

contained in Aluminum cylinders and produced by AIRCO Products. The gas mixtures obtained from Union Carbide were in steel containers and it was found that carbonyls were plated on the glass components of the reactor system. The water traps employed in the reactor systems trapped these compounds. Most CO/H₂ mixtures contained a trace amount of methane (0.7 to 0.5 mole %). In these cases methane product yields were corrected by this amount. The olefin containing CO/H₂ mixtures were routinely checked to insure that no cracking, hydrogenation or isomerization occurred inside the tank.

Table 3.3.1

Feed Mixture Compositions (mole %)

- 1) Ultrahigh purity H₂ (99.999%)
- 2) Ultrahigh Purity He (99.999%)
- 3) 25% CO (99.5%) 75% H₂ (99.999%)
- 4) 46% CO (99.5%) 54% H₂ (99.999%)
- 5) 24% CO (99.5%) 71% H₂ (99.999%) 5% C₂H₄ (99.9%)
- 6) 24.8% CO (99.3%) 74.7% H₂ (99.999%) .5% 1-Pentene (99.9%)

Note: The numbers in parenthesis refer to the minimum purities.

3.3.3 Gas Chromatograph Calibration Procedure

Three calibration mixtures containing various synthesis products were used to calculate the chromatograph response factors. The components of these mixtures as well as their analyzed mole fractions are given in Appendix I. The component concentrations in these mixtures correspond to values typically encountered under differential reaction conditions. The response factors (mole fraction/chromatograph peak area)

for each product measured at two different concentration levels are typically with 5% indicating a linear chromatograph response (Appendix 1). Response factors for products not contained in either of the calibration mixtures were determined using the relative response factors of Dietz (35). He reports that the relative response factors are accurate for all thermal conductivity detectors. However, if one uses for instance propylene as the calibrated material to calculate the methanol response factor according to the data of Dietz (35) a value is obtained which is 25% smaller than the response factor obtained by a direct methanol calibration. Similar errors were found when relative response factors were used to calculate chromatograph response factors of hydrocarbons of two or three carbon atoms more than the hydrocarbon used in the direct calibration. These errors most likely arose from peak shape differences among the products. Many peaks were merged (Figures 3.3.3 and 3.3.4) and deconvolution was accomplished by use of digital integration. Additionally, temperature programming was employed in order to get desired product separation. Dietz (35) obtained his data under isothermal conditions using pure components. Due to the peak broadening of product molecular weights, the heavier components had a lower height/width ratio necessitating continual changes in electronic integration parameters during the course of an injection. Thus the use of calibration mixtures encompassing the molecular weight range of the products formed in the synthesis allowed for the accurate determination of chromatograms.

3.3.4 Gas Chromatographs

Two gas chromatographs were employed in product analysis for the bulk of the experiments. A Perkin Elmer Sigma 3 was used predominately

for the analysis of the low molecular weight products (C_1-C_4 , CO_2 , CH_3OH) while a Hewlett Packard 5730 handled the higher molecular weight products. Both chromatographs possessed a liquid nitrogen subambient system for cooling purposes. The low molecular weight products were separated using a poropak Q column (10' by 1/8" OD, Supelco Inc.) with a temperature programming schedule of 30 to 170°C at 20°C/Min. A SP 2100 column (10% on chromosorb, 100/120 mesh, 10' by 1/8" OD -Hewlett Packard) separated the heavier products using a typical programming schedule of 0°C (4 min hold), 4°C/min to 100°C.

The Sigma 3 chromatograph (Figure 3.3.3) exhibits a reproducible base line drift which does not interfere with accurate peak area evaluation. This chromatograph was obtained using a 3390A digital integrator (Hewlett Packard) which has a wide range of integration functions and sensitivity thresholds which can adequately make up for non-ideal baseline behavior and peak shapes. The water peak accounts for that produced under reaction conditions since a molecular sieve trap (Linde 5A) was used to remove water from the helium carrier gas line. Nevertheless the spectral area of this peak was not determined quantitatively due to its broad tailing. The second C_4 peak labelled C_4 paraffin also contains the product areas of the 2-butene isomers. The high molecular weight separation was able to resolve these isomers allowing for the identification of the C_4 paraffin. The $C_n > 5$ products would generally come out as broad unresolved peaks making analytical measurements dubious. Occasionally it was necessary to bake the Porapak Q column (at 170°C) in order to remove accumulated high molecular weight products. Figure 3.3.4 shows a typical high molecular weight chromatograph obtained with the HP 5730 chromatograph using a HP 3880A digital integrator

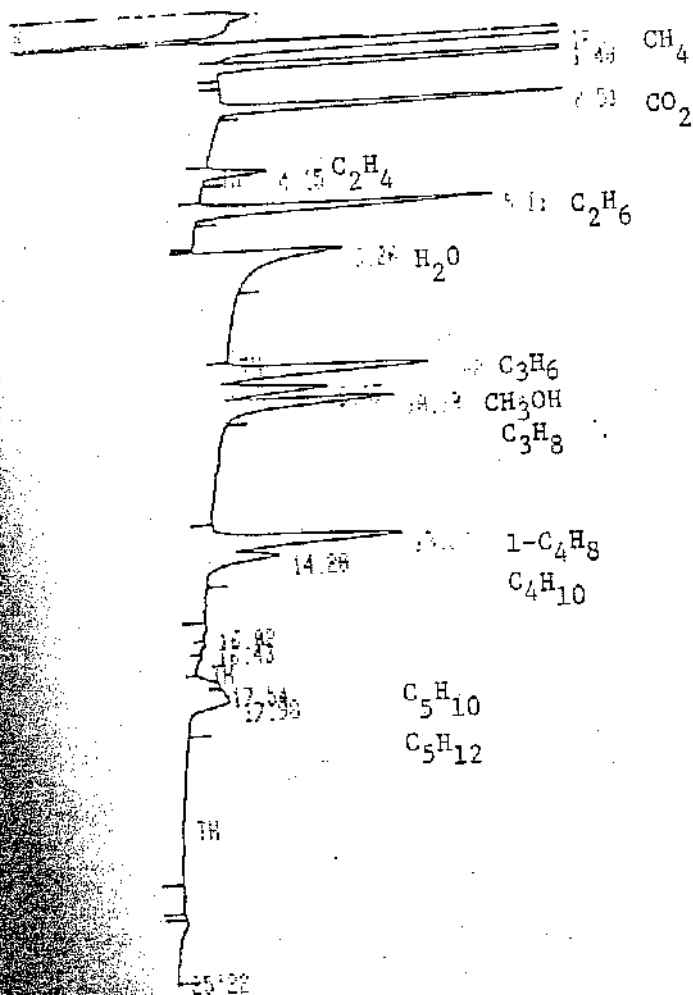


Figure 3.3.3 Typical chromatograph for the low molecular weight products. Obtained with Sigma 3 chromatograph with a poropak Q column under temperature programming conditions of 30 to 170°C @ 20°C/min. FeCo catalyst, 1/3 CO/H_2 feed at 14 atm and 250°C.

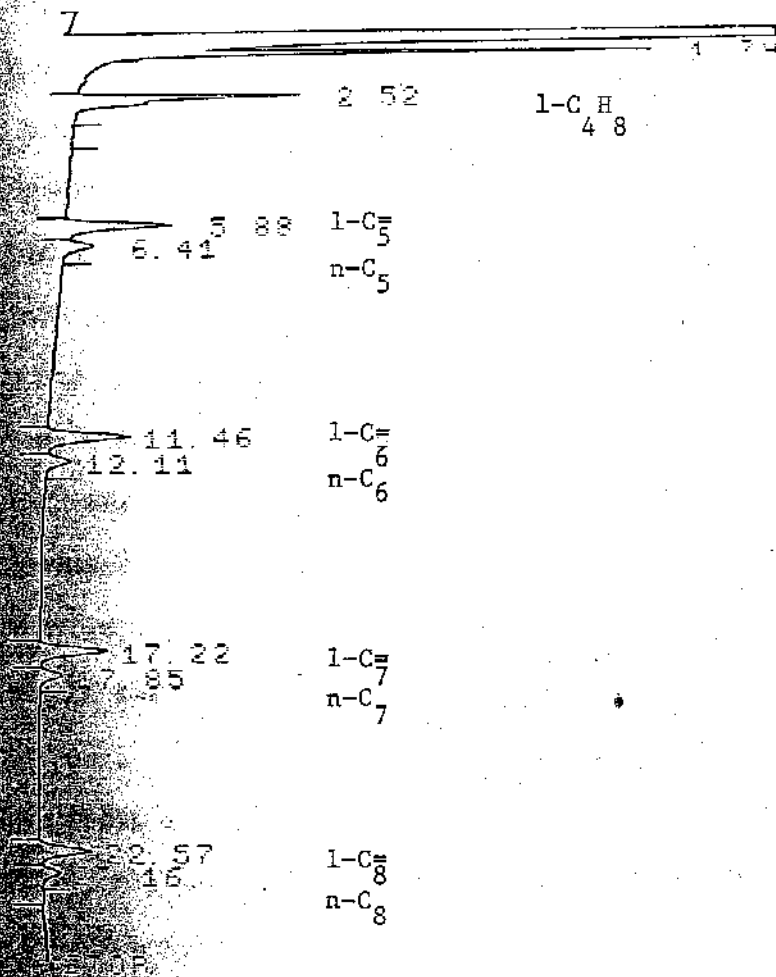


Figure 3.3.4. Typical chromatogram for the high molecular weight products obtained with the HP #5730 chromatograph with a SP2100 column under temperature programming conditions of 4°C to 100°C at 4°C/min. CO catalyst, 1/3 CO/H₂ feed at 7.8 atm and 250°C.

(Herzberg Backlund). One can see that the isomers of 2-butene can be readily identified, however, quantitative evaluation of the 1-butene and pentane peaks was not possible due to incomplete separation. All major hydrocarbons were separated and identified. These included the straight chain paraffin, α -olefin, cis- and trans-2-pentene and in some cases the branched paraffin. The heavier products were separated into straight chain olefin and n-paraffins. The branched isomers and internal olefins are generally minor products and are lumped into a total mole fraction corresponding to the carbon number. The SP-2100 column yielded a very broad and poorly defined water peak thus affecting the accurate integration of the areas for the $C_n > 9$ hydrocarbon products. During the course of an experiment it was often necessary to heat this column up to 150°C to remove any collected water and heavy hydrocarbon products. Ordinarily the product analysis of this column included at least the C_5 to C_{10} carbon fraction.

Both chromatographs employed heated six port sample valves. The Sigma sample valve is a Carle Model 4018 valve with a sample loop volume of 1 cc. The 6730 employed a factory installed valve equipped with either a 1 or 2 cc sample loop. Since the chromatograph response factors were determined on a mole fraction basis the actual volume of sample injected into the column was not needed as long as the total molar amount injected into the column was identical under both calibration and reaction conditions.

It was found that a measurable pressure increase occurred in both sample valves at flow rates greater than 40 cc/min (1 atm, 25°C). This resulted in an increase in the total molar amount injected for analysis. At the highest flow rates used (800 cc/min, 1 atm, 25°C), the amount of sample injected was approximately 60% more than that injected at

flow rates. Typically the increase was approximately 5-50% of the total product areas in reaction measurements. Consequently it was necessary to correct for this additional molar amount as a function of flow rate. A series of sample injections were performed by passing the calibration mixture through the sample valves at gas flow rates typically encountered in reaction studies. The increase in area for each measured flow was then normalized to the area obtained at flow rates where no flow induced pressure increase occurs (10-30 cc/min at 1 atm and 25°C). By this method one obtained flow correction constants which reflect the magnitude of product area increase as a function of flow. A plot of these correction constants as a function of flow rate is given in Appendix I. The data were fit to a fourth order polynomial in flow rate (cc/min, 1 atm, 25°C). Flow correction values for CO/H₂ feed rates used in reaction studies were computed by use of the polynomial function. The flow rates used in experimental studies was within the range of calibration mixture flow rates used to establish the flow correction constants.

3.5 Rate Data Analysis

Reaction rates were calculated on a product mole fraction basis by knowing the reactant flow rate and feed composition. The reactor was treated as a differential reactor using the model equation shown below

$$R_i = x_i F/W$$

where

R_i = production rate of component i (moles/gm cat-sec)

x_i = moles of component i formed/moles of reactant fed.

F = molar feed rate (moles/sec)

W = catalyst weight (gm)

CO conversions were typically kept below 4% for reaction rate analysis. The mole fraction X_i must be determined by a mass balance around the reactor since the total molar flow changes due to reaction. The computational method used in performing the mass balance and calculating reaction rates is given in Appendix II. Turn over frequencies (activities) are based on hydrogen chemisorption values obtained on the reduced catalyst(5).

3.3.6 Reactor Operation

A measured amount of catalyst (calcined oxide, typically .4-.6 gms) was placed in the reactor and reduced at 425°C in flowing hydrogen at one atmosphere. Flow rates were typically 50 cc/min measured at 1 atmosphere and 25°C. The total reduction time varied between eighteen to twenty four hours. It was found that this variation in reduction time did not affect the exposed surface area as measured by hydrogen chemisorption. In fact it had a negligible effect on the extent of reduction (119). Prior to cooling to the standard reaction temperature (250°C) the water traps were activated and the hydrogen flow was increased to allow any residual water to flush out of the system. The catalyst bed was then brought to reaction temperature under a continuous hydrogen flow. The cooling process took approximately forty five minutes to insure thermal equilibrium. The desired feed gas was then introduced generally at gas hourly space velocities (GHSV's) exceeding 10,000 hr⁻¹.

The CO/H₂ mixtures were introduced at delivery pressures close to one atmosphere. The reactor pressure was then quickly brought up to higher pressures if desired by increasing the delivery pressure of the feed gas regulator. Some experiments involved changing the reactor

pressure. These changes were generally accomplished in less than one hour to minimize any deleterious effects due to subjecting the catalyst to high conversion conditions (i.e., wax formation). Upon termination of a particular experiment the system was brought to atmospheric pressure and the reactor was cooled in flowing hydrogen. However, if a Mossbauer spectrum was to be taken on a particular catalyst after reaction the system was flushed and cooled in Helium at the pressure used in the experiment. It has been shown that exposure to Helium at one atmosphere at reaction temperatures does not affect the Mossbauer spectrum of the particular oxide phase formed under reaction conditions (76).