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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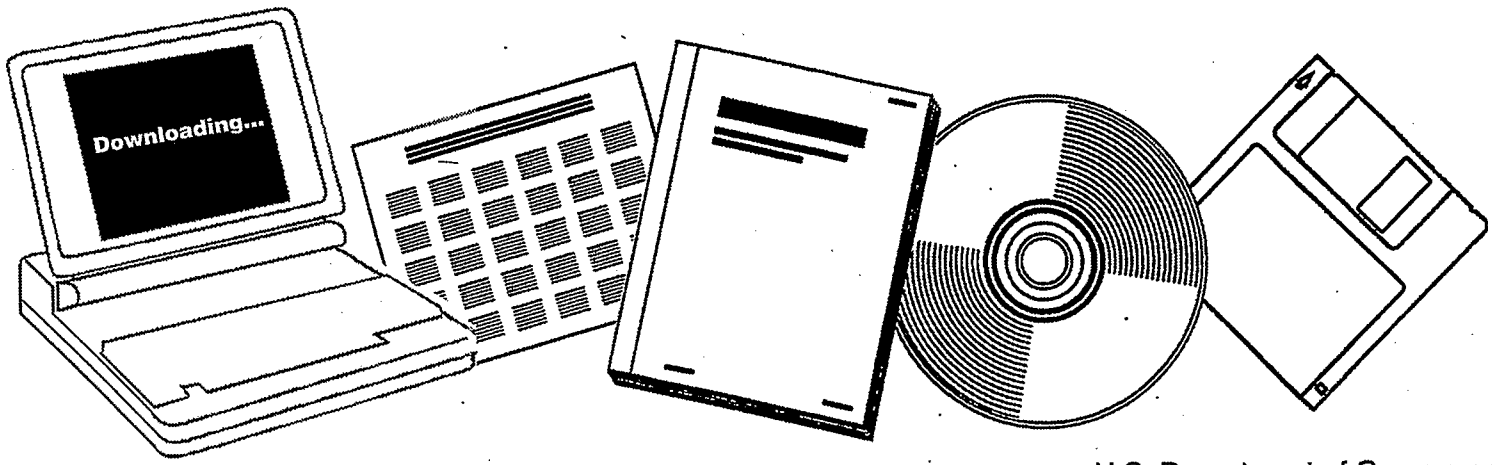

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PROBE MOLECULE STUDIES:

ACTIVE SPECIES IN ALCOHOL SYNTHESIS

4th Quarterly Report

July 1991 - September 1991

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DISCLAIMER

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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.

$Cu/ZnO/Al_2O_3$, 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 $H_2/CO/CO_2$ over $Cu/ZnO/Al_2O_3$ 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 $Cu/ZnO/Al_2O_3$ 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 $Cu/ZnO/Al_2O_3$, 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 $Cu/ZnO/Al_2O_3$. The empty reactor was inert in all cases. The He/CH_3NO_2 blank over $Cu/ZnO/Al_2O_3$ 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 CO_2 was detected in this case.

Reaction of $CO/H_2/CO_2$ over $Cu/ZnO/Al_2O_3$ 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 CH_3NO_2/H_2 blank run was again observed.

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

1) No CO_2 was formed from CH_3NO_2 in either He or H_2 blanks on supported Ru.

2) No compounds were detected in which the carbon-nitrogen bond of CH_3NO_2 was retained in any reactions over supported Ru.

The interaction of CH_3NO_2 with $Cu/ZnO/Al_2O_3$ is clearly different from its interaction with Ru. The formation of amines from CH_3NO_2 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 $Cu/ZnO/Al_2O_3$.
- Prepare alkali promoted $Cu/ZnO/Al_2O_3$.
- Determine the optimum conditions for C_2^+ alcohol formation.
- Compare the results from both unpromoted and promoted $Cu/ZnO/Al_2O_3$ catalysts.

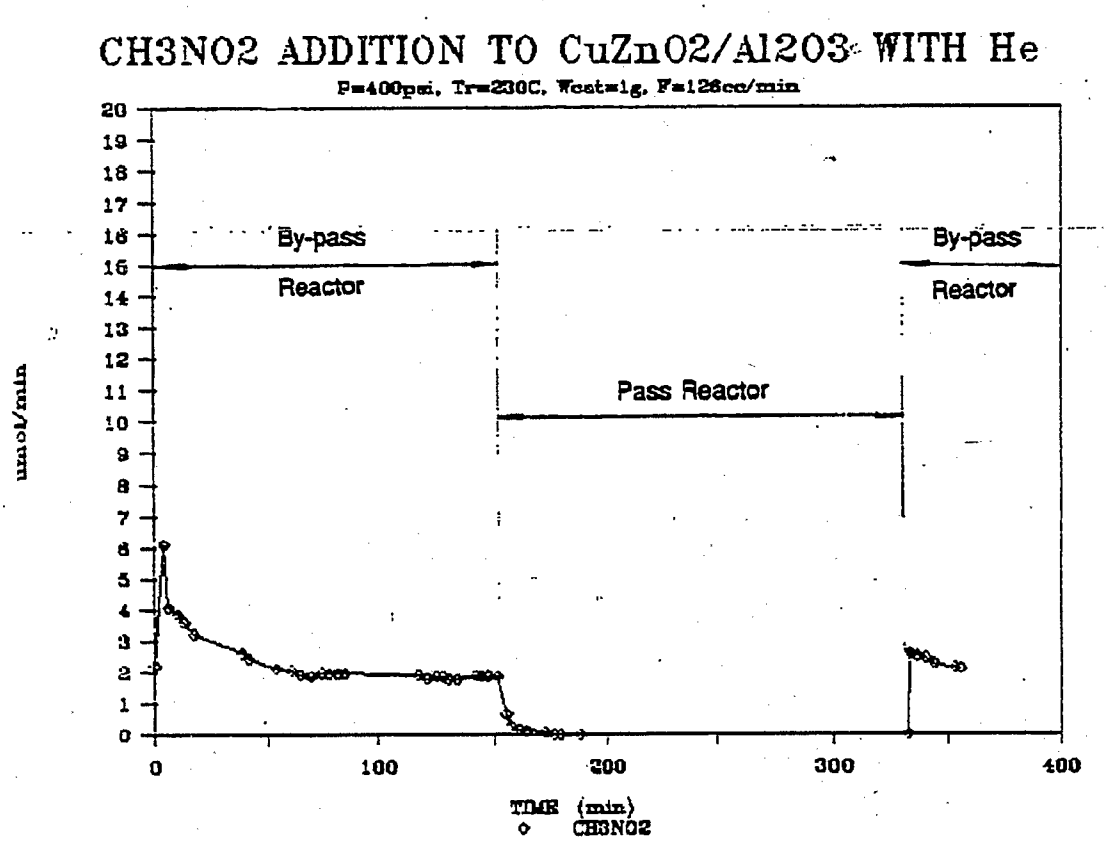
CH3NO2 ADDITION TO CuZnO2/Al2O3 WITH He
P=400psi, Tr=230C, Wcat=1g, F=126cc/min
umol/min
By-pass
Reactor
Pass Reactor
By-pass
Reactor
TIME (min)
◇ CH3NO2

Figure 1.

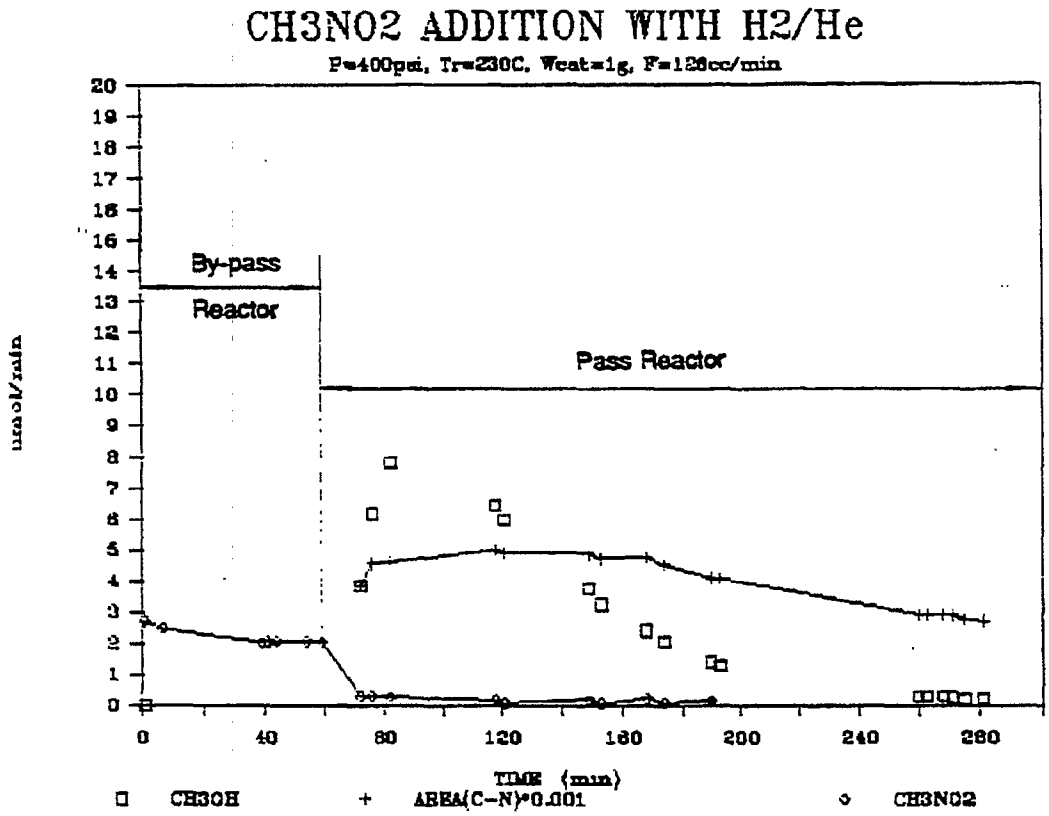
CH3NO2 ADDITION WITH H2/He
P=400psi, Tr=230C, Wcat=1g, F=126cc/min
By-pass
Reactor
Pass Reactor
umol/min
TIME (min)
CH3OH
AREA(C-N)*0.001
CH3NO2

Figure 2.

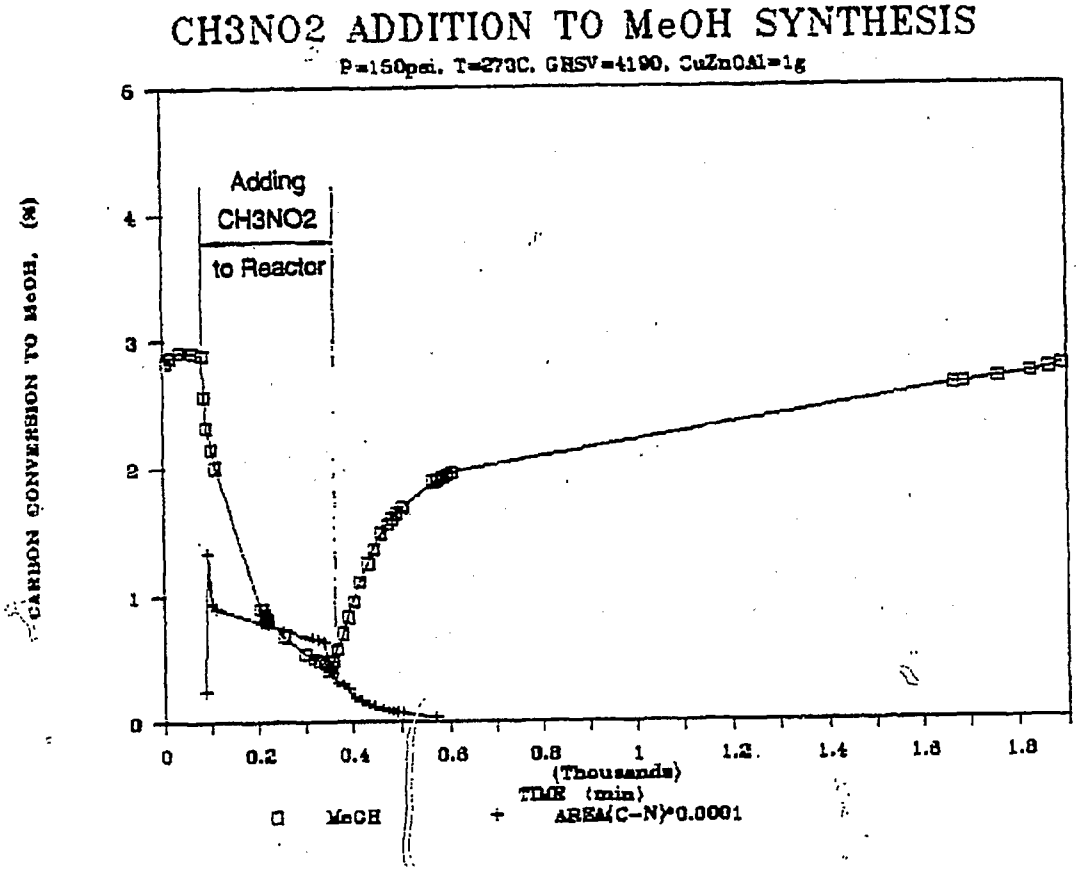
CH3NO2 ADDITION TO MeOH SYNTHESIS
P=150psi, T=273C, GHSV=4190, CuZnOAl=1g
CARBON CONVERSION TO MeOH, (%)
Adding
CH3NO2
to Reactor
0
1
2
3
4
5
6
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
(Thousands)
TIME (min)
MeOH
AREA(C-N)*0.0001

Figure 3.

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