PROBE MOLECULE STUDIES: ACTIVE SPECIES IN ALCOHOL SYNTHESIS. THIRD QUARTERLY REPORT, APRIL 1991--JUNE 1991

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

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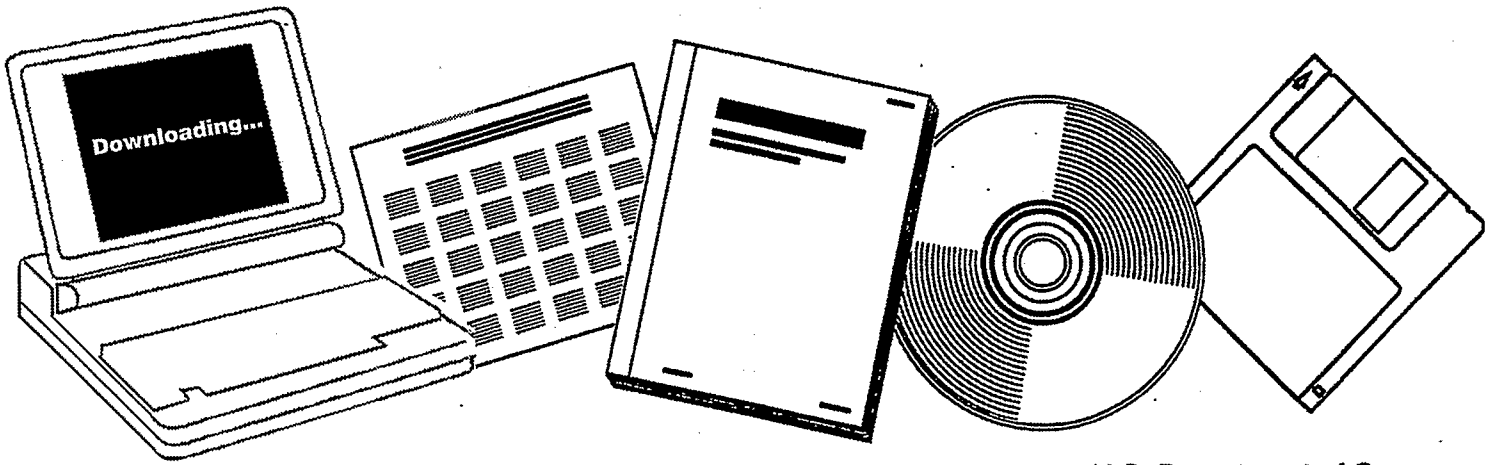

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PROBE MOLECULE STUDIES: ACTIVE SPECIES IN ALCOHOL SYNTHESIS

3rd Quarterly Report

April 1991 - June 1991

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DISCLAIMER

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. Different probe molecules are planed to add in situ during the reaction to help delineate reaction path ways 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.

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. A reaction and analysis system capable of carrying out the experiments for this study has been set up, modified, and tested.

First, the commercially important Cu/ZnO/Al2O3 catalyst for methanol synthesis is being studied. Other catalysts, such as Pd and Rh with and without alkali or oxide promoters which are known to produce oxygenates from syngas, are being prepared and characterized for this study.

Based on the observation of a previous study that nitromethane is an effective source of CH2 groups, it will be one of the primary probe molecules to be studied. In addition, acetylenic compounds are primary choices for this

study also. These compounds were found by other workers to be effective as a source of chain initiators.

2. SUMMARY OF PROGRESS

Methanol synthesis reactions over Cu/ZnO/Al2O3 with and without 1-hexyne ($C_4H_9-C\equiv CH$) have been carried out. Complete reduction of 1-hexyne ($C_4H_9-C\equiv CH$) to n-hexane (C_6H_{14}) without significant perturbation of the MeOH synthesis process was observed. Nitromethane (CH_3NO_2) has been used as the next probe molecule for the same reactions.

Due to problems encountered during this period, the reaction system was modified to allow more effective studies.

3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Methanol synthesis reactions over Cu/ZnO/Al2O3 under 350 psi at 250 °C with CO/H2 ratio of 1:1 to 1:4 were carried out to reach a stabilized conversion to MeOH. About 20% 1-Hexyne in cyclohexane was added to the syngas inlet at ~ 0.01 cc/min through the liquid pump.

The typical experimental results are shown in Figure 1. Major observations and problems we have had during this period are stated as below.

Observation 1: 1-Hexyne does not incorporate into the

product during the process of MeOH synthesis over Cu/ZnO/Al2O3.

Observation 2: 1-Hexyne was completely reduced to n-hexane over Cu/ZnO/Al2O3 under the condition used without disturbing the MeOH formation (see Figure 1).

Problem 1: Without addition of CO2 to the syngas mixture, CO conversion to MeOH under the selected reaction condition is very low.

Problem 2: Operating at the lowest rate of 0.01 cc/min, the syringe pump was still introducing too much liquid into the reactor. Although the solvent used did not show any significant side effect on the reaction path way, it can still affect the surface processes, such as adsorption, reaction etc. Besides, the low pumping rate makes it hard to operate at a steady flow rate.

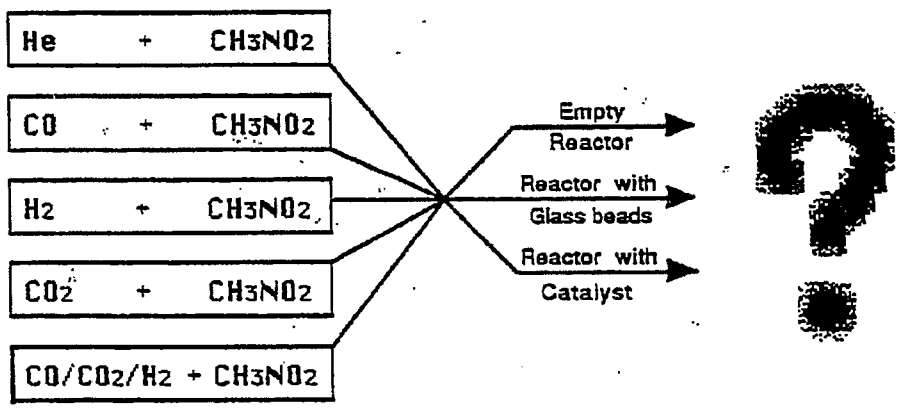
In order to obtain more reliable and meaningful results, it was decided to modify the reaction system in order to use a saturator instead of a liquid pump for probe molecule introduction. A schematic of the modified system is shown in Figure 2. In addition, this system allows addition of CO2 for MeOH synthesis over Cu/ZnO/Al2O3 to obtain a standard CO conversion to MeOH.

During this period the saturator was tested with CH3NO2 under various conditions of pressure, temperature and gas flow rate.

4. PLANS FOR THE NEXT REPORTING PERIOD

In the next period further studies of MeOH synthesis reaction over Cu/ZnO/Al2O3 wil be performed. CO/CO2/H2, instead of CO/H2, mixture will be used to improve CO conversion. CH3NO2 will be used as the probe molecule.

In order to clarify what happens when CH3NO2 is added to the catalyst surface, enough blank runs have to be performed prior to reactions. This is shown schematically as follows:



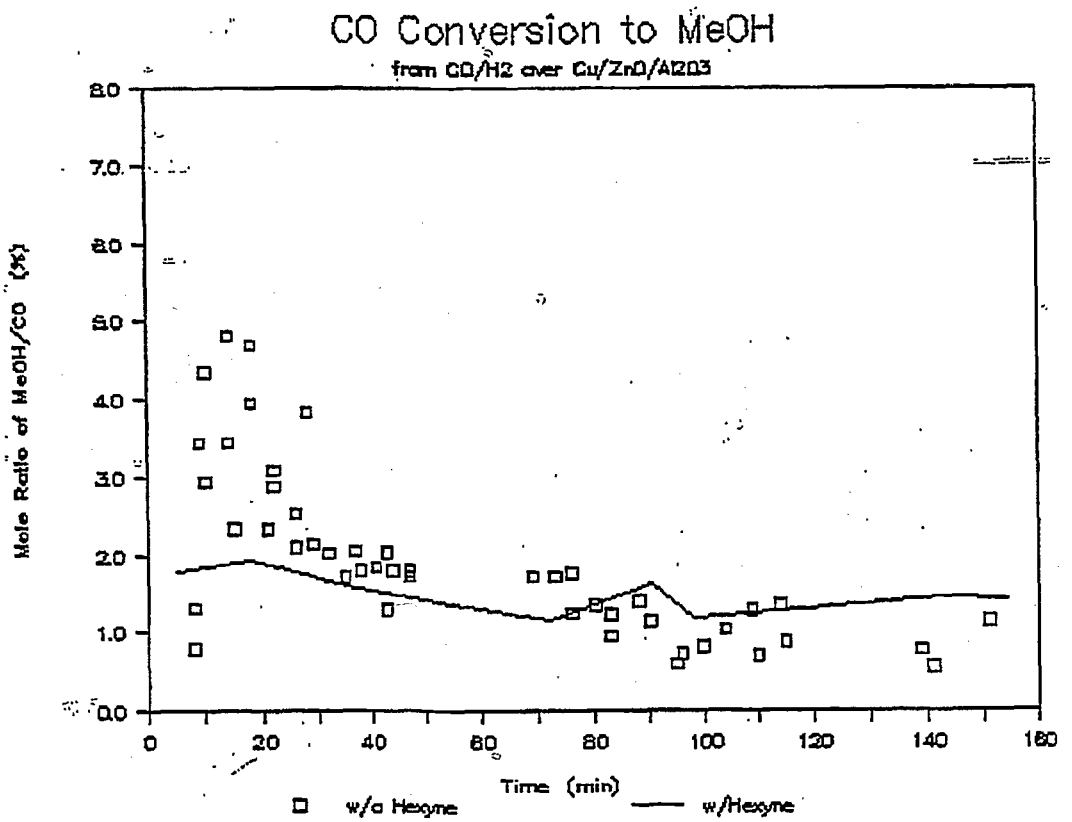
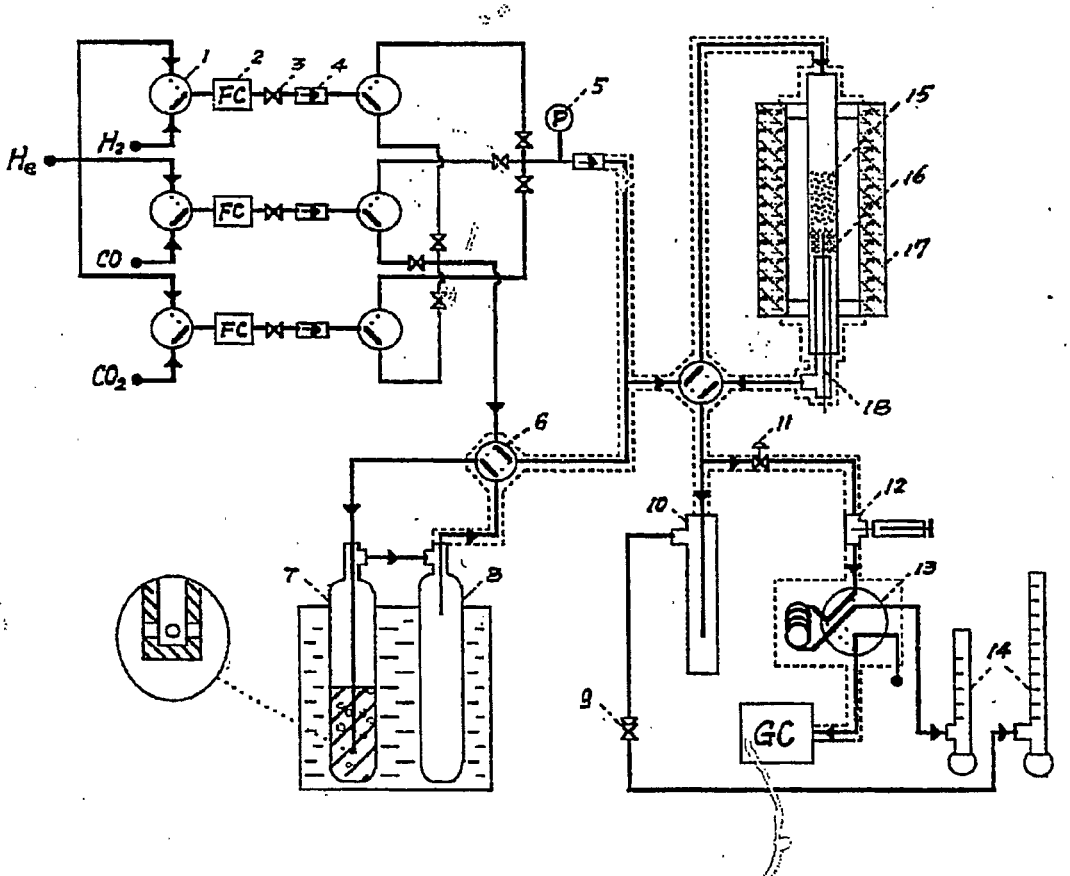


Figure 1. CO conversion to MeOH from CO/H2 (1:3) over Cu/ZnO/Al2O3 at 350 psi, 250 °C, 4000 hr^{-1} (HGSV) without and with Hexyne ($C_4H_9C{\equiv}CH$) addition.



1: 3-way valve, 2: flow control meter, 3: on/off valve, 4: check valve, 5: pressure gauge, 6: 4-way valve, 7: probe molecule saturator, 8: trap, 9: backup pressure regulator, 10: trap, 11: leaking valve, 12: sampler, 13: 6-way sampling valve, 14: bubble flow meter, 15: catalyst, 16: glass wool, 17: furnace, 18: thermocouple.

Figure 2. The reaction system set-up for probe molecule studies on mechanisms of oxygenates synthesis from CO hydrogenation..

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