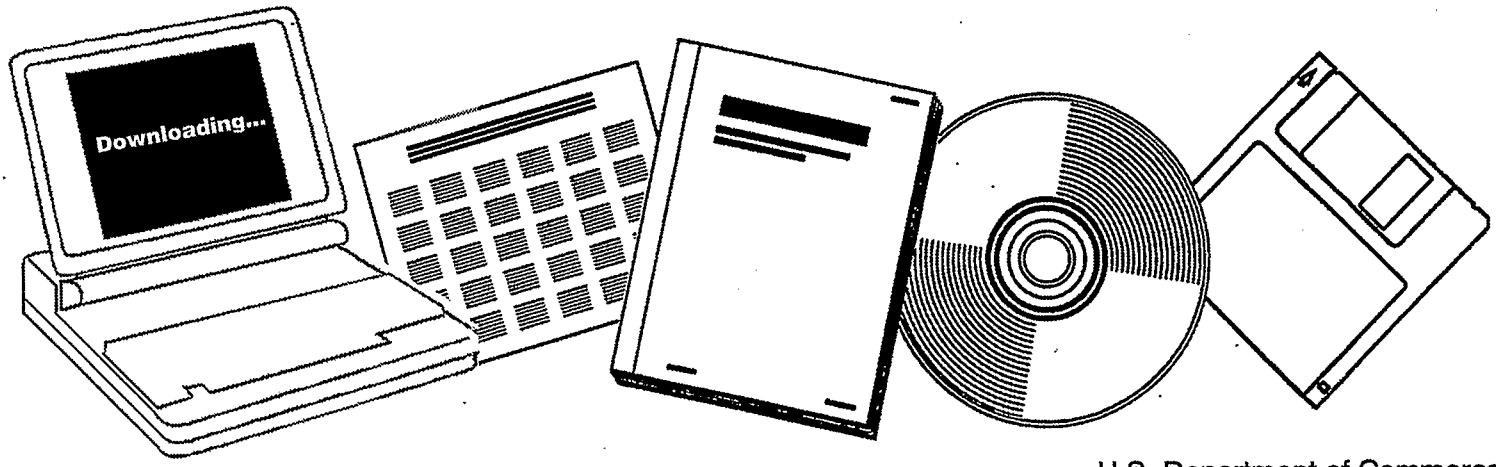
PROBE MOLECULE STUDIES: ACTIVE SPECIES IN ALCOHOL SYNTHESIS. FIRST QUARTERLY REPORT, SEPTEMBER 1990-DECEMBER 1990

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

JAN 1991



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PROBE MOLECULE STUDIES: ACTIVE SPECIES IN ALCOHOL SYNTHESIS

1st Quarterly Report

September 1990 - December 1990

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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 oxygenate formation from syngas over supported catalyst by in-situ addition of probe molecules. Alternation of the reaction pathways by probe molecule addition will be observed and analized to reveal mechanistic information.

A reaction and analysis system capable of carrying out the experiments for the proposed research has been set up and will be used to run CO/H2 reactions in both the presence and the absence of each probe molecule under conditions which favor the formation of oxygenated products. Rh and/or Co, which are known to produce oxygenates from syngas, with SiO2 as support will be prepared and characterized for this study.

Analysis and studies of our experimental results are expected to provide us enough information to propose mechanistic hypothesis of the oxygenates formation from CO/H2 and probably suggest novel ideas for design of highly reactive/selective catalysts and even synthesis processes.

2. SUMMARY OF PROGRESS

During the first quarter, a complete CO/H2 reaction system with on-line quantification analysis system was set up and tested.

3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

- Experimental System Set-up

The experimental system for reaction and products analysis was set up and schematically shown in the attached Figure. It consists of six major parts, namely, the gas handling system, the probe molecule introduction system, the reactor, the products trapping/collection system, the on-line sampling and GC analysis system, and the off-line component identification system. Detailed descriptions for each part are given below.

(A) Gas Handling System

UHP H2 from Harvey Co. and UHP CO from Matheson Co. are employed as reaction gases. UHP He and H2, and HC-free compressed air from Harvey Co. are used for the Varian 3000 GC with both FID and TCD detectors. 4A Linde high pressure purifiers are installed on each gas introduction line to remove traces of H2O. An Activated Carbon high pressure purifier is used on CO line to remove traces of hydrocarbons. An oxygen trap from Scott Specialty Gases is used on the GC H2 line.

The flow rates of reaction gases (CO and H2) are controlled by mass flow controllers and calibrated with bubble flow meter. CO and H2 are premixed and introduced to the reactor from the top.

(B) Probe Molecule Introduction System

Liquid probe molecule in selected solvent is holden in a

burette and introduced by a high pressure syringe pump to the same reactor inlet as for CO and H2. The flow rate of the solution can be measured by recording the liquid level in the burette.

(C) Reactor

The reactor is a fixed bed with a 14" long by 3/8" O.D. stainless steel tube. Glass wool is used to hold the catalyst particles. Reactants are introduced from the top of the reactor and the reaction products leave the reactor from the bottom.

The system pressure is controlled by a back pressure regulator down stream of the reactor and measured by a pressure gauge up stream before the reactor. The reactor is placed inside a furnace which can be programed to ramp and hold at desired temperatures. The temperature inside the reactor is measured by a thermocouple right beneath the glass wool bed.

(D) Products Trapping/Collection System

The outlet flow from the bottom of the reactor can be conveyed through a heated line with a 4-port valve to a water cooled trap first and a dry-ice in acetone cooled trap secondly for condensation of liquid products. The heated line can be maintained at maximum of 573 K, which is above the boiling point of C16H34 and C14H30O at 1 atm. Another pathway of the 4-port valve leads the outlet gas from the reactor directly to the vent (bypassing the traps), which is in use when liquid products collected in the traps need to be

removed and bottled.

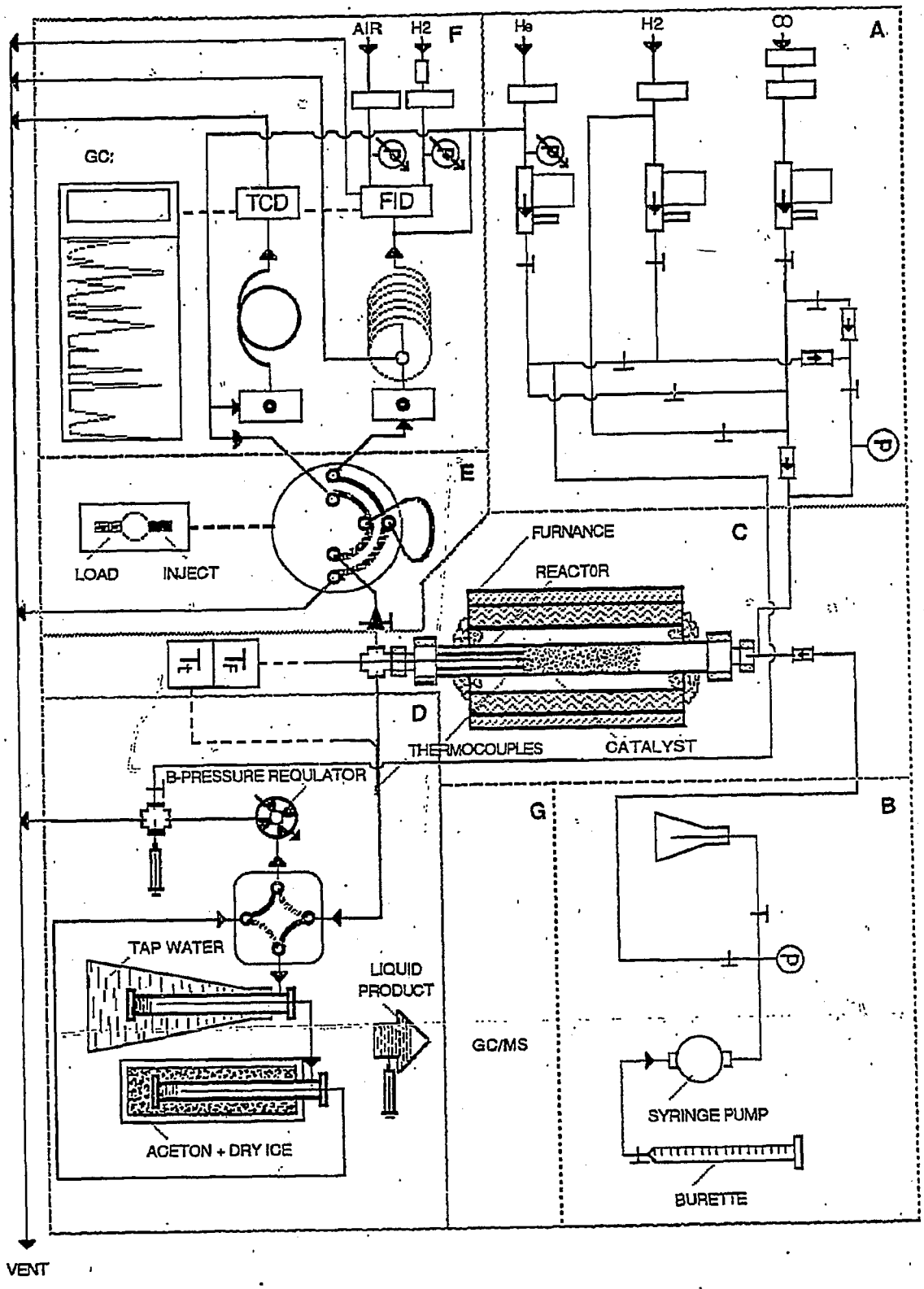
(E) On-Line Sampling and GC Analysis System

In order to trace the dynamics of the reaction and analyze the whole range of product distribution, an on-line sampling system is fixed between the reactor outlet and the first trap. A high pressure rating (3000 psi at 21 °C), high temperature rating (-29 °C ~ 232 °C), and chemicals-resistant metering valve is installed on a diverted line before the first trap to allow only small amount of gas flow through without losing the system pressure control. A heated metering valve is connected to a Varian 3000 GC equipped with a FID. A capillary column (DB5) is used to separate the products. A packed column connected to the TCD is available for manual injection of the gas samples taken after the traps. All lines for on-line sampling can be heated up to ~573 K.

The concentration of components in the reaction products will be calculated by external-standard method from the data collected by the integrator.

(F) Off-Line Component Identification System

An Extrel 800 MS (IE/Quadruple) interfaced with another Varian 3000 GC is used to identify the components in all product samples (liquids and gases). The same capillary column as the one in the GC on the reaction system is installed in the GC/MS. To get consistent information from both GC/MS and GC/FID, the GC operation conditions for two GCs must be matched up very well.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PRODUCT
GC/MS
SYRINGE PUMP
ACETON + DRY ICE
BURETTE
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4. PLANS FOR THE NEXT REPORTING PERIOD

The next step of this study will involve:

1) Catalyst preparation and characterization;

2) Determining the detailed methods and procedures for products analysis;

3) Starting reaction studies without probe molecule addition in order to optimize the operating conditions for a better oxygenate selectivity over our catalysts.

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