3.2.2 Catalyst Characterization

3.2.2.1 Fe Catalsyt

The iron catalysts exist as α-Fe_2O_3 after calcination in air (118,4). Upon reduction in flowing hydrogen at 425°C for 24 hours the catalyst is converted predominantly to the BCC iron phase (118,3). However, there is a sizeable fraction of superparamagnetic iron oxide. This is most likely due to some back oxidation due to exposing the catalyst to air (passivation) while obtaining the MES data. Figure 3.2.2 presents the Mossbauer spectra for the calcined oxide and reduced phase (1) at 25°C. MES data obtained at liquid helium temperatures (1,4) for the passivated catalyst reveal that the superparamagnetic fraction is due to an oxyhydroxide phase. The formation of this phase is most likely due to back oxidation of the catalyst surface due to the exposure to air. MES studies conducted in a controlled atmosphere cell (4) reveal that the calcined oxide is completely reduced to BCC metal (4).

Under synthesis conditions (250°C, 1/3 CO/H_2 feed, 1 atm) the reduced catalyst is converted to a mixture of ε and ε' carbide, since MES parameters agree with values obtained for these carbide phases (117,3) The Mossbauer spectrum under these conditions is included in Figure 3.2.2. The dominant six line pattern with the smaller hyperfine field is associated with the ε' phase.

Figures 3.2.3 and 3.2.4 present Mossbauer spectra for the Fe catalyst at higher pressures using the 1/1 and 1/3 CO/H_2 feeds respectively at 250°C. There is no apparent change in the MES parameters associated with the dominant six line pattern of the ε' phase. Table 3.2.3 presents these parameters for the spectra obtained at 1 atm using a 1/3 CO/H_2 feed (1,3) and at 7.8 atm. using a 1/1 CO/H_2 feed . (Figure 3.2.3).

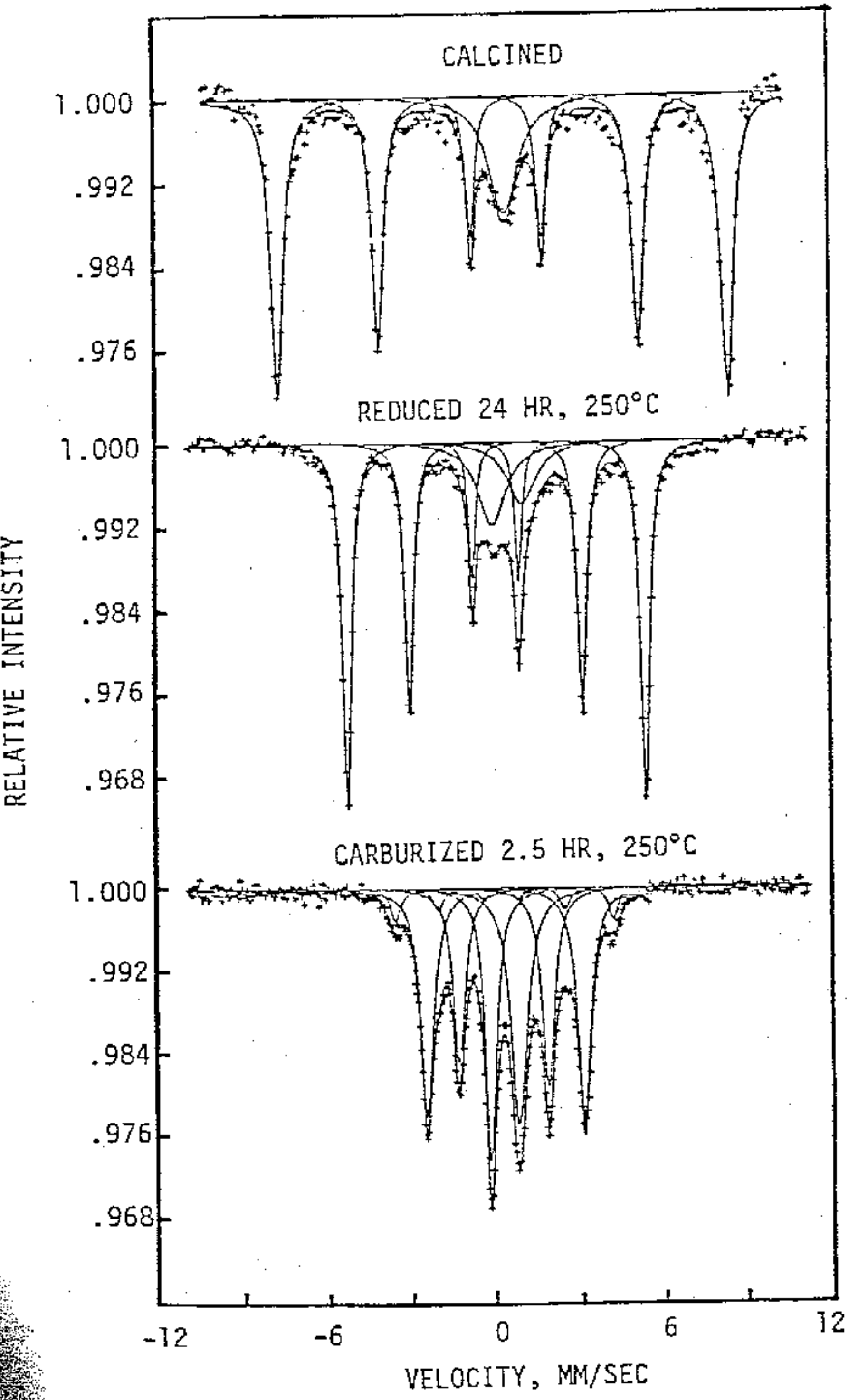

Figure 3.2.2 Mössbauer spectra for the Fe catalyst in various chemical phases. Spectra taken in air at 25°C (1).

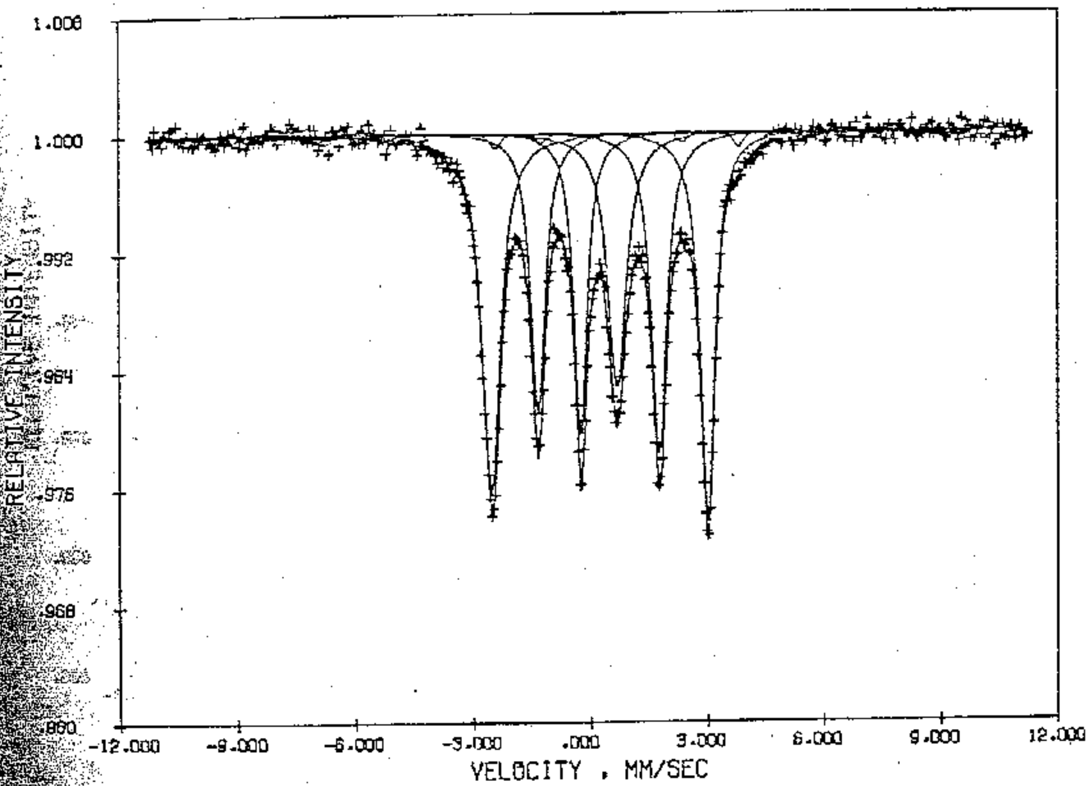

Figure 3.2.3 Mössbauer spectrum for the Fe catalyst after exposure to 1/1 CO/H_2 feed at 7.8 atm and 250°C. Spectrum taken in air at 25°C.

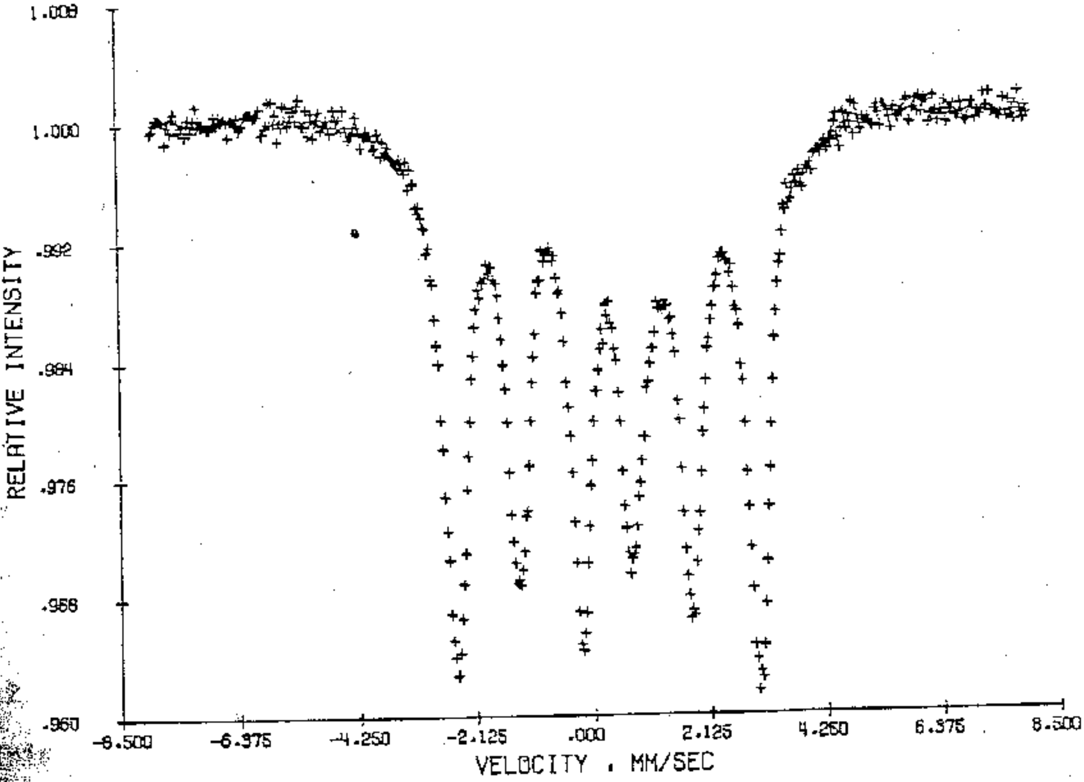

Figure 3.2.4 Mössbauer spectrum for the Fe catalyst after exposure to 1/3 CO/H_2 feed at 14 atm and 250°C. Spectrum was not computer fitted as was taken in air at 25°C.

Table 3.2.2

Mossbauer parameters for the Fe catalyst after exposure to either 1/3 or 1/3 CO/H_2 feed gas at 250°C
(Parameters are for Six Line Pattern)

Pressure	Feed	δ(mm/sec)	ΔEq(mm/sec)	H(kOe)
1	1/3	.24(1)	-.12(1)	173(1)
7.8	1/1	.24	-.15	172

(1) from reference 1

The principal difference in the MES spectra obtained at different feed and pressure conditions appears in the relative fractions of the ε carbide phase. At the higher pressure the presence of ε carbide in the bulk phase is barely detectable (Figures 3.2.2 and 3.2.3). The formation of this phase appears to be independent of the CO/H_2 feed ratio but is dependent on pressure since its relative fraction is greatly reduced at 14 atm. compared to 1 atm. when using the 1/3 feed at 250°C.

3.2.2.2 FeCo catalyst

This catalyst has been thoroughly investigated by Unmuth et al. (119) and Amelse et al. (5) and using both x-ray diffraction and Mossbauer spectroscopy. Alloy formation has been confirmed from these studies. The broad linewidth encountered in both these spectroscopies indicate that the BCC alloy composition is extremely non-uniform (116). The Mossbauer spectra for this catalyst in the oxide and reduced state presented in Figure 3.2.5 (5). This material does not carburize under synthesis conditions. This is expected in the case of an FeCo alloy since Co destabilizes the bulk iron carbide phase (48). The hyperfine field (356 kOe) associated with the catalyst after exposure to the 1/3

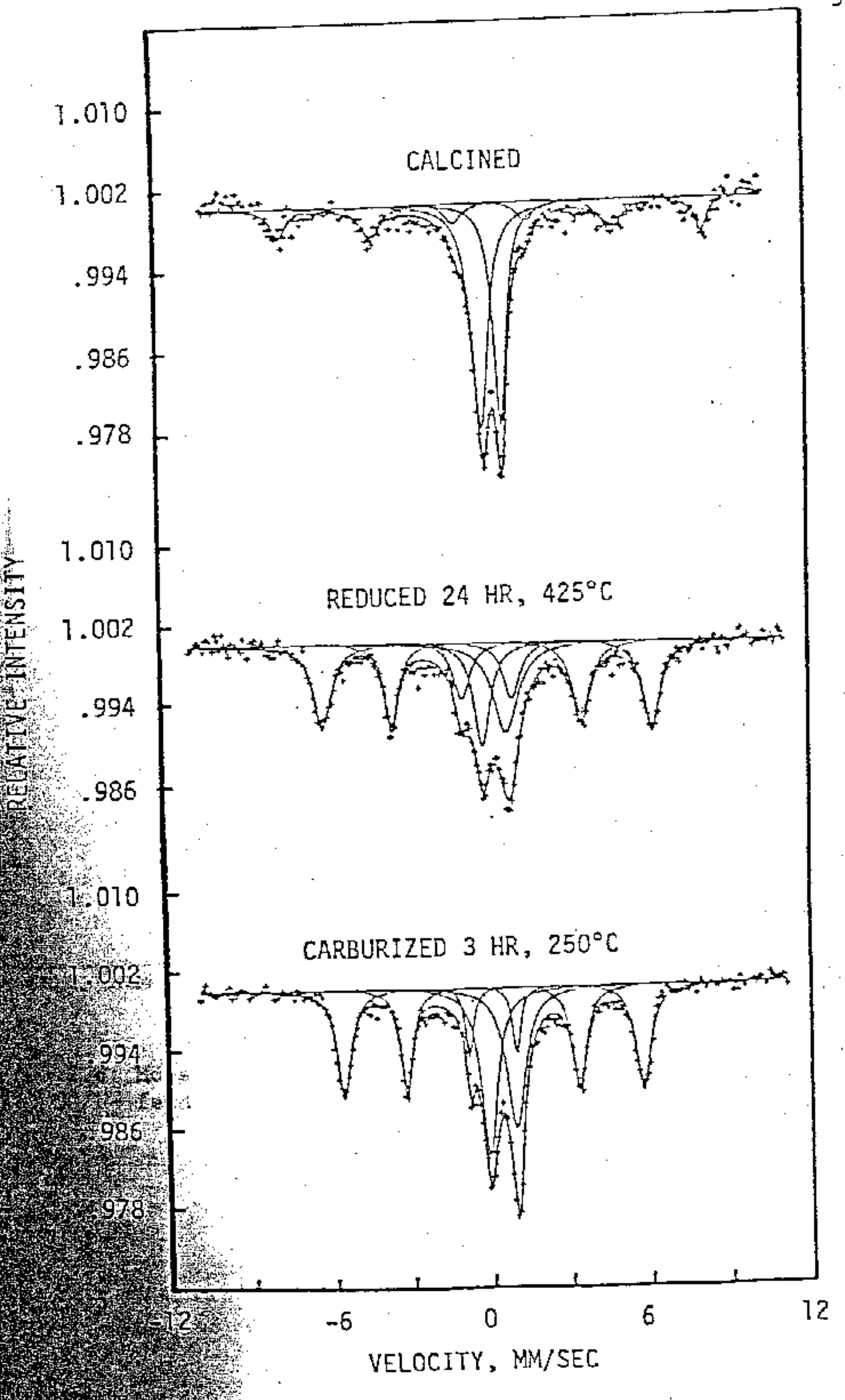

Figure 3.2.5 Mossbauer spectra for the FeCo catalyst in various chemical states. Spectra taken in air at 25°C (1).

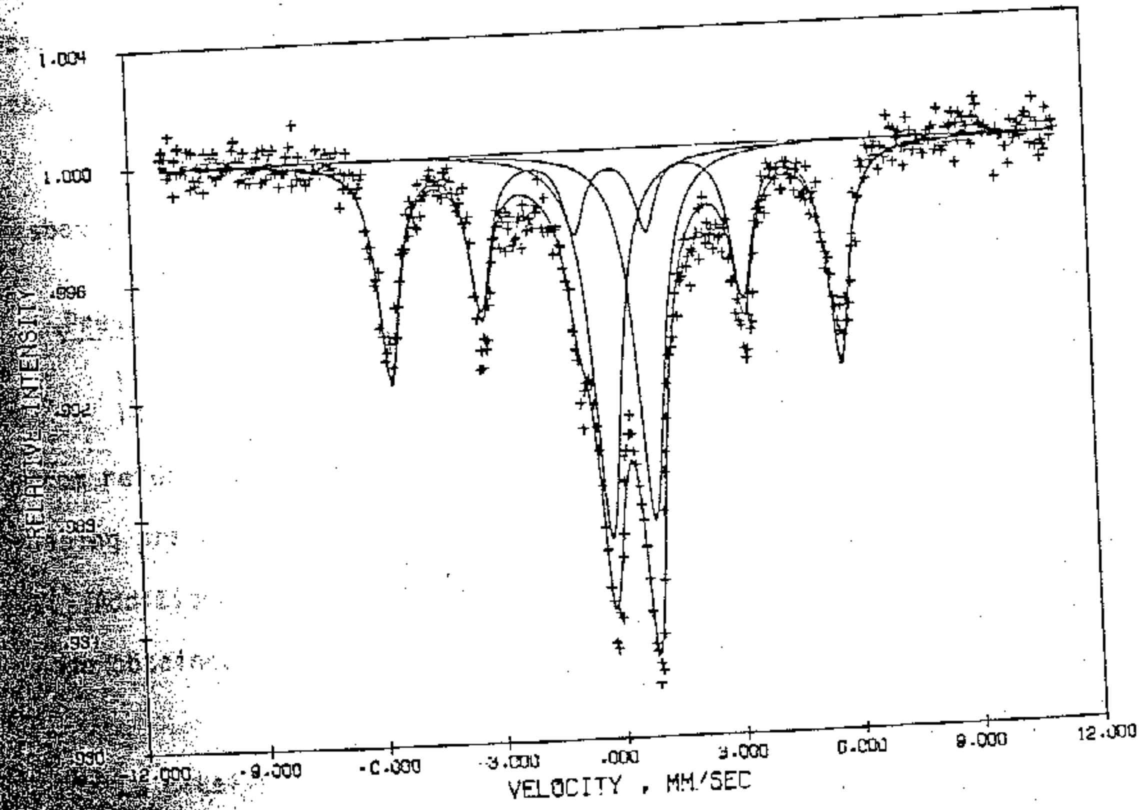

Figure 3.2.6 Mössbauer spectrum for the FeCo catalyst after exposure to the 1/3 CO/H_2 feed at 14 atm and 250°C. Spectrum obtained in air at 25°C.

CO/H_2 mixture at 1 atm. and 250°C is essentially identical to the BCC alloy (354 kOe) (1). Amelse et. al. (1,5) attributed the increase in the superparamagnetic fraction to back oxidation due to exposure to air. Figure 3.2.5 presents the Mossbauer spectrum for the FeCo after exposure to the 1/3 CO/H_2 mixture at 250°C and 14 atm. The Mossbauer parameters associated with the BCC six line splitting are presented in Table 3.2.3 for the samples exposed to 1/3 CO/H_2 pressures of 1 (4) and 14 atm.

Table 3.2.3

Mossbauer Parameters for the FeCo catalyst exposed to 1/3 CO/H_2 feed
(Six Line Pattern)

Pressure	δ mm/sec	ΔEq mm/sec	H(kOe)
1	.02(1)	-.03(1)	354(1)
14	.02	-.03	354

(1) from reference 4

Increasing pressure has no effect on the Mossbauer parameter of the bulk phase. Additionally the spectra obtained with the 1/1 feed were similar to those obtained with the 1/3 feed (Figure 3.2.6).

3.2.2.3 Co Catalyst

Since cobalt does not exhibit the Mossbauer effect the phase identification for this catalyst was conducted through X-ray diffraction. The calcined oxide was Co_3O_4 and upon reduction a mixture of FCC and HCP metallic phases exist (119). This catalyst does not form a bulk carbide since the diffraction pattern of the reduced catalyst remained unchanged after exposure to reaction conditions (1 atm, 250°C, 1/3 CO/H_2 feed) (119).

3.2.3 Catalytic Surface Area Measurements

In order to obtain specific activities in the kinetic studies the number of active catalytic sites need be determined. Hydrogen chemisorption on the catalyst in the reduced state was chosen as the method for determining the number of active sites on a per gram basis. The method was developed by Amelse et al. (5) and is thoroughly discussed in his doctoral dissertation (1). The method involves reducing the calcined oxide at 425°C for 24 hours in flowing H_2. The temperature is then lowered to 0°C in H_2 so as to minimize any kinetic limitations imposed by the adsorption/desporption process(1). After exposure to flowing H_2 at 0°C for 20 minutes the system is completely flushed with argon. The catalyst sample is then rapidly heated to 425°C and the moles of desorbed H_2 are measured.

This technique cannot be applied to catalysts existing in the carbide phase since exposure to hydrogen at these temperatures would produce hydrocarbons (Section 2.2). The method however can provide a useful comparison for specific activities with respect to alloying and varying dispersions involving the same metal components.

The number of active sites associated with each catalyst on a weight basis is presented in Table 3.2.4. (5) The number of sites is equal to twice the H_2 uptake assuming one hydrogen adsorbs on an active site.

Table 3.2.4

Dispersion Measurements

Catalyst	moles H_2 adsorbed$^{(1)}$ / gm	No. of active sites / gm	Fraction metal exposed Dh$^{(2)}$
	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-2}$
Fe	19.8	39.6	4.75 ± .24
Co	23.1	46.2	6.8 ± .15
FeCo	22.7	45.4	5.6 ± .3

(1) From reference (1)

(2) Based on weight fraction of oxide reduced as determined by thermogravimetric measurements.

3.3 Reactor and Analytical Equipment

3.3.1 The Differential Flow Reactors

The high pressure reactor and the support gas handling system are shown in Figure 3.3.1. The reactor itself consisted of a 1/4" O.D. stainless steel U tube completely encased in a resistance heater. A thermo couple connected to an Omega model #491 Proportional Temperature controller was located adjacent to the center of the U-tube to allow for accurate temperature control. The oven casing was heavily insulated and 1/8" O.D. stainless steel lines were used for the reactor inlet and outlet in order to minimize any heat loss. By moving the thermocouple through the oven over the length of the reactor it was found that the internal volume was isothermal within the limits of the temperature indicator on the controller (±3°C).

The use of a stainless steel reactor raised some questions concerning iron carbonyl formation and catalytic activity along the inside wall. Indeed it was found that some methane and CO_2 formed on a clean reactor surface and there was a noticable amount of deactivation in initial experiments at high pressure. To counteract these problems the interior wall of the reactor was plated with gold using a technique developed by P. Forsythe (46). These reactors maintained stable activity and exhibited no wall reactions. During the latter stages of experimentation it was found that pretreating a clean stainless steel reactor with a CO/H_2 mixture at 600°C produced the same results.

The low pressure system shown in Figure 3.3.2 is similar to that used by Amelse (3,5). It contains an oven and temperature control system similar to the high pressure system except a 1/4" O.D. glass U-tube is employed as the reactor. At one atmosphere both systems yielded identical

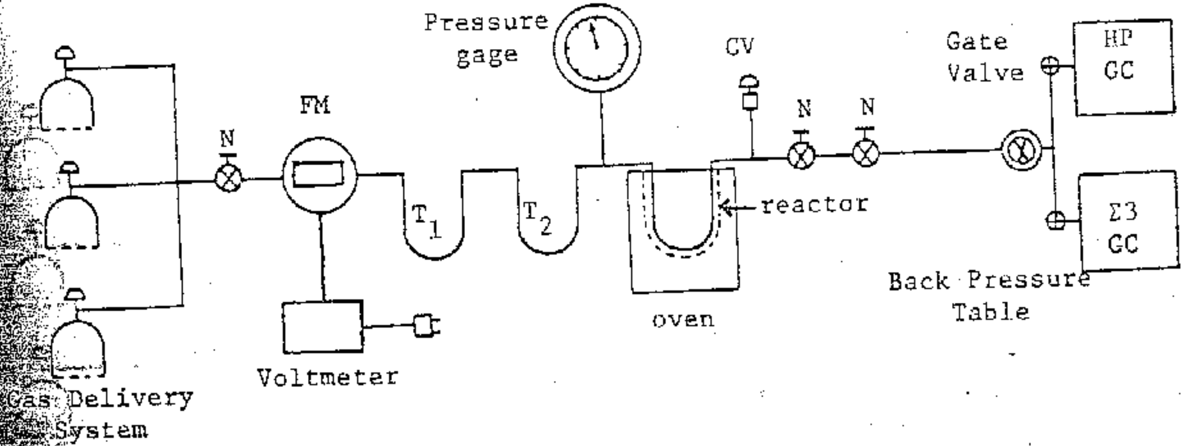

Figure 3.3.1 Reactor Scheme used for kinetic experiments at pressures greater than 1 atm.

N - Micrometering

FM - Mass Flow Meter

T_1 - Cold Trap

T_2 - Oxygen Trap

CV - Check Valve

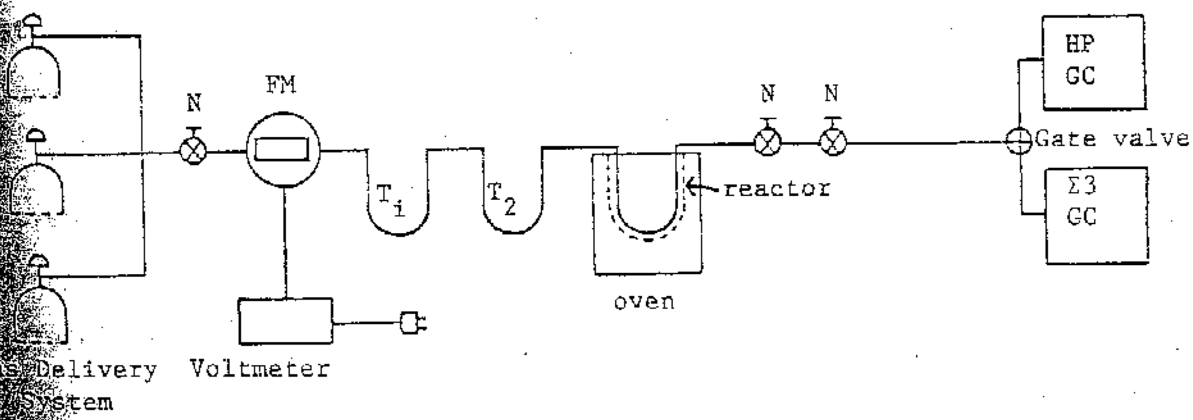

Figure 3.3.2 Reactor scheme used for kinetic experiments at 1 atm. pressure.

N - Micrometering valve
FM - Mass flow meter
T_1 - Cold Trap
T_2 - Oxygen Trap
CV - Check Valve

kinetic results while using either a glass or a treated stainless steel reactor. The delivery pressure of the feed gas was generally set at 10 psig above the desired reactor pressure in order to insure high gas flow rates. The low pressure reactor had a single needle valve to control the feed flow rate upstream of the reactor. Needle valves in both the upstream and downstream side of the high pressure reactor were used to control flow while the bulk of the pressure drop was across the back pressure regulator (Tescom model #25T562). The pressure drop across the catalyst bed was tyipcally 5 psig and the pressure gauge was located upstream of the catalyst bed in order to minimize downstream dead volume.

Prior to passage over the catalyst the condensables in feed gas were removed by passage through a silica (<120 mesh) trap placed in a dry ice/acetone bath. A NaCl/ice-water bath was employed for experiments involving the 1-petene feed mixture. Oxygen was removed by a MnO_2/SiO_2 trap which was reduced prior to the experiment in flowing H_2. The trap reportedly removes oxygen to less than 1 ppb (77). All lines downstream of the reactor were heated in order to avoid condensation of reaction products. Occassionally dodecane was passed through the heated lines in a H_2 carrier to insure that no condensation of product gases occurred. Reactant flow rates were measured by a thermal mass flow meter (Brooks Instrument Division, Emerson Electric Co., Model 5310) and checked by a soap bubble flow meter at the exhaust side of the systems.

3.3.2. Feed Mixtures

The feed mixtures used in this study are given in Table 3.1. Mixtures 1 and 2 were provided by the Linde Division of Union Carbide, while 6 was from Matheson Gas Products. The remaining mixtures were