

3.2 Catalyst Characterization

A complete analysis of the dried zeolites and the decomposed and reduced Ru catalysts was carried out by atomic absorption (AA) to determine the aluminum and alkali cation contents of the zeolites as well as the metal loading. The sodium content was determined by flame-emission spectroscopy. The Ru catalysts were then characterized by chemisorption of hydrogen and carbon monoxide. The crystallinity of the catalysts was examined by X-ray diffraction at various stages of preparation, pretreatment and after reaction. Details of the various characterization techniques are given in the following sections.

3.2.1 Atomic Absorption

The composition of the various catalysts was determined by atomic absorption and flame-emission spectroscopy using a Perkin Elmer 380 atomic absorption spectrometer, before and after exchanging the ruthenium. For the zeolites not containing Ru, approximately 100 mg of each sample, accurately weighed into a teflon beaker, was dissolved in 10 ml HCl and 4 ml concentrated H_2SO_4 . HF (49%), in excess to the stoichiometric amount, was added to react away any silicon present. The mixture was heated to dryness on a hot plate. The residue was then re-dissolved with 25 ml of HCl and about 25 ml of distilled water by heating for a few

minutes, before transferring the mixture to a 250 ml volumetric flask. Distilled water was added to bring the volume to 250 ml. Two mg of potassium/ml of solution in the form of KNO_3 were added in order to reduce ionization of the analyzed elements and avoid any interferences during the AA analysis.

In order to determine the silicon content of the zeolites, the water content was determined by calcining approximately 1 g of zeolite at 1000 K for 4 hours.

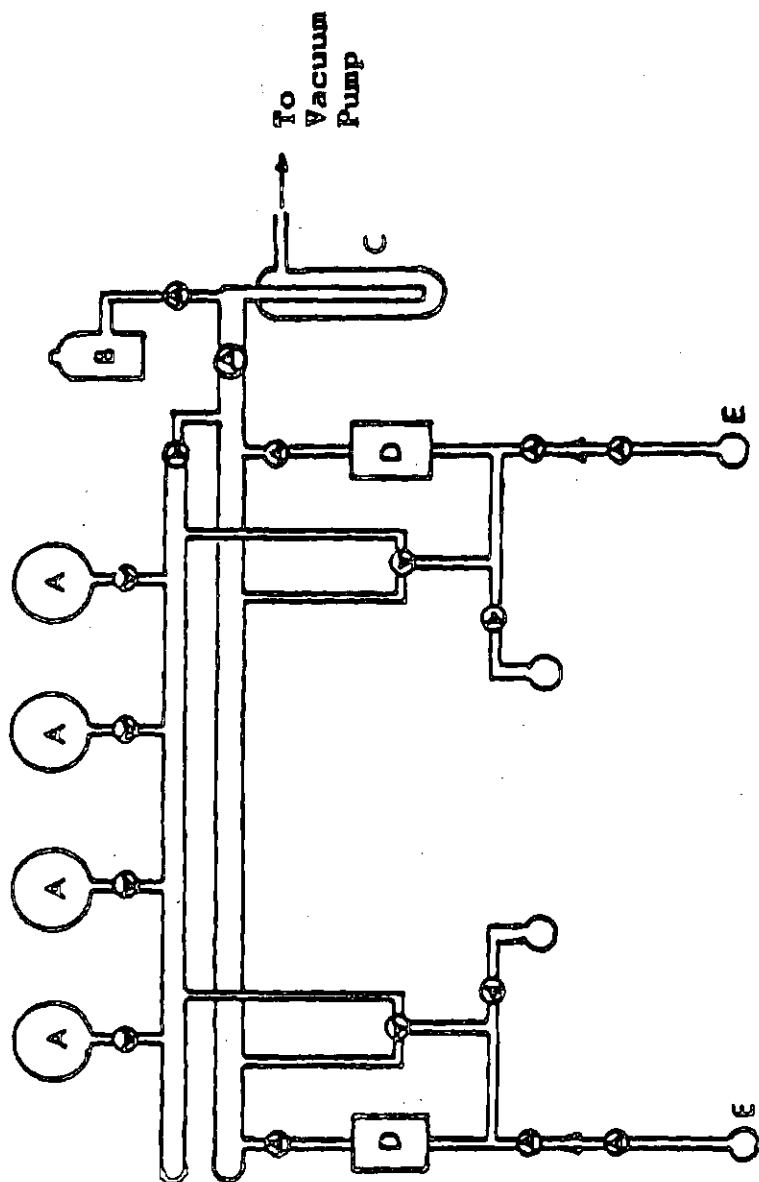
The concentration of ammonium cations was calculated from the known aluminum and alkali contents assuming that all the negative charges in the zeolite framework were neutralized by either the alkali cations or the ammonium ions. A Kjeldhal analysis of the ammonium concentration in the zeolites gave similar results.

A quantitative analysis of Ru in all the ruthenium catalysts was also performed by atomic absorption. The method applied was essentially the same as that described by Fabec⁽⁷⁵⁾ with minor modifications. Approximately 40 mg of the reduced catalyst were dissolved in 2 ml H_2SO_4 . HF was added in excess of the stoichiometric amount necessary to react off the silicon present in the zeolite. The mixture was allowed to stand overnight on a hot plate at approximately 373 K. Thereafter, the contents were transferred to a 50 ml volumetric flask and brought to volume with a 10% HCl solution containing 2mg/ml of aluminum

ions. Calibration curves were obtained using controlled dilutions of a standard 1000 mg of Ru/l solution. All additives (HCl, H₂SO₄, Al(NO₃)₃·9H₂O) are taken into account for the instrument calibration.

3.2.2 Chemisorption

Chemisorption of hydrogen and carbon monoxide were carried out at ambient temperature in a conventional volumetric apparatus (Figure 3.1) where a vacuum of 1×10^{-6} torr was achieved. Air Products UHP-grade hydrogen and helium were passed through a liquid nitrogen trap and carbon monoxide through a dry ice trap before being admitted to their respective reservoirs. Helium was used for dead-volume determination. The prereduced catalyst (0.5-1 g) was evacuated at room temperature, heated slowly (0.5 K/min) to 673 K, at which point hydrogen (approximately 300 torr) was added and held at that temperature for two hours. The sample was then evacuated for two hours at 673 K and cooled to room temperature. The total uptake of hydrogen or carbon monoxide was determined from approximately 100 to 300 torr and the linear part of the isotherm was extrapolated to zero pressure. Since the isotherm was measured by desorption, the system was allowed to equilibrate during 20 to 24 hours for the first point of the isotherm; for the subsequent points equilibrium was reached in about one hour. A second



A. Gas Reservoirs
 B. Ion Gauge
 C. Liquid Nitrogen Trap

D. Pressure Sensors
 E. Sample Cells

Figure 3.1 Chemisorption System

isotherm was performed in the same manner after evacuating the catalyst for a short period of time (ca. 5 min.). It has been shown that there was no significant difference in the quantity of adsorbed hydrogen removed with evacuation time ranging between 2 and 20 min.⁽⁷⁶⁾ The difference between the two isotherms, extrapolated to zero pressure, gave the amount of irreversibly (strongly) chemisorbed hydrogen (H_{irr}) or carbon monoxide. The use of the strongly held hydrogen has been shown to be more appropriate for Ru dispersion calculations when dealing with highly dispersed systems, since it seems to form a complete monolayer, assuming $H_{irr}/Ru_s = 1$.⁽⁷⁷⁻⁷⁸⁾

Hydrogen chemisorption measurements were used to calculate the surface area assuming a stoichiometry of $H_{irr}/Ru_s = 1$ ⁽⁷⁷⁾ and an average Ru surface area of 8.17 \AA^2 ($10 \text{ \AA} = 1 \text{ nm}$).⁽⁷⁹⁾ Assuming the particles to be cubic with five sides exposed to the gas phase, the relationship $d_p = 5/S\rho$, where ρ is the density of the metal and S the surface area of Ru per gram of Ru, was used to assess the average Ru crystallite size, d_p . The Ru dispersion was calculated by $D(\%) = (Ru_s/Ru_T) \times 100$.

Although such determinations have been found to compare favorably with T.E.M. measurements⁽⁷⁷⁾ for Y-zeolites, suppression of irreversible hydrogen chemisorption may be significant for zeolite-supported ruthenium catalysts prepared by ion-exchange.⁽²¹⁾ Thus, H_2 chemisorption alone

may not be very reliable for characterization. Although CO adsorption cannot be used for determination of ruthenium dispersion, since its stoichiometry is function of the metal particle size,⁽⁸⁰⁾ the CO chemisorption measurement were carried out mainly because consideration of CO/H and CO/Ru_(total) ratios may be used to indicate H₂ chemisorption suppression.⁽²¹⁾

3.2.3 X-Ray Diffraction

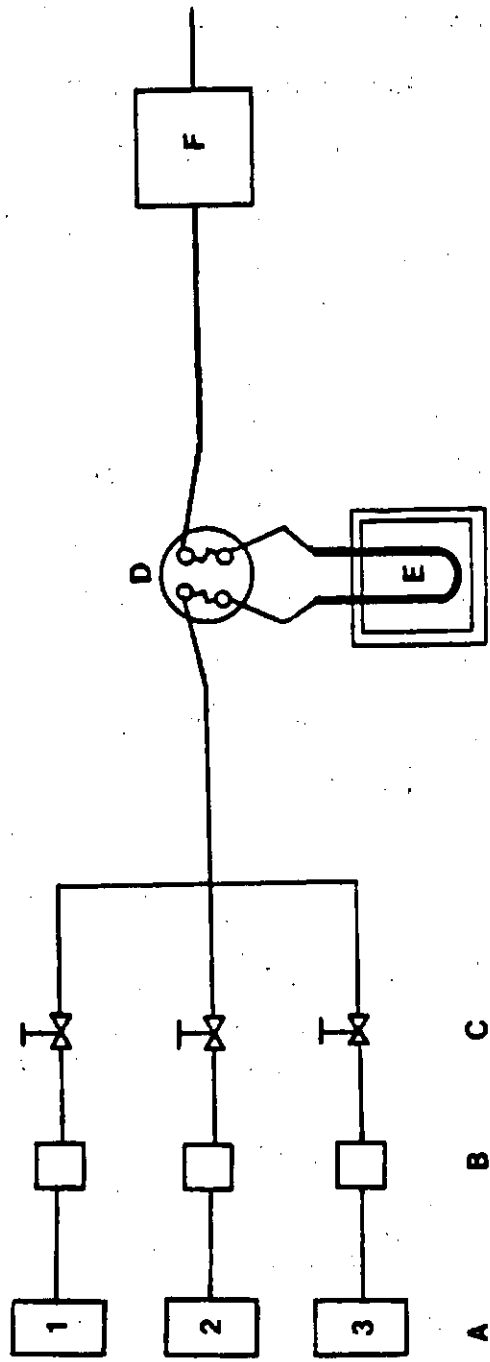
In order to check whether the crystallinity of the zeolites was affected during the various stages of preparation, pretreatment and use for CO hydrogenation reaction, the various catalysts were examined at each stage by X-ray diffraction. X-ray powder diffractograms were obtained on a GE XRD-700 unit using Cu/K α radiation and a graphite monochromator.

3.3 Reaction Studies

3.3.1 Experimental Setups and Procedure

3.3.1.1 CO hydrogenation

Fischer-Tropsch synthesis was carried out in tubular microreactor made from a stainless steel tube of 3/16 in. diameter (1 in. = 2.54 cm). The feed of the reactant gases was controlled by mass flow controllers (see Figure 3.2 for



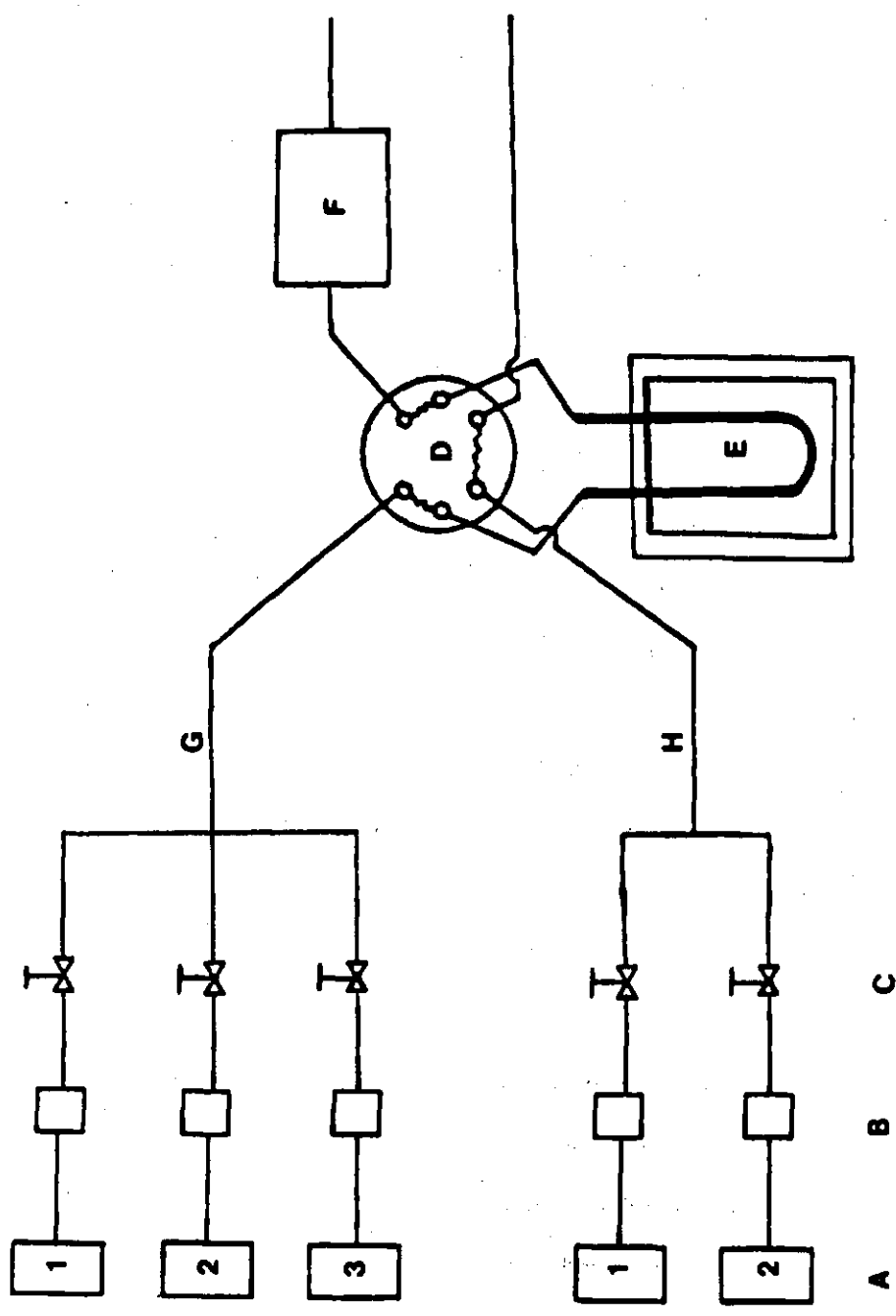
- A. Gas Supply: 1. Helium
- 2. Hydrogen
- 3. Carbon Monoxide
- B. Gas Purifiers
- C. Mass Flow Controllers
- D. 4-Way Valve
- E. Furnace + Microreactor
- F. Gas Chromatograph

Figure 3.2 Schematic Diagram of Reactor System for CO Hydrogenation

flow diagram). The reaction temperature was controlled by a thermocouple inserted into the catalyst bed. The prereduced catalyst (0.2-0.5 g) was loaded into the reactor and heated under a hydrogen stream of 3.6 l/h. The temperature was ramped to 673 K at 2 K/min and held there for two hours before cooling to reaction temperature. Ultrahigh purity H₂ and CO supplied by Air Products were passed through molecular sieve traps to remove water. Prior to passage through the molecular sieve trap, the hydrogen was passed through a deoxo unit to react any oxygen present to water. Reaction was carried out at atmospheric pressure and 483-573 K using a 1:1 mixture of H₂/CO flowing at 2.4 l/h. Under these conditions, CO conversion was found to be lower than 10%, even at the highest temperatures used in this study. A sample of the effluent gas was analyzed on-line by gas chromatography after 5 min of reaction. This time was found to be long enough to establish the product distribution. The hydrogen bracketing technique, which added a 40 minute hydrogen exposure after every five minutes of reaction, was found to be sufficient to maintain a clean metallic surface, thus giving reproducible results.

3.3.1.2 Hydrocarbon Reactions

Olefin (propylene and 1-butene) transformations were carried out in a similar system to that used for CO hydrogenation (see Figure 3.3). To avoid any hydrocarbon



- A. Gas Supply: 1. Helium
- 2. Hydrogen
- 3. Carbon Monoxide
- B. Gas Purifiers
- C. Rotameters
- D. 6-Way Valve
- E. Furnace + Microreactor
- F. Gas Chromatograph

Figure 3.3 Schematic Diagram of Reactor System for Hydrocarbon Reactions

reaction on metallic reactor walls, a quartz microreactor was used for these experiments. The catalysts, in this case the zeolites without any metal, were first pretreated at 673 K for two hours under a hydrogen stream in order to decompose the ammonium cations and produce the protonic-form zeolites HY, H-mordenite and MHY (M = Li, Na, or Rb). The same pretreatment procedure was also followed in the case of the alkali-form zeolites LiY, NaY, and RbY, NaX, KL, and Na-mordenite, mainly to eliminate any water present. The reactor was then cooled down to a reaction temperature of 523 K, chosen in order to compare the properties of these zeolites with those of the zeolite-supported Ru catalysts for CO hydrogenation. A flow rate of 100 ml/min of a reactant mixture containing approximately 1% olefin in helium was used with a catalyst charge of 0.1 g. Samples of the reactor outlet were analyzed by on-line gas chromatography after 5 min of reaction, as during the CO hydrogenation experiments.

3.3.2 Product Analysis

The reaction products were analyzed on-line using two chromatographs. A Varian 3700 gas chromatograph (GC) fitted with a flame ionization detector and a 12 m SP-1700 column maintained at 353 K permitted separation of all hydrocarbons and most isomers in the C₃-C₆ fraction. A second chromatograph (Varian 1400) equipped with a thermal

conductivity detector and a 2 m stainless steel column packed with Porapak Q was used, when necessary, to separate CO, CO₂, CH₄, C₂H₄, C₂H₆, and H₂O. Calibration of the GC response was carried out with known mixtures of gases obtained from Scott Specialty Gases. Peak areas and product concentrations were determined by an electronic integrator (Varian CDS 111).

3.3.3 Activity and Selectivity Determination

3.3.3.1 CO hydrogenation. The activity of the catalysts for CO hydrogenation was determined from CO conversion to the various hydrocarbons. In most cases, only C₁- to C₆-hydrocarbons were formed in measurable amounts. The conversion to CO₂ was not taken into account in the calculations since, under the reaction conditions chosen here, the formation of CO₂ was low, thus making its measurement by GC less accurate.

Therefore, the CO conversion was calculated as follows:

$$\text{CO Conv.} = \frac{\sum_i n_i}{n_{\text{CO}}} \times 100 \quad (3.1)$$

$$= \frac{\sum_i P_i}{P_{\text{CO}}} \times 100 \quad (3.2)$$

where i is the number of carbon atom per hydrocarbon molecule, n_i the numbers of moles of hydrocarbons in the

injected sample of known volume, P_i their partial pressure in atm which were determined directly by the GC integrator, n_{CO} the number of moles of CO in a comparable volume of reactants, P_{CO} its partial pressure in the reactant mixture. Equation 3.2 can be obtained using the ideal gas law since the volume and the temperature of the injected samples are constant, and the partial pressure of CO is known.

Knowing the conversion, the rate of CO conversion can be derived from:

$$\text{Rate (mol/h.g.)} = \frac{F}{22.4} \times \frac{273}{293} \times \frac{1}{W} \times \frac{\text{CO Conv.}}{100} \quad (3.3)$$

where F the CO flow rate in l/h, W the catalyst weight in grams. The turnover frequencies (TOF) for CO conversion were then determined, using these rates of CO conversion and the hydrogen chemisorption measurements.

The selectivities of the various catalysts were determined as the weight fractions, C_i , of converted CO into hydrocarbon C_i with i carbon atoms:

$$C_i = \frac{i P_i}{\sum i P_i} \times 100 \quad (3.4)$$

3.3.3.2 Olefin Reactions. A similar calculation procedure was used to determine catalyst activities and selectivities for the olefin reactions. The olefin concentration in the

feed was determined each time before starting the reaction, after setting all the gas flow rates. This permitted the determination of the total olefin conversion, including the amount retained by the catalyst in the form of either strongly adsorbed species or coke, by a simple mass balance.