4.12 Surface Science Analysis of Spinel Oxide Based Catalysts

This work was performed in collaboration with Professor Gar Hoflund and his research group in the Department of Chemical Engineering at the University of Florida.

4.12.1 Techniques employed

A number of surface science techniques were employed to investigate the composition and nature of freshly prepared and used catalytic materials. Ion Scattering Spectroscopy (ISS), Auger Electron Spectroscopy (AES), X-Ray Photoelectron Spectroscopy (XPS), and Electron Stimulated Desorption (ESD) were used to probe the surface of both fresh and used catalysts. Each technique provides a specific type of information about the these complex catalysts. The information is complementary, and when taken together, yields an improved understanding of the composition and chemical nature of the materials.

ISS, AES and XPS provide compositional information with varying degrees of surface sensitivity. ISS is highly surface sensitive, detecting atoms only in the outermost layer. AES and XPS are much less surface sensitive, generally probing 40-60 angstroms beneath the surface, depending on the kinetic energies of the electrons being detected and the experimental geometry. In general, AES probes less deeply (i.e., is more surface sensitive) than XPS. High resolution XPS data can provide chemical state information about the elements present in the near surface region.

ESD allows the detection of surface hydrogen. The role of surface hydrogen, which is a very important component of the catalytic reaction, is not well understood or even usually examined because of detection difficulties. ESD uses 1 KeV electrons to cause emission of ionic and neutral species. The m/e spectra (ESD) and ion energy distribution (ESDIED) of the desorbing ions are obtained using a quadrupole mass spectrometer with an energy prefilter.

4.12.2 ISS, AES and XPS Data

2.25 wt% K, 5.9 wt% Pd on ZnCrMn spinel oxide with excess ZnO (16-DMM-68)

The "as prepared" catalyst was examined "as is" and after reduction *in situ* using 1.4 x 10^{-5} Torr of hydrogen while ramping the temperature from 20°C to 350°C over a 100 minute time period. The "as prepared" catalyst is relatively featureless, mainly showing ZnO. Dramatic changes occur during the reduction step. Both K and Pd become highly concentrated near the surface, and the data suggest that they are closely associated in the same particle. Sputtering of the sample shows increasing Cr and Mn concentrations in the subsurface region.

Surface analysis of the fresh vs. spent catalyst shows that alkali, Cr and Mn concentrations increase and Pd and Zn concentrations decrease during operation. Potassium

is observed, as expected, but sodium, an impurity, is also seen — probably carried over from the metal nitrate salts during catalyst preparation.

5 wt% K, 5.9 wt% Pd on ZnCr spinel oxide with excess ZnO

Zinc, oxygen and small amounts of Pd, K and Cr are present in the near surface region. Zn is present as ZnO and there is a significant concentration of hydroxyl groups bound to the Zn. No carbon is present on the sample surface.

Reduction of the sample results in a significant increase in the surface Pd concentration, and the K appears to be associated with the Pd. Zn is still present as ZnO but the hydroxyl group concentration bound to the Zn has diminished substantially.

Surface analysis of the fresh vs. used catalyst shows a reduction in the surface Pd. The potassium promoter is spread uniformly over the outermost surface of the used catalysts. In fact, the outermost atomic layer consists of Zn and K. As the sample is sputtered, the K concentration decreases and the O and Pd concentrations increase until a Pd rich layer is found; then the Pd concentration decreases. A substantial amount of carbon has appeared. There are less hydroxyl groups present: zinc is present primarily as Zn metal and oxygen associated with zinc is present as hydroxyl groups. The Cr has been reduced to Cr metal and its concentration has increased in the near surface region.

7 wt% K, 5.9 wt% Pd on ZnCr spinel oxide with excess ZnO

The fresh catalyst is similar to the 5 wt% material: zinc, oxygen and small amounts of Pd, K and Cr are present in the near surface region. Zn is present as ZnO and there is a significant concentration of hydroxyl groups bound to the Zn. No carbon is present on the sample surface.

Reduction of the sample results in the formation of multiple forms of Zn; this differs from the 5 wt% K catalysts where only ZnO was present. There is also more oxygen present in the near surface region.

The used sample shows a reduction in the surface Pd. The outermost atomic layer consists of Zn and K, but Pd and Na are also present. As the sample is sputtered, the K concentration decreases and the O and Pd concentrations increase until a Pd rich layer is found; then the Pd concentration decreases. A longer sputtering time was necessary to reach the Pd-rich layer than for the 5 wt% K catalyst. A substantial amount of carbon has appeared. Zinc is present primarily as Zn metal and zinc oxide. The Cr has been reduced to Cr metal and its concentration has increased in the near surface region.

3 wt% Cs, 5.9 wt% Pd on ZnCr spinel oxide with excess ZnO

The fresh catalyst shows that zinc, oxygen and small amounts of Pd, Cs and Cr are present in the near surface region. Zn is present as ZnO and hydroxyl groups are also observed. A small amount of carbon is already present on the sample surface.

Reduction of the sample under hydrogen removes the carbon and enriches the near surface region in Cs. More hydroxyl groups are seen. Zinc is still present as ZnO.

The used catalyst has Zn, O, Cs and Cr in the near surface region. Some of the ZnO has been reduced to Zn metal. The surface is further enriched in Cs and the Pd concentration has decreased. The outermost atomic layer consists mainly of oxygen with Cs, Pd and Cr present as well. As the sample is sputtered, the Cs and Pd concentrations increase until a steady Pd concentration is reached; this Pd layer contains significant amounts of Cs and Cr. The Pd is concentrated in the outermost layers and diminishes with continued sputtering.

4.12.3 ESD/ESDIED Data

Four samples were examined:

1. ZnCrMn spinel oxide with excess ZnO, with K and Na impurities
2. 16-DMM-68 fresh catalyst (composition 1 promoted with extra K and with Pd)
3. 16-DMM-68 used catalyst
4. A ZnCr spinel oxide with excess ZnO, with K and Na impurities

The ions desorbing consisted of H^+, H_2^+, O^+, OH^+, H_3O^+, CO^+ and Cl^+. Most of the H-containing ions may relate to the surface acidity and all originate from the outermost atomic layer of the samples. Differences in the relative sizes of the m/e spectra and the peak shapes in the ion energy distribution indicate differences in the chemical nature of the surface with regard to hydrogen.

The two support surfaces are similar with respect to the H^+ ion energy distribution, but the width is greater for sample 4, and the H^+/H_3O^+ ratio is larger suggesting higher acidity for ZnCr spinel oxide versus ZnCrMn spinel oxide.

Addition of Pd to the ZnCrMn spinel oxide results in large changes: in addition to hydrogen chemical states associated with the spinel, two other, higher kinetic energy states are present corresponding to hydrogen adsorbed on palladium.

Under reaction conditions, the amount of hydrogen associated with the support is decreased and that associated with the palladium has increased. These results show that the chemical state of the hydrogen adsorbed on the catalyst surface can be observed and changes can be correlated with catalytic performance.

4.12.4 Conclusions from the Surface Science Analysis

- The surface of the catalysts is predominately ZnO and alkali.
- ZnO is reduced to Zn metal with use.
- The palladium forms a layer lying just beneath the outermost atomic layer.
- Sodium is carried over from the spinel oxide preparation.
- The alkali is initially associated with the Pd, but with use becomes spread out over the surface of the Pd/spinel. Too thick (or too thin) a layer results in inefficient higher alcohol synthesis.
- Cesium associates with the Pd in used catalysts to a greater extent than does K.
- Chromium migrates to the surface with time, and is probably responsible for increased hydrocarbon formation due to increased surface acidity. Mn addition tends to lower overall spinel acidity.
- Hydrogen can be observed on the catalyst surface. Hydrogen on the active catalyst is associated with the palladium.

5. Experimental Details

5.1 Catalyst Preparation

The ZnCr and ZnCrMn oxides were prepared by coprecipitating the metal nitrate salts in aqueous medium at a constant pH. An aqueous solution containing the metal nitrate salts and a basic solution were dripped slowly into ~200 mL of the basic solution using two peristaltic pumps. Care is taken to assure that the resulting solution is well stirred during the addition and the pH of the solution is monitored continuously. The flow of the basic solution is adjusted to keep the solution at a constant pH. The resulting mixture is then heated for a given time and then solid precipitate is filtered and washed with at least three liters of water, mixing well during the washing. The solid is dried at 110-120°C overnight and calcined for the desired time at the appropriate temperature. The catalysts were impregnated using the incipient wetness method.

5.2 Catalyst Testing

The reactor tubes were made from 1/4 inch copper tube inserted into 3/8 inch stainless steel tubes. The copper tubing was rinsed well with acetone before use. (Experiments not noted to have been run in copper reactors were conducted in reactors constructed of 1/4 inch stainless steel tubing that had been treated overnight with a 50/50 solution of hydrochloric acid and water. The tubes were rinsed with water for 5 minutes followed by an acetone rinse.) Reactors were dried under vacuum. One gram of catalyst was mixed with 3 cm^3 of glass beads until the mixture was uniform. The reactors were then loaded while tapping on the sides of reactor tube. Due to the V-like nature of the reactor tubes, each side of the V was loaded with one-half of the catalyst mixture at a time. Glass wool was then put into place on both sides of the reactor. The catalysts were reduced with 5% hydrogen in nitrogen for four hours at the desired temperature.

The reduced catalysts were then loaded into the sand bath and the system was pressurized with nitrogen. Once the reactor reached the correct temperature, the nitrogen was turned off and the syngas feedstream was turned on and adjusted to the correct pressure.

5.3 Microreactor System for Screening Catalysts

The Syngas Microreactor system was designed to screen heterogeneous catalysts for the conversion of synthesis gas to methanol and higher alcohols over a pressure range of 15-1500 psig, a temperature range of 25-400°C, and feed gas flow rate range of 50-1000 sccm. Up to three fixed-bed reactor tubes may be operated independently, except for reaction temperature. The unit consists of three sections: the feed section, the reaction section, and the analytical section (Figures 5.3-1, 5.3-2, and 5.3-3).

1. Feed Section. The feed section is designed to allow the operator to select any one of four premixed feed gases independently for any reaction tube. In addition, a nitrogen purge and pressure testing stream is available for selection. After stream selection, the feed gas for a reaction tube is passed through a molecular sieve/activated carbon trap to remove water and metal carbonyl contaminants. The purified gas then passes through a mass flow meter and into the reaction tube inlet.

2. Reaction Section. Each reaction tube is manufactured from 0.5" stainless steel and can hold up to ten milliliters of catalyst. The reaction tubes are heated using an air fluidized sandbath which is operated by a PID controller that senses the process temperature via a thermocouple positioned directly in the sandbath. The temperature of each reaction tube is also monitored using a thermocouple positioned axially inside the reaction tube. The reaction tube offgas passes into a spring-loaded back pressure regulator (used to elevate reaction pressure) equipped with a bypass valve.

3. Analytical Section. From the back pressure regulator, the product gas stream enters into the analytical section of the unit. The analytical section consists of automated, air-actuated, gas sampling valves (GSVs) to provide on-line offgas sampling, followed by knock-out drums to collect liquid product for future analyses. In a modification of the unit after initial construction, an aluminum box was fabricated to house the gas sampling system components. These included the back pressure regulators, gas sampling valves (GSV-1& GSV-2), reactor down-stream pressure gauges and the calib./ gas sample 3-way valves. Independent block heaters were used on the gas sampling valves and provide some of the heat required by the box. However, the majority of heat is provided by a 4 ft section of heat tape attached to the inside of the box cover and regulated by a Payne Controller.

Figure 5.3-1. Feed System of Syngas Microreactor System

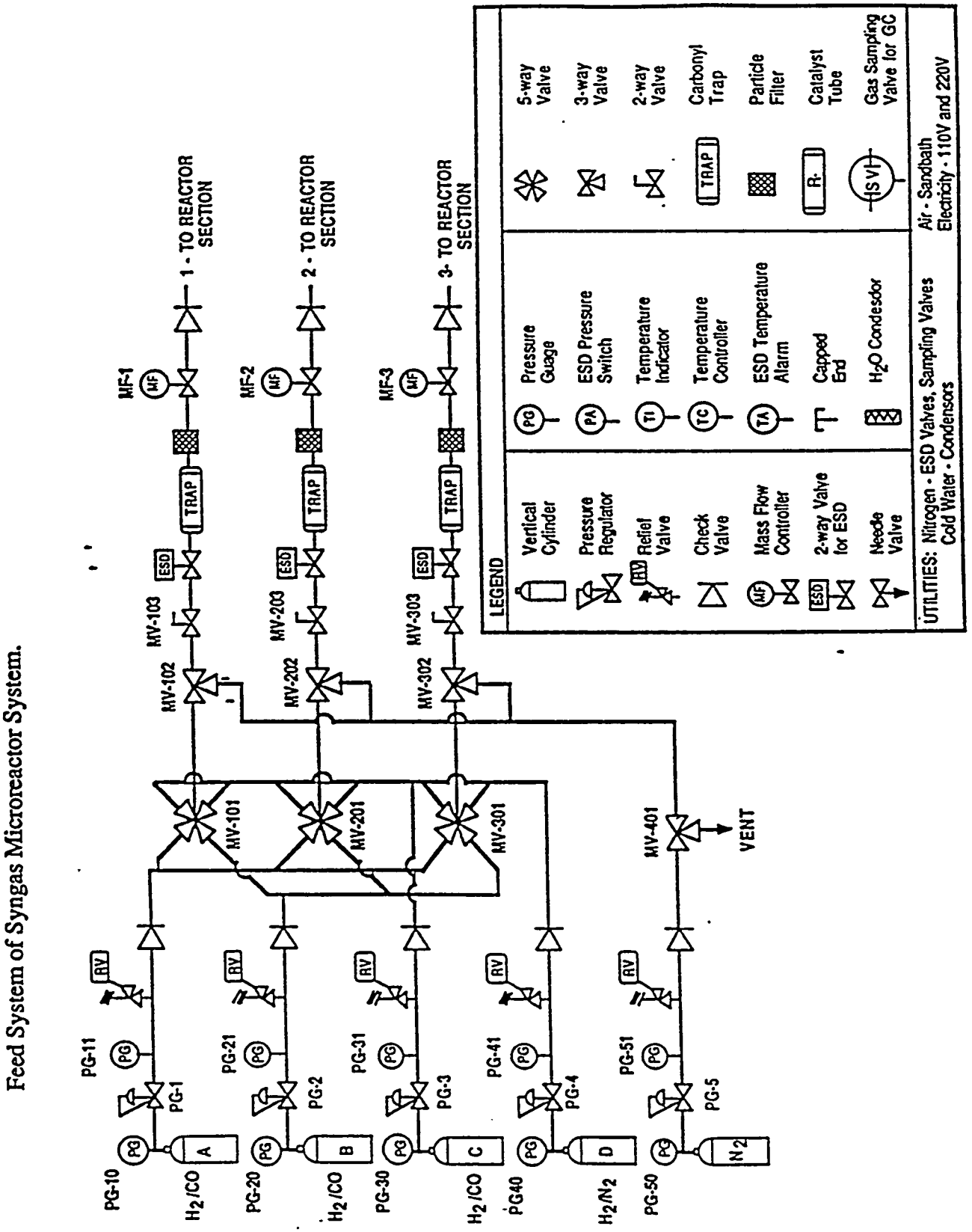


Figure 5.3-2. Reactor System of Syngas Microreactor System

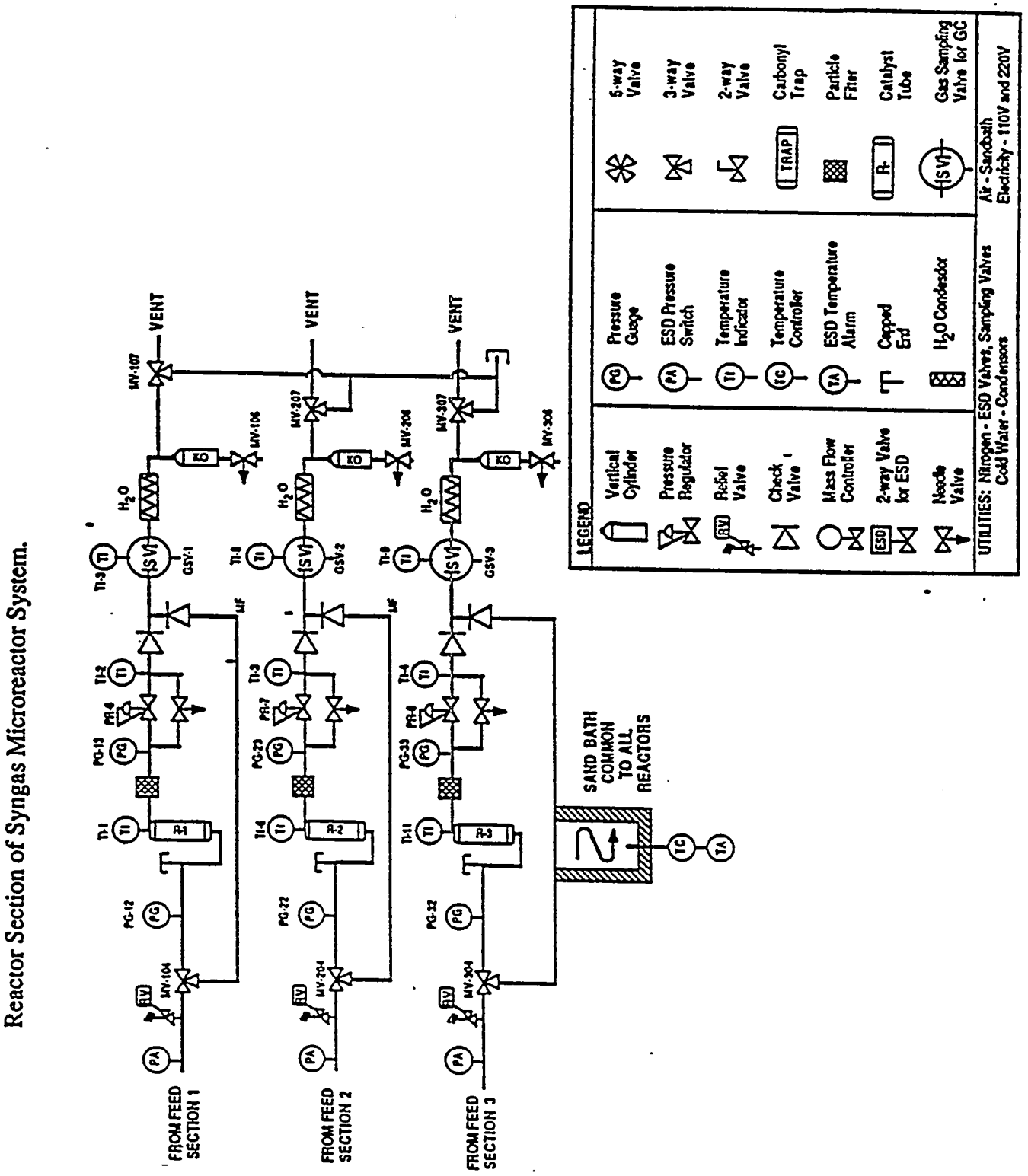
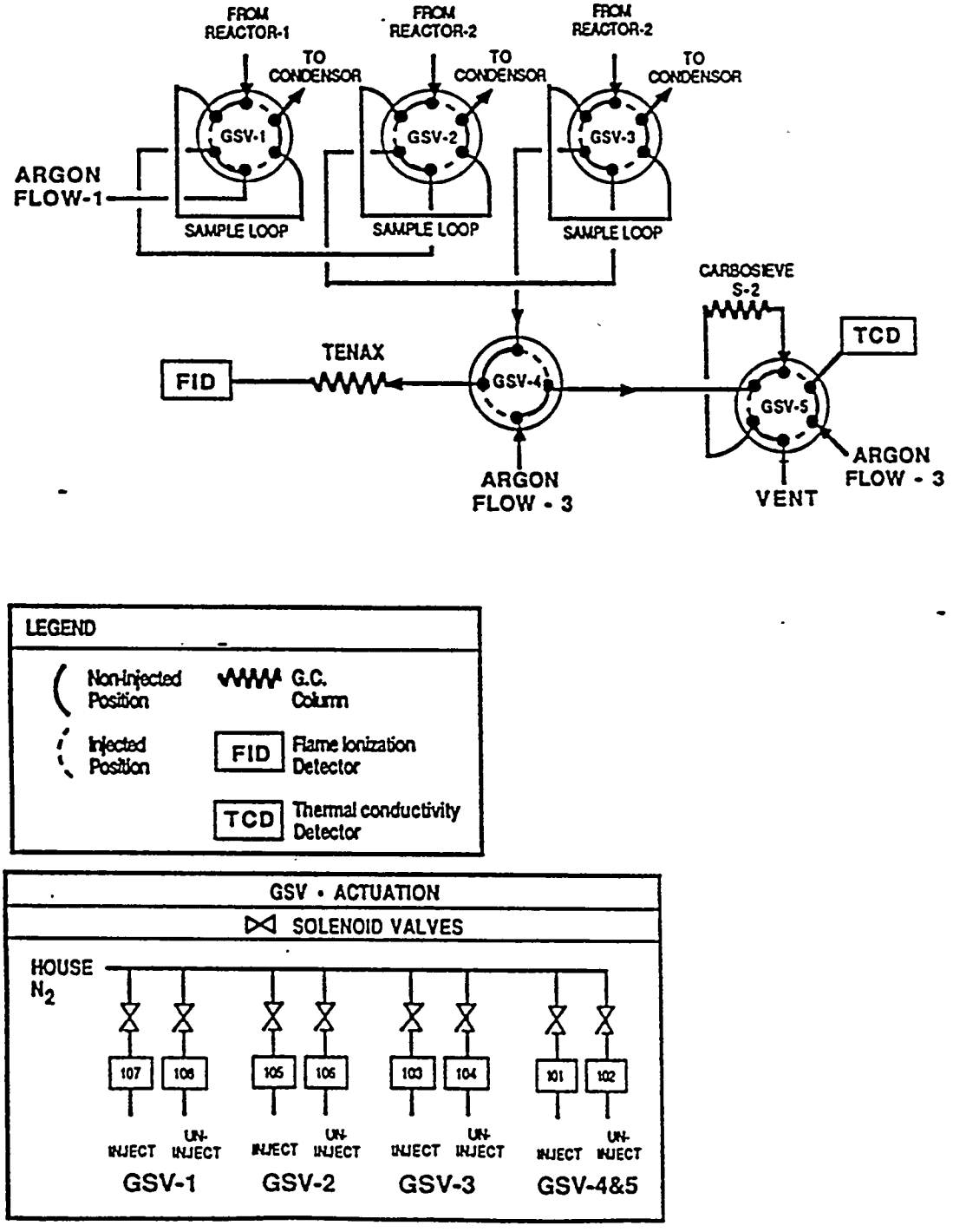


Figure 5.3-3. Analytical System of Syngas Microreactor System



5.4 Product Analysis

Each reaction line in the microreactor system passes through an independent six port, two position, gas sampling valve (GSV-1, GSV-2, or GSV-3). These valves alternatingly provide 0.6 ml reactor offgas samples to a Varian 3700 gas chromatograph. All valves are pneumatically actuated using a collection of solenoid valves controlled via the UCC computer automated laboratory system (CALS).

Once a sample enters the argon carrier gas stream (see Figure 5.3-3), it is transported outside of the fume hood to a four-port two-position air-actuated switching valve (GSV-4) located at the GC. This valve directs the sample to either the organics separation (Tenax column) and detection leg of the analysis scheme or to the inorganics separation (Carbosieve S-2 column) and detection section. While GSV-4 is directing samples to the Tenax column, GSV-5, a six-port two-position gas sampling valve back-flushes the Carbosieve column of accumulated organic compounds from previous analyses. GSV-4 and GSV-5 are bridged so that they actuate at the same moment. The analytical section is designed to have GSV-1, 2 or 3 send two samples to the GC two minutes apart. The first sample goes to the organics analysis section. On the second sampling, GSV-4 and 5 are actuated to divert the second gas sample to the inorganics analysis section.

5.5 Gas Chromatographic Analyses

A single Varian 3700 gas chromatograph equipped with two detectors is used for offgas analysis. Inorganics (H_2, N_2, CO, and CO_2) are separated on a 10'x1/8" 80/100 mesh Carbosieve S-2 column purchased from Supelco and detected by thermal conductivity. All organic products are resolved on a 12'x1/8" 80/100 mesh Tenax column obtained from Alltech and detected using flame ionization. The Tenax column has been calibrated on an absolute weight basis using quantified mixtures of C_1-C_6 normal hydrocarbons, normal and branched alcohols, and normal aldehydes. Argon is used as the carrier gas for both columns. The following parameters are used for the GC oven and the two columns and detectors:

Temperature ramp: 50°C to 225°C at 8°C/min with a 10 minute hold at the upper temperature

Column	Flow Rate	Injector Temp.
Tenax	20 sccm	220°C
Carbosieve (sample)	20 sccm	170°C
Carbosieve (reference)	20 sccm	170°C

Detector	Temperature	Sensitivity	Attenuation	Other
TCD	200°C	5.0 mV	4X	Filament Temp. = 350°C
FID	250°C	10^{-10}	8X	H_2 flow = 30 sccm
				Air flow = 300 sccm

5.6 Data Analysis

Upon collecting the dual channel GC chromatogram for a reactor tube, CALS determines the identity and area of all components eluted and passes the results to a VAX mainframe computer. The operator accesses the VAX using a terminal in the laboratory and enters a FORTRAN program that has been written to provide further data analysis. The operator inputs the feed and offgas flow rates, reaction conditions, and catalyst reference numbers. The program calculates the catalyst activity and selectivity as well as performing carbon, hydrogen, and oxygen mass balances. In general, the oxygen and hydrogen mass balance is not 100% because the analytical system is unable to quantitate the H_2O concentration in the offgas. A summary of the results may then be printed in a convenient format.