DESIGN OF A HIGH ACTIVITY AND SELECTIVITY ALCOHOL CATALYST. SECOND QUARTERLY REPORT, NOVEMBER 7, 1990 TO FEBRUARY 6, 1991

DELAWARE UNIV., NEWARK. CENTER FOR CATALYTIC SCIENCE AND TECHNOLOGY

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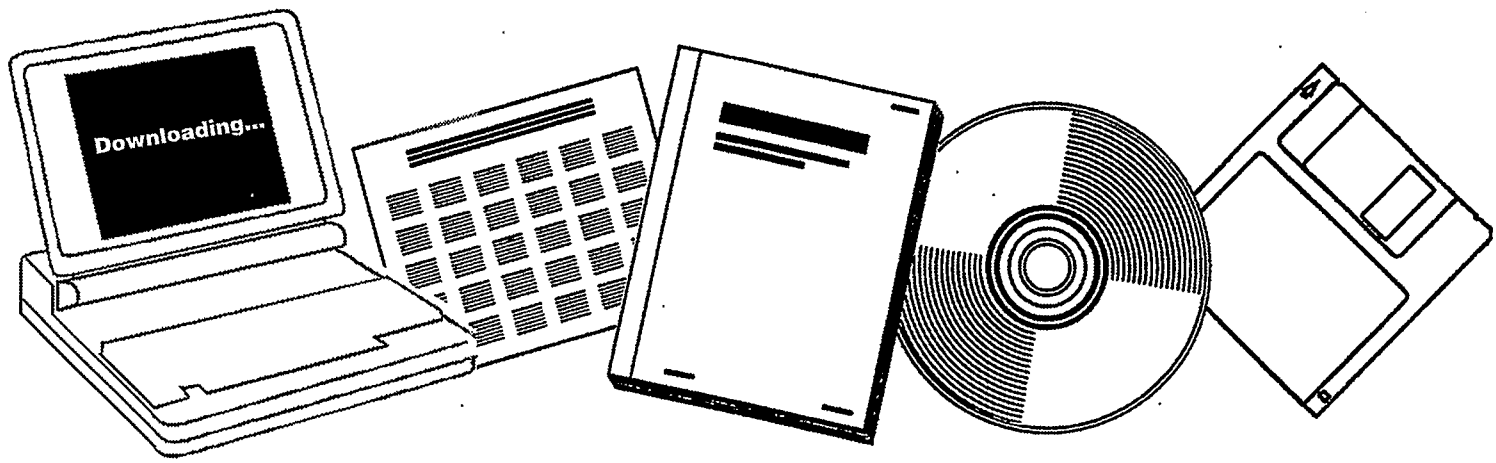

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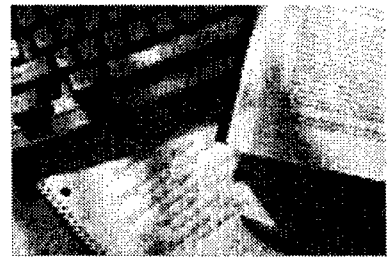

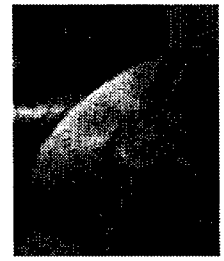

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DESIGN OF A HIGH ACTIVITY AND SELECTIVITY ALCOHOL CATALYST

Second Quarterly Report for Period November 7, 1990 to February 6, 1991

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Design of a High Activity and Selectivity Alcohol Catalyst
DE-90PC 90291
Second Quarterly Report

During the second quarter the work of the project focussed upon the design and construction of various pieces of equipment to be used in the service of this program.

First, as part of the research we will be using the chemisorption of metal carbonyl complexes on the surface of alumina support media as a means to the synthesis of highly dispersed, bimetallic catalysts consisting of rhodium and molybdenum oxides, as well as other metals. These steps involve reacting the support surface under inert conditions with the precursor compound. The sequential chemisorption and oxidation steps are shown below:

$$Mo(CO)_6 + (HO)_2\text{-}AlO_x \rightarrow Mo(CO)_4 - (O)_2\text{-}AlO_x \quad (1)$$

$$Mo(CO)_4 - (O)_2\text{-}AlO_x \rightarrow Mo(O)_2 - (O)_2\text{-}AlO_x \quad (2)$$

$$Rh(CO)_2(acac) + Mo(O)_2 - (O)_2\text{-}AlO_x \rightarrow Rh(CO)_2 - Mo(O)_2 - (O)_2\text{-}AlO_x \quad (3)$$

$$Rh(CO)_2 - Mo(O)_2 - (O)_2\text{-}AlO_x \rightarrow Rh - Mo(O)_2 - (O)_2\text{-}AlO_x \quad (4)$$

Reactions (1) and (3) must be run anaerobically to prevent the predecomposition of the metal carbonyl compound. That is, in order for the chemisorptive step to take place the metal compound must be in a low to zero formal oxidation state. The chemisorptive chemistry is important as a means to a highly dispersed supported metal catalyst. Steps (2) and (4) are mild oxidations.

To carry out these steps the catalysts are prepared under dry nitrogen and in hydrocarbon solvents. During this time we have assembled an ACE-Burlitch inert atmosphere system. This system, coupled with a model 2008AC Alcatel mechanical vacuum pump, provides the essential dry, oxygen-free nitrogen and light vacuum service (down to 5×10^{-4} torr) needed for the air-sensitive chemistries employed in the catalyst synthesis. The nitrogen is purified by passing it over a column packed with BASF R3-11 copper on alumina to convert oxygen to water, and then it proceeds through a packed bed of 4A molecular sieve which adsorbs the water.

Handling and storage of sensitive catalyst samples is facilitated by an inert atmosphere glove box. Since our requirements for such a system are not severe in this work (at this point), we have installed a Manostat Glove Box (Aldrich Z16,994-3) which will be maintained with dry argon. This can be combined with glove bag operations to satisfy most of our requirements for the

handling of materials under anaerobic conditions. Eventually, as need dictates more rigorous inert atmospheres may need to be used and then the experiments will be conducted in a rigorously ained inert atmosphere box.

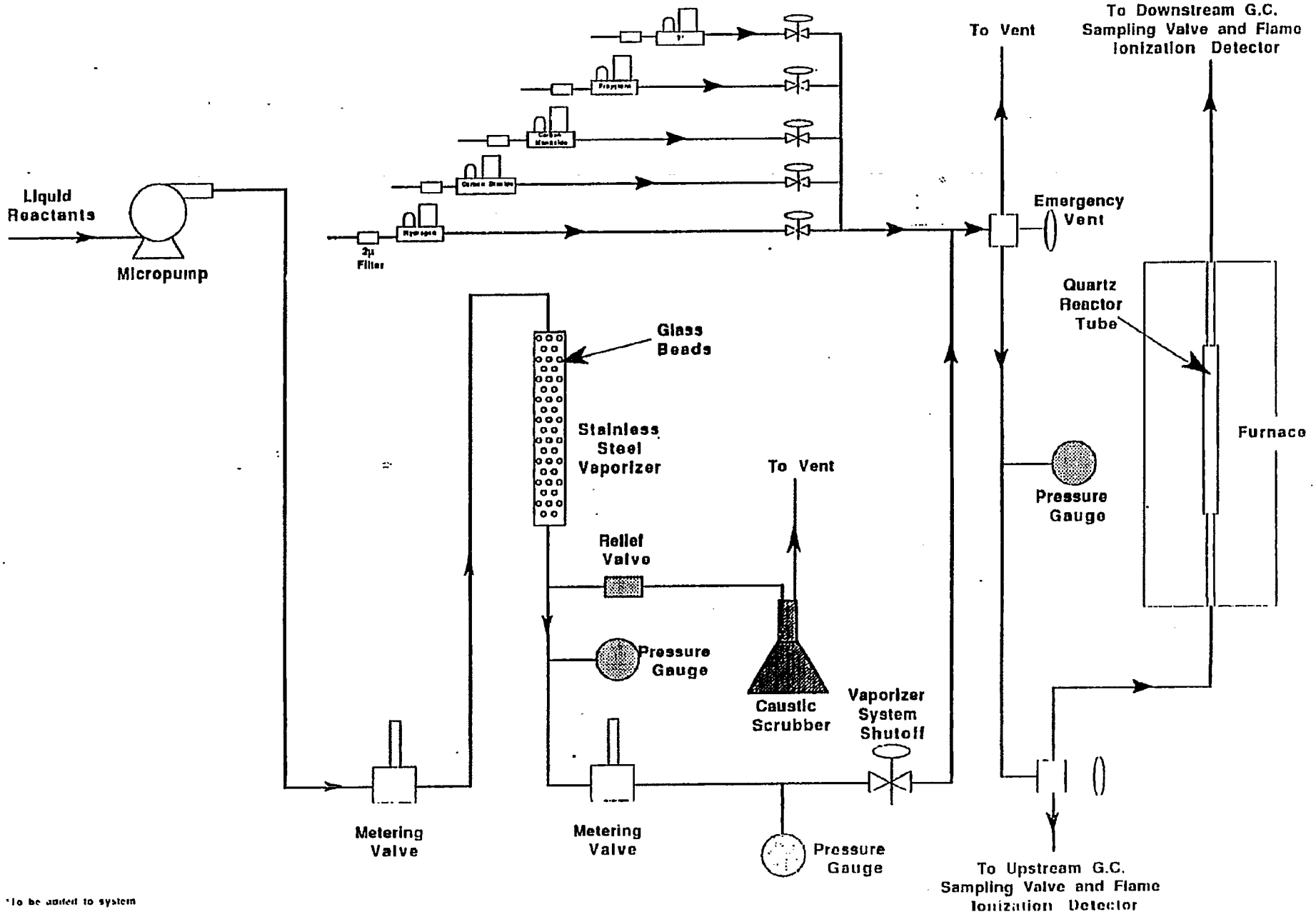
→ The third effort during this quarter focussed upon installing and bringing on-line a low-pressure flow reactor for catalytic investigations, aimed, especially, at the generation of fundamental kinetics data for structure-activity relationships.

A flow sheet for the system is attached. The system has ... careful control of up to five feed gases using Brooks 5850 mass flow contr ... reactor can be used to feed liquids in the form of vapors entrained in gas flows. The reactor is a quartz tube (approx. 0.25 in. I.D. × 10 in.) heated by a close-fitting furnace.

During the months of January and February, the graduate student (Eric Lowenthal) further augmente → with a Hewlett-Packard model 5710 gas chromatograph equipped with a flame ionization detector and a model 3890 integrator. This instrumentation is currently being calibrated for the first reactor experiments.

The first reactor experiments will focus upon a simple model reaction—methanol dehydration to dimethyl ether. ... tant to examine first from two points of view. It is simple in kinetic order a ... ned by other workers earlier. Second, and perhaps more important, this reaction occurs over the Rh-Mo/Al_2O_3 catalyst converting primary product alcohols into ethers. We have proposed to investigate means to curtail this reaction and we will do this as part of the initial reactor studies. More specifically, we will examine the quantitative effect of alkali metal oxides on the rate and selectivity of this reaction. In this way this simple dehydration reaction will allow us to re-examine well-established kinetics, thus developing our experimental reactor techniques, and at the same time we can attack a first-order issue in the catalytic chemistry of these interesting bimetallic catalyst materials. Upon completion of this initial work we will examine structure-sensitive and insensitive reactions over these catalysts as a function of metal loading and in the same low pressure reactor.

Process Flow Sheet for Low Pressure "Probe Reaction" Studies



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