown in Figure 1. CH_3NO_2 decomposed to produce CO_2 , the only product detected. When CH_3NO_2 was added to the catalyst surface in the presence of H_2 in He (Figure 2) under the same conditions, a small amount of CH_3OH and a carbon-nitrogen compound tentatively identified as trimethylamine were

formed. No CO₂ was detected in this case.

Reaction of CO/H₂/CO₂ over Cu/ZnO/Al₂O₃ was studied at 150 psi, 503 K, with GHSV=4190 hr⁻¹. As shown in Figure 3, a steady-state rate of near 4% conversion to MeOH was observed. When nitromethane was added to the reaction mixture, the conversion to methanol decreased and the formation of the same carbon-nitrogen compound observed in the CH₃NO₂/H₂ blank run was again observed.

These results differ from those of the supported Ru case in a number of ways:

- 1) No CO₂ was formed from CH₃NO₂ in either He or H₂ blanks on supported Ru.

- 2) No compounds were detected in which the carbon-nitrogen bond of CH₃NO₂ was retained in any reactions over supported Ru.

The interaction of CH₃NO₂ with Cu/ZnO/Al₂O₃ is clearly different from its interaction with Ru. The formation of amines from CH₃NO₂ is suggested from the carbon-nitrogen compound we have identified. The route by which this compound forms may help us to understand the surface chemistry of this catalyst and hence may provide information about the mechanisms of alcohol synthesis over this catalyst.

4. PLANS FOR THE NEXT REPORTING PERIOD

In the next period, the following topics will be addressed:

- Confirmation of the carbon-nitrogen compound by standards.
- In depth investigation of the interaction of CH₃OH with nitromethane over Cu/ZnO/Al₂O₃.
- Prepare alkali promoted Cu/ZnO/Al₂O₃.
- Determine the optimum conditions for C₂⁺ alcohol formation.
- Compare the results from both unpromoted and promoted Cu/ZnO/Al₂O₃ catalysts.

CH₃NO₂ ADDITION TO CuZnO₂/Al₂O₃ WITH He

P=400psi, T=230C, Wcat=1g, F=126cc/min

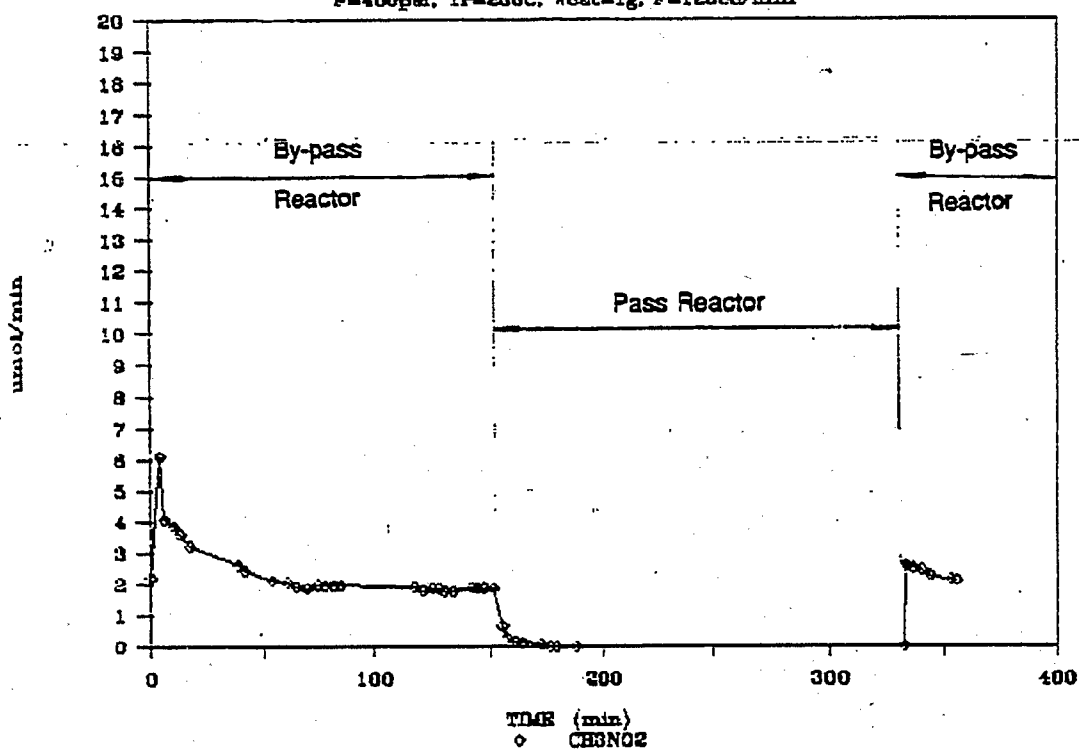


Figure 1.

CH3NO2 ADDITION WITH H2/He

P=400psi, T=230C, Wcat=1g, F=1.26cc/min

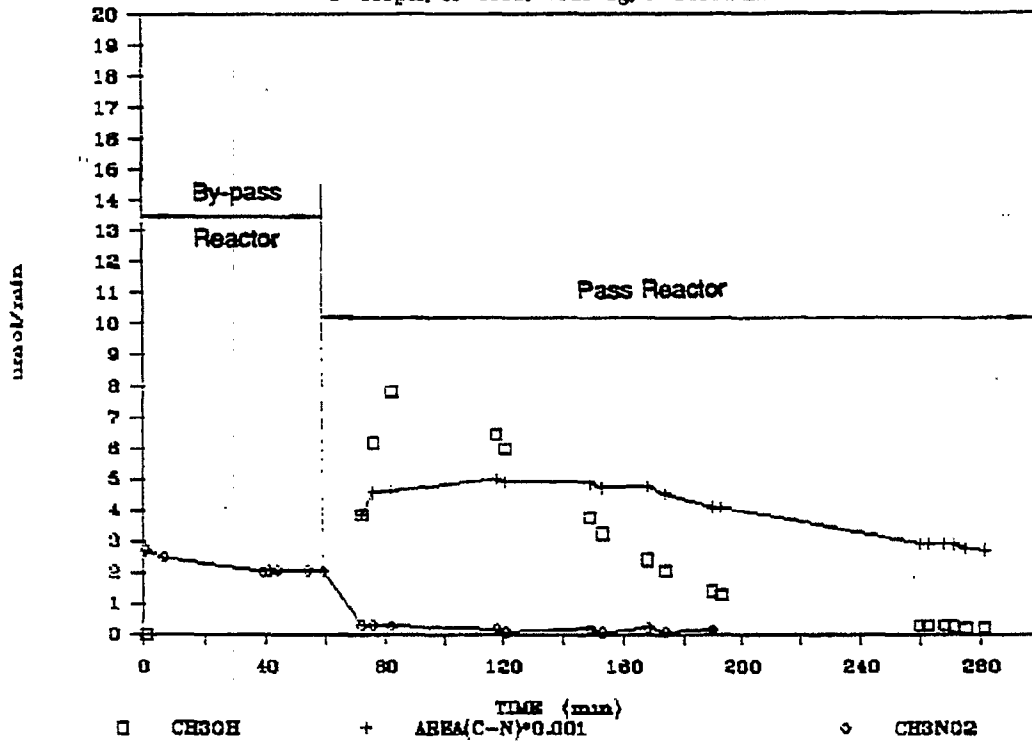


Figure 2.

CH₃NO₂ ADDITION TO MeOH SYNTHESIS

P=150psi. T=273C. GHSV=4190. CuZnOAl=1g

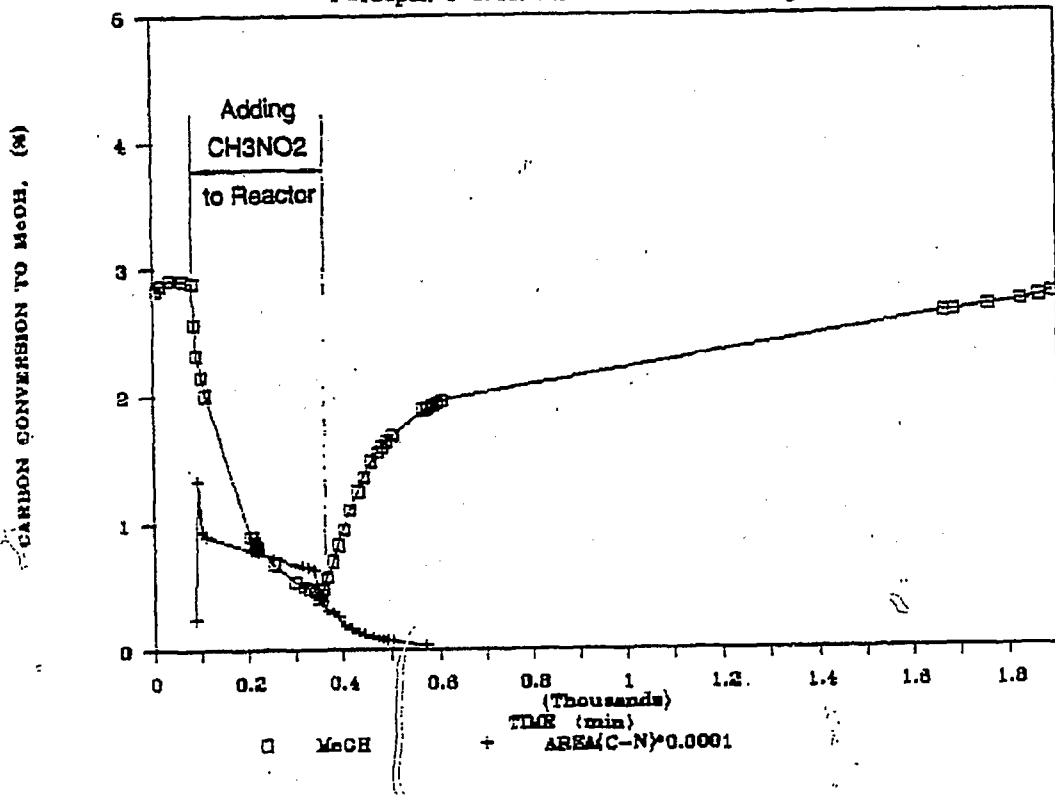


Figure 3.

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