

5.0 EXPERIMENTAL

5.1 Catalyst Preparation

Catalyst precursors and supports were purchased from commercial sources. The following supports were used after a calcining treatment at 500°C for 3 hr in air: γ - Al_2O_3 (Catapal® SB, 217 m^2/g , 45 μm), SiO_2 (Davison 952, 339 m^2/g , 70 μm), $\text{MgO} \cdot 3.6 \text{ SiO}_2$ (Florisil®, 298 m^2/g , 75 μm) and TiO_2 (Degussa P-25, 50 m^2/g , 2 μm). The catalysts and precursors were protected from air and moisture using standard Schlenk techniques(25) and a Vacuum Atmospheres dry box. All solvents were reagent grade and distilled from sodium benzophenone ketyl in a nitrogen atmosphere. Immediately prior to use, the supports were further dried in vacuo at 110°C for 1-2 hr. Catalysts were prepared by impregnation (to incipient wetness) of the supports with separate solutions containing the promoter and metal carbonyl. All of the catalysts that were prepared are listed in Table 1 along with the metal loadings. Details of the preparation of individual catalysts are found in the quarterly reports.

5.2 Gas-Phase Testing

Prior to slurry-phase testing, gas-phase tests were conducted to screen catalyst activity. Those catalysts with gas-phase activities greater than 20 mol of syngas converted/kg of catalyst/hr were selected for further slurry-phase testing.

A simplified flow diagram of the fixed-bed gas phase screening system is shown in Figure 34. A section of the system, including the reactor, exit line, system pressure regulator, and product traps, is assembled in a vertical configuration with flow in a downward direction. Inert (N_2 or He) and process (H_2 , CO) gases are delivered to the reactor through thermal mass flow controllers equipped with digital meter readouts. Flow ranges are 0-1000 SCCM for each gas and, thus, synthesis gas can be blended in any proportion. A trap of alumina, heated to $250^\circ C$, is located in the CO line upstream from the flow controller and decomposes any metal carbonyls that may be present.

The reactor is made of 0.500 in. O.D. by 0.049 in. wall, 316SS seamless tubing with flange connections welded at either end. It is about 8 in. long with an effective bed volume of 15 cc. An aluminum heating block, 2.5 in. O.D. by 0.5 in. I.D. is bolted to the reactor tube and wrapped with a heat tape. A thermocouple is located inside the heating block midway along its length and midway across its radius. This thermocouple serves as the sensor for a temperature programmer, which is capable of multi-ramp operation at effective heating rates from 0 to about $30^\circ C/min$. Actual bed temperatures are monitored by a multipoint thermocouple located inside the reactor tube. The five thermocouple junctions are spaced at 1 in. intervals to span the entire bed length (Figure 35). A reactor bypass is valved into the system and is used for calibration of feed gas flow and composition. The exit line, including the body of the spring loaded system pressure regulator, is wrapped with heat tape from the

reactor to the product traps. A temperature controller is used to maintain the temperature at 150°C.

Each of two product traps consists of a series of two 125 cc pyrex two-piece vacuum traps immersed in a bath of glycol and water. An immersion circulator controls bath temperature at -30°C. A valving arrangement, using two three-way ball valves, permits selection of either trap. A wet test meter, located downstream of the traps, measures total gas flow through the system. A tee in the line between the product traps and the wet test meter is used to divert a portion of the gas stream to a GC system.

Pressure relief valves and gauges are located on both high and low pressure sides of the system. A pressure switch located on the high pressure side shuts off power and gas flow to the system in the event either a high or low setpoint is exceeded. A low setpoint bypass permits operation at ambient pressures. Each heated zone is protected by a temperature alarm in addition to a controller. Separate thermocouples are used for the alarms, which shut off the system if a high setpoint is exceeded. Solenoid shut-off valves are located on all gas lines supplying the reactor. A multi-point recorder provides a permanent record of system pressure and temperatures during a run. Electrical instrumentation is mounted in a cabinet located just outside the hood housing the reactor.

A 10 cc sample of catalyst was loaded into the 15 cc reactor using glass wool plugs to fix and contain the catalyst bed. This procedure

was done in a glove box under N_2 when air sensitive catalysts were being tested. The reactor was connected in place in the system which had been purged with N_2 flow for at least 10 minutes. The system was then pressurized to 600 psig and leak tested.

Catalyst activation was initially performed using a CO/H_2 blend according to a procedure developed under the previous program, as described in Section 3.1.4, Catalyst Activation Studies. The activation was changed to pure H_2 at $300^\circ C$ and 1000 hr^{-1} GHSV after finding that this procedure gave better catalyst performance. Most gas-phase tests used a CO/H_2 feed ratio of 1 at 300 psig and were conducted at 500-2000 GHSV (v/v based on 10 cc catalyst volume). Temperature was varied in the range of 220 to $280^\circ C$.

To begin a material balance period, the time and wet test meter reading were noted while simultaneously the exit gas flow was diverted through a clean, tared liquid product trap. Material balance periods were typically 6 to 16 hours in length during which one or two samples of the uncondensed exit gas was analyzed by GC. This was accomplished by opening a valve and temporarily diverting a small sidestream to the chromatographs. At the end of the material balance period, the time and wet test meter reading were again noted and the exit gas flow was diverted from the tared trap. The product trap, containing wax and liquid products was removed from the system, sealed, allowed to equilibrate to room temperature, and then weighed. A Pasteur pipette and micro-spatula were used to separate the product into three fractions: wax, organic liquid and aqueous

liquid. The fractions were collected in tared vials and weighed. Discrepancies between the combined weight of the fractions and the weight of the trap were usually less than 0.5% and were accounted for by normalizing the individual fraction weights. Table 1 summarizes the results for all catalysts tested in the gas phase reactor. Testing of each catalyst took 3 to 5 days.

5.3 Slurry-Phase Testing

Two continuous, stirred, 1 liter autoclave reactors were used for slurry tests. Figure 36 shows a schematic diagram of one of these units. Inlet CO and H₂ streams are passed through separate oxygen removal and drying stages, and an additional iron carbonyl removal stage using a heated alumina trap is employed for the CO before the streams are mixed and preheated. Any desired ratio of CO to H₂ can be fed to the stirred reactor system with the help of mass flow controllers. During the course of the program one of the reactors was modified to allow the use of a third feed gas component. The reactor is fully baffled, and the gas inlet point is located directly beneath the flat-bladed impeller to maximize gas shear. The reactor operates in a temperature range of 220-330°C, pressures of 160-510 psi, and gas hourly space velocities (GHSV) up to 1000 h⁻¹, based on a 500 cc slurry volume. Products, together with unreacted syngas, are taken overhead through a heated partial reflux condenser maintained at a top temperature of about 200°C to return vaporized slurry liquid to the reactor.

Hydrocarbon product can be removed from the reactor directly via a heated sidestream, filtered through a 5- μ m stainless steel sinter, and analyzed. The supported catalysts used in this study caused no clogging of the filter and thus wax removal was performed easily, without the need to stop the stirrer or gas flow. No catalyst was lost during wax removal. Wax was generally withdrawn on a daily basis, but the specific frequency depended on the catalyst activity. The level of the dip tube determined the level of liquid remaining in the reactor. By determining the amount of slurry liquid withdrawn to maintain a constant level at a particular set of process conditions, the higher molecular weight hydrocarbons that do not distill with the gas phase product can be quantitatively included in the material balance of the system. This procedure is essential to obtain an overall product selectivity.

The product stream from the partial reflux condenser flows via a heated line to a pressure reduction stage, and then to a C₅/C₆ splitting column, to produce a condensed liquid phase and a gaseous phase. The splitting column was a single stage glass industrial coil condenser (Kontes, Vineland, NJ) cooled with ethylene glycol (-10°C) from a refrigerated circulating coolant bath (Lauda, Brinkman/Sybron, Westbury, NY). Gas entered the condenser at 30°C and exited at 10°C. The gaseous stream consists of unreacted syngas, CO₂, and products with carbon numbers from C₁ to C₅. The condensed liquid product consists of hydrocarbons with carbon numbers C₆ and above and an aqueous phase containing dissolved oxygenates. This method of product collection avoids the use of high-pressure traps, is more

suited to continuous operation, and, by reducing the number of product fractions, is more accurate in obtaining material balances.

The entire system is designed to run continuously and automatically when unattended, with automatic sampling of the split gas phase stream and collection of liquid samples. After any change in process parameters, the reactor system is allowed to equilibrate for 14 to 16 hours before carbon and hydrogen material balances are obtained over an additional 8 hour period.

For the slurry phase tests, catalysts were activated in a separate, 150 cc fixed bed tubular unit using either pure H_2 or 20% syngas in N_2 . Activated catalyst was then slurried in deoxygenated paraffin oil (Fisher #0-122) in the dry box and transferred to the slurry autoclave reactor under a N_2 blanket. Slurry screening tests were performed continuously for up to 21 days. Inlet CO/H_2 ratios were 2, 1.5, and 0.5, with emphasis on CO-rich feeds. Space velocities were 1 and 2 NL/g of catalyst/hr. Operating pressures and temperatures ranged from 300 to 600 psig and 220 to 280°C, respectively. The solids content of the slurry was 15 to 35 wt%.

5.4 Product Analysis

Because of the complexity of the Fischer-Tropsch product, equilibration of the reactor and the product collection systems, a flexible quantitative analysis scheme incorporating all products including waxes was required to produce good carbon and hydrogen

material balances and prevent misleading results. This procedure routinely produces material balances for carbon and hydrogen in the range of 95-105%.

A versatile analytical and computerized data handling system has been developed for this program (see ref. 26). The currently used method is illustrated schematically in Figure 37, and consists of four separate gas chromatographs linked via a Perkin Elmer Sigma 15 computing integrator/controller to a Tektronix 4052 microcomputer equipped with a 1.9-megabyte disk system. Unreacted synthesis gas, CO₂, and C₁ to C₅ hydrocarbon isomers were analyzed as a single gas phase sample by a Carle 400 analytical gas chromatograph specifically designed for simultaneous TCD/FID analysis of refinery gas. Low concentrations of C₆ to C₁₀ hydrocarbons appearing in the gas phase product due to inefficiencies in the C₅/C₆ splitting condenser were analyzed by a Perkin Elmer Sigma 300 gas chromatograph equipped with a 25-m x 0.53-mm fused silica capillary column coated with 95% dimethyl/5% diphenyl polysiloxane.

After the condensed liquid phases were separated and weighed, aqueous phase samples were analyzed for C₁-6 alcohols, aldehydes, ketones, and acids using a Perkin Elmer Sigma 1 gas chromatograph equipped with a 0.2% Carbowax 1500 on 80/100 Carbopak C, 6-ft x 1/8-in., stainless steel, packed column. The separated organic phase was analyzed for C₅-C₄₀ hydrocarbons on a Perkin Elmer Sigma 1B gas chromatograph using a 10-ft x 1/8-in., stainless steel column packed with SP2100 on Supelcoport. Filtered slurry wax product removed

directly from the reactor was also analyzed for C₉₋₄₀ hydrocarbons on the same instrument. Any contribution from the initial slurry liquid was subtracted from the analysis. Products >C₄₀ were not added to the product distribution.

The analytical data were collected and temporarily stored in the Sigma 15 integrator before direct transfer to the Tektronix disk system. After compilation into matrix format, the six data files for each sample point were assembled by the computer into an overall product matrix, and weight percent, mole percent, and Schulz-Flory distributions, selectivity and conversion fractions, and C and H material balances were calculated. The Tektronix graphics routines provided immediate plots of the hydrocarbon weight and Schulz-Flory product distributions.

5.5 Catalyst Characterization

Metal loadings were determined in-house by inductively coupled plasma-atomic absorption and at Schwarzkopf Microanalytical Laboratories (Woodside, NY). XPS data was obtained on a Physical Electronics 560 XPS/AES instrument. Catalyst samples for XPS were reduced in the 10 cc fixed bed reactor and transferred to the sample holder in a dry box. H₂ chemisorption experiments were conducted on a Micromeritics Chemisorb 2800 using catalyst samples prereduced in the 10 cc reactor. After transfer of the samples to the chemisorption sample tubes, they were treated with H₂ at 300°C and 1 atmosphere prior to data acquisition. B.E.I. surface areas were obtained using a Micromeritics Digisorb 2500.