H, OH, C, M (enol) or H, H, C, M (carbidic)

4.5.3

The possibility of a common surface intermediate can also be responsible for the deviation in C_1 product yield with respect to SF kinetics since the sum of the termination rate constants k_1^0 and k_1^H need not be equal to the termination rate associated with the longer chain products. Additionally the secondary chain initiation by methanol can be responsible for non SF behavior.

4.6 Transient Studies in the Product Distribution on Fully Carburized Iron Catalyst

4.6.1 Reaction or Conditions Necessary for Transient

One will recall that the extent of CO conversion is varied by changing the reactant mixture flow rate (Gas Hourly Space Velocity). The time needed to reach a steady state product distribution on a fully carburized catalyst is found to depend upon the magnitude of the change in the flow rate (GHSV). Normally the change in the GHSV would be done in small increments in order to obtain a steady state in a reasonable amount of time (typically two hours). This behavior is observed at all conditions employed in this study however, the effect is considerably more pronounced at higher pressures with the 1/1 CO/H_2 feed. Before presenting some typical results a brief descripton of the experimental procedure used in performing the transient studies is given.

The catalyst is carburized at 250°C and allowed to reach steady state at a relatively low CO conversion (<2%). Multiple G.C. injections

are taken in time increments typically between twenty-five to fifty minutes at a constant GHSV in order to ensure a steady state product distribution is attained. Once steady state is achieved the GHSV is then reduced by at least one order of magnitude. The product gas at these new conditions is then analyzed in time intervals ranging from twenty to sixty minutes during the course of an experiment. If a particular experiment is conducted long enough to reach steady state at the reduced gas hourly space velocity, the flow rate is then increased to the original GHSV intitially employed for the transient experiment. Activity and selectivity studies at this GHSV are again conducted to ensure that no deactivation occurred during the course of an experiment. In all experiments where this sequence was performed the final activity and selectivity matched that obtained initially.

4.6.2 Transient Studies Using the 1/1 CO/H_2 Feed

Typical product yields obtained during the transient period are presented in Figures 4.6.1 through 4.6.3. This transient response corresponds to a change in CO conversion (GHSV) from an initial value of .2% (2250hr^{-1}) to 2% (178 hr^{-1}) with a total pressure of 7.8 atmospheres with the 1/1 CO/H_2 Feed. Figures 4.6.1 and 4.6.2 show the transient behavior of the methane and olefin yields. The change in flow rate occurs at zero time.

The methane, ethylene, and propylene yields attain their new steady state values within fourty five minutes while the 1-butene yield reaches approximately 80% of its steady state value within this time span (Figure 4.6.1). Similar behavior is observed for the corresponding paraffin yields. The higher molecular weight olefin yields respond to the change in GHSV more slowly (Figure 4.6.2). For example, after two hours at the
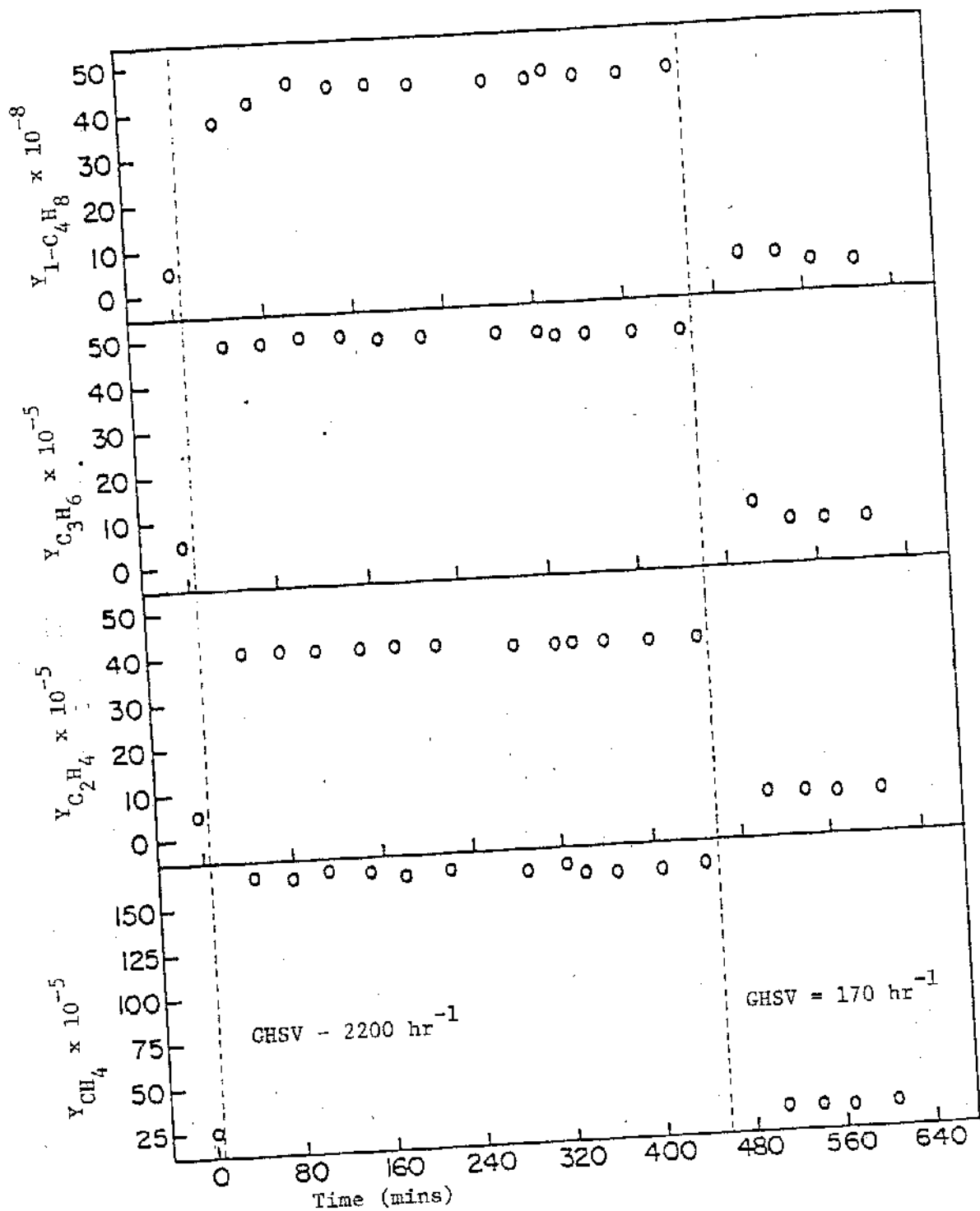
Figure 4.6.1 Methane, ethylene, propylene and 1-butene product yields as a function of time during transient experiment for the Fe catalyst at 7.8 atmospheres and 250°C using the 1/1 CO/H_2 feed. At zero time the GHSV chaged from 2200 hr^{-1} to 170 hr^{-1}.
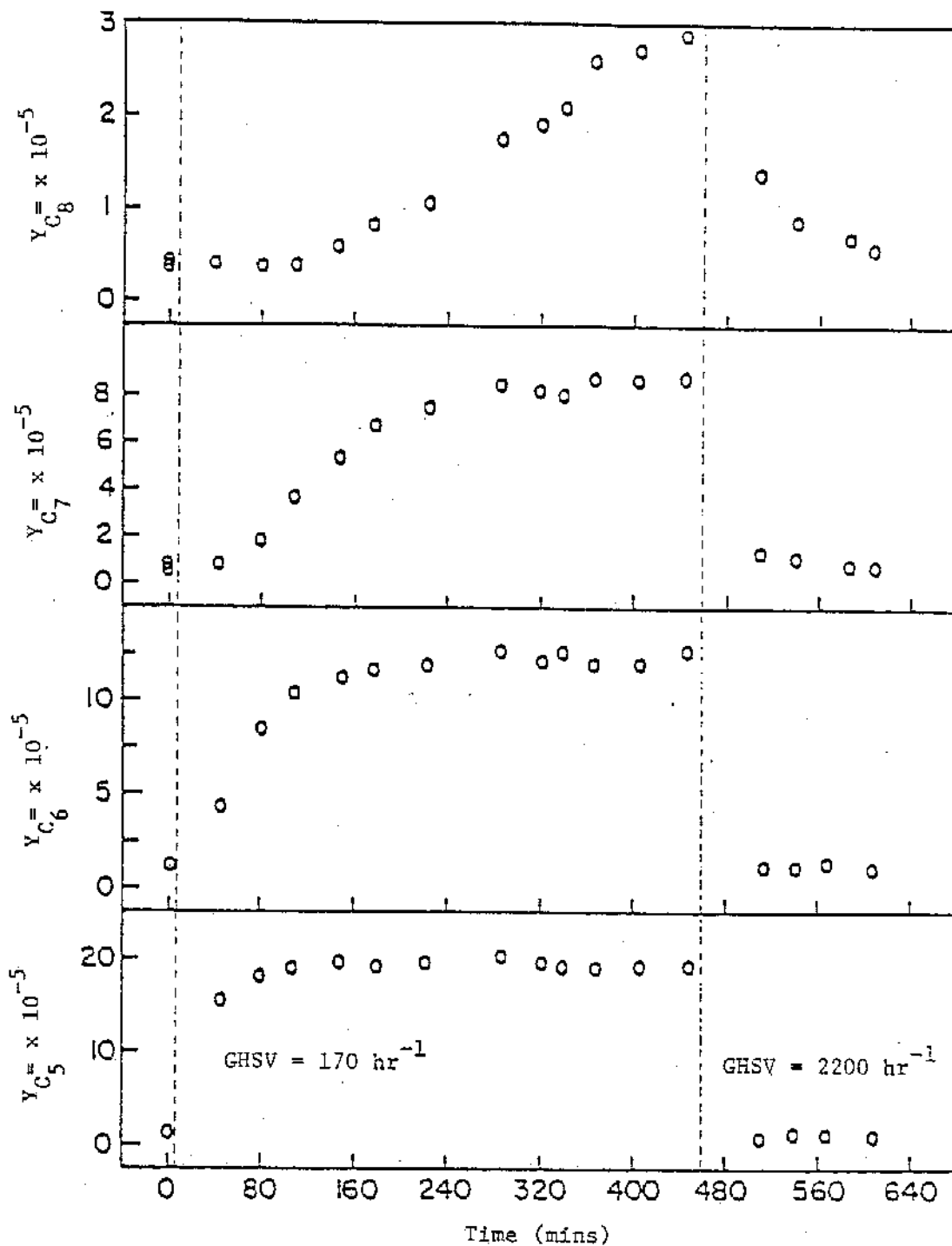
Figure 4.6.2 α olefin yields (Yi) for the C_5 through C_8 products as a function of time during transient experiment for the Fe catalyst at 7.8 atmospheres and 250°C using the 1/1 CO/H2 feed. At time zero the GHSV changed from 2200 hr^{-1} to 170 hr^{-1}.

low GHSV the 1-heptene yield is at approximately 50% of its steady state value and there is no observable change in the 1-octene yield.

The increase in olefin product yields occurs sequentially with increasing carbon chain length. Similar behavior is observed with the high molecular weight paraffins as shown in Figure 4.6.3. It is interesting to note that there is a small time lag between the increase in a given olefin yield compared to the corresponding paraffin yield. For example after eighty minutes the 1-heptene yield increases to 23% of its steady state value while there is no corresponding increase in the n-heptane yield. Both kinetic and physical adsorption effects are discussed in the next section in an attempt to explain the observed transient behavior.

4.6.3 Possible Explanation for Observed Transient Behavior

4.6.3.1 Adsorption by the Silica Support

Adsorbed FT hydrocarbon products on the support surface have been detected (31,42) through the use of IR spectroscopy. This physical adsorption may be responsible for the observed transient behavior. For the relatively non-polar hydrocarbon products, the total adsorption capacity of the support will increase with higher molecular weight compounds. If one assumes that all the intrinsic hydrocarbon product yields respond instantly to the change in flow rate due to reaction kinetics one can expect the sequential increase in observable yields with longer carbon chain length if physical adsorption on the silica surface is occurring.

The reaction products can be broken into two groups. The first being the hydrocarbon products while the second group includes the polar compounds of methanol and water. During the course of an experiment the catalyst is initially exposed to high GHSV where the relative molar
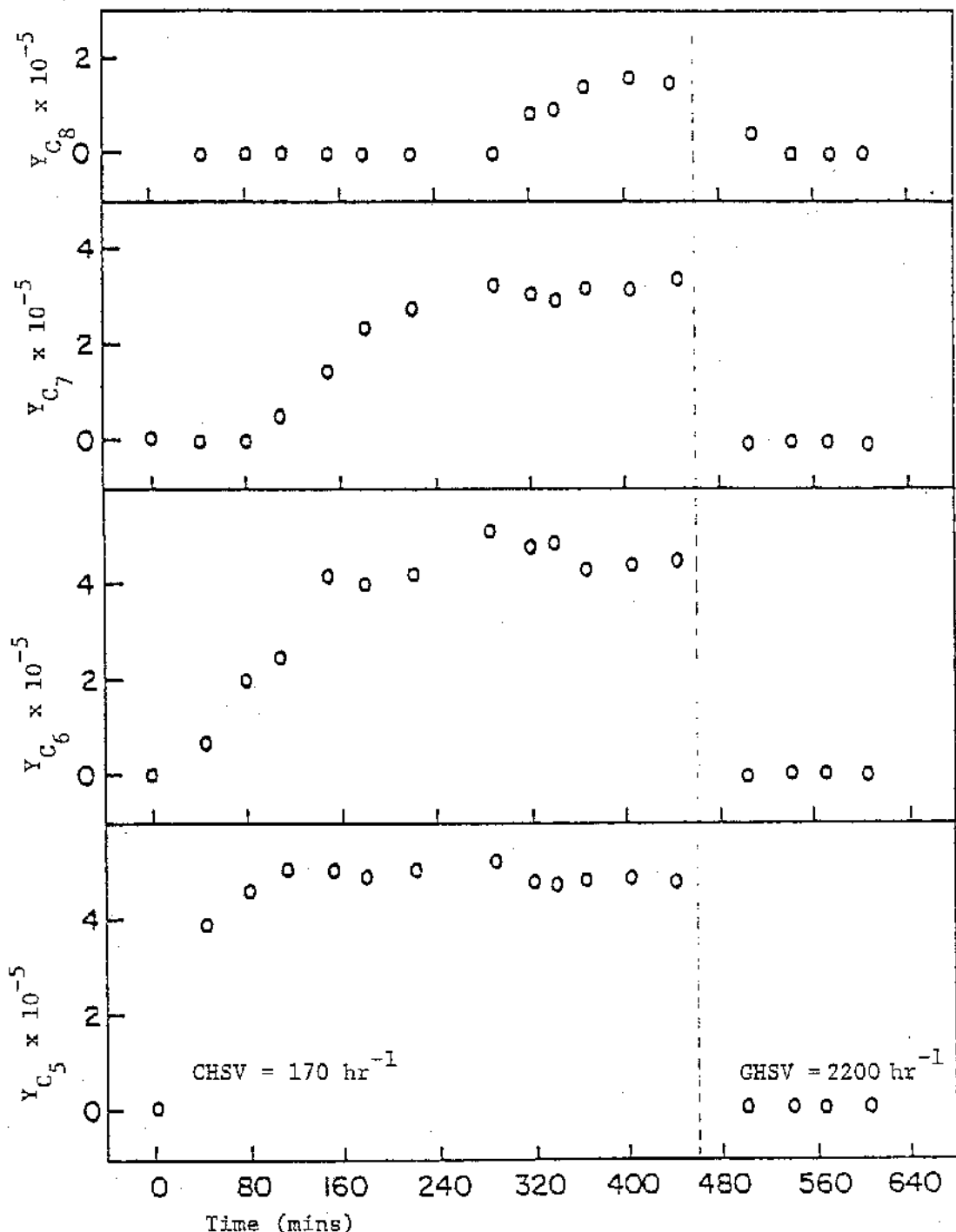
Figure 4.6.3 Paraffin Yields (Y_i) for C_5 through C_8 as a function of time during transient experiment for the Fe catalyst at 7.8 atmopsheres and 250°C using 1/1 CO/H_2 feed. At zero time the GHSV changed from 2200 hr^{-1} to 170 hr^{-1}.

amounts of water and methanol exceed those of the high molecular weight hydrocarbon products (Section 4.4.2). Consequently during the interval of time in which the catalyst is carburizing and reaching the initial steady state the silica surface is predominantly exposed to water and methanol. Since these two products are capable of hydrogen bonding and the silica surface is very polar in nature due to the presence of surface hydroxyl groups it is reasonable to assume that a certain fraction of the support is covered with methanol and water.

Based on the strong affinity between the polar products and the support surface one would expect the methanol yield to exhibit a similar transient response to that of the $C_{n \geq 5}$ hydrocarbon products if physical absorption is indeed responsible for the observed behavior. However, as shown in Figure 4.6.4, at both 7.8 and 14 atmospheres, the methanol yield reaches its steady state value within 45 minutes, much faster than that observed for the high molecular weight hydrocarbons. It appears that the surface is saturated with respect to methanol adsorption with a relatively short time scale. Any hydrocarbon adsorption would have to occur on at least a partial methanol/water overlayer on the silica surface since it highly unlikely that relatively non-polar hydrocarbons would displace polar species (CH_3OH and H_2O) adsorbed on a polar surface.

Based on surface area calculations, at 2% CO conversions it would take approximately two hours to saturate the silica surface with a monolayer of adsorbed methanol and water (Appendix IV). Since the transient product yields do not collectively show significant changes after this time period one can assume that physical adsorption may not be responsible forthe transient response of the methanol or hydrocarbon products.
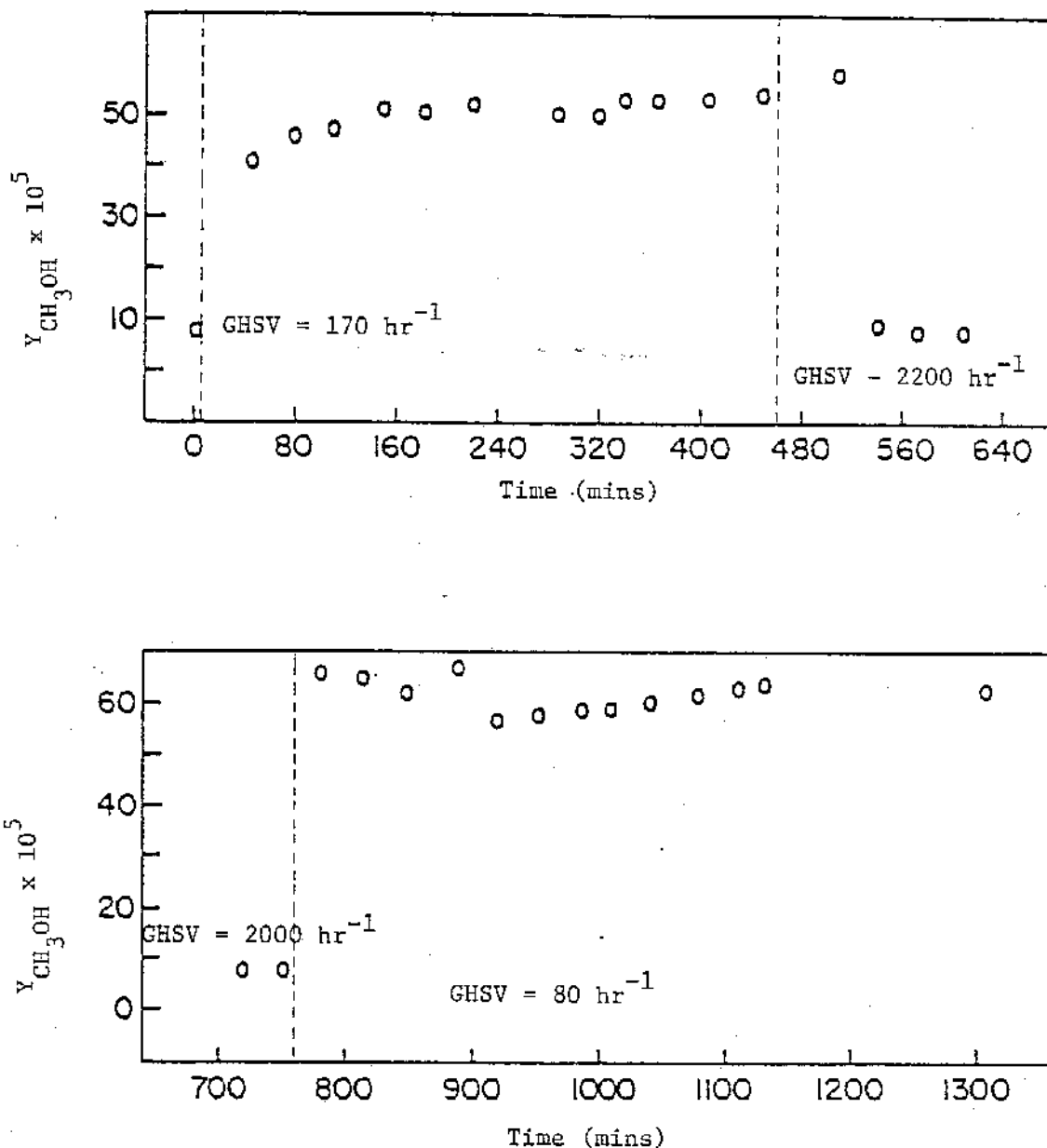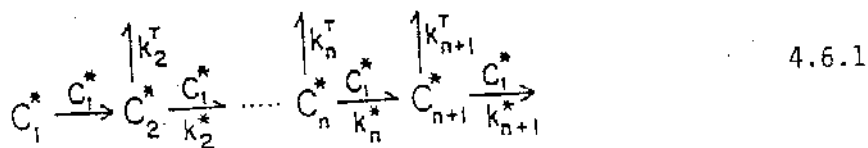
Figure 4.6.4 Methanol yield as a function of time during transient experiment for the Fe catalyst at 7.8 atmospheres (top) and 14 atmospheres (bottom). At time zero GHSV = 2200 hr^{-1}. 1/1 CO/H2 feed T = 250°C.

4.6.3.2 Hydrocarbon Chain Growth Mechanism

The transient response of the olefin product yields can be due to the intrinsic kinetics of hydrocarbon chain growth. A proposed reaction scheme presented is based on the work of Dautzenberg et al. (33).

$$C_1^* \xrightarrow{C_1^*} C_2^* \xrightarrow[k_2^*]{C_1^*} \cdots\cdots C_n^* \xrightarrow[k_n^*]{C_1^*} C_{n+1}^* \xrightarrow[k_{n+1}^*]{C_1^*} \qquad \uparrow k_2^T \quad \uparrow k_n^T \quad \uparrow k_{n+1}^T \tag{4.6.1}$$

where C_i^* surface intermediate for the formation of a C_i hydrocarbon product

k_i^* rate constant for addition of carbon unit to C_{i-1}^* intermediate

k_i^T rate constant for production of C_i hydrocarbon product (SF termination rate constant)

In terms of the Schulz Flory polymerization model, the rate constant for propagation is k_i while the rate contant for termination is k_i^*. The growth probability α is then defined as

$$\alpha = \frac{k_i c_i^*}{k_i^* c_i^* + k_i c_i^*} \tag{4.6.2}$$

Under steady state conditions α is found to be relatively constant throughout the C_4 to C_8 hydrocarbon products. Since the $\ln(Y_i)$ values of these products fall along the same straight line (section 4.5) the values of the propagation and termination rates for these compounds must be equal

$$k_4^* C_4^* = k_5^* C_5^* = \cdots = k_n^* C_n^* \tag{4.6.3}$$

$$k_4 C_4^* = k_5 C_5^* = \cdots = k_n C_n^* \tag{4.6.4}$$

Figure 4.6.5 presents a series of SF plots of the hydrocarbon product distribution obtained at steady state and under transient

conditions, for the Fe catalyst at 7.8 atmospheres with the 1/1 feed. Curve A corresponds to the initial steady state obtained at .2% CO conversion. The value of α obtained at these conditions is 0.54, comparable to the values obtained at higher conversions (Table 4.5.1). Curves B, C and D are SF distribution plots obtained under transient conditions. The α value obtained at forty five minutes after the flow rate (curve B) is 0.28. (Note that α is determined only through the most apparent linear portion of the plot). This value is much lower than that obtained at steady state conditions.

The value of α increases to its maximum steady state value as the hydrocarbon yields approach their steady state values. As discussed in Section 4.6.1 steady state product yields are first reached for C_1 through C_4, then C_1 through C_5 and so on. This is observed by comparing curves D and E in figure 4.6.5. After 222 minutes the constant α value of 0.56 through the C_4 to C_7 products is obtained. A complete steady state product distribution (C_4 throuch C_8) is reached after 451 minutes (Curve E) with an α value of 0.53.

The sequential attainment of steady state product yields with increasing carbon chain length is expected if one assumes a series reaction sequence as depicted in equation 4.6.1. During the transient period one would expect a build up of surface intermediates, C_n^*, to occur sequentially with increasing chainlength n. Dautzenberg et al. (T8) used transient reaction conditions to measure the propagation rates, k_i^*. By varying the pulse duration of a CO/H_2 mixture (typically 4 to 12 minutes) they were able to modify the transient product distribution of A Ru/Al_2O_3 catalyst operating at 10 atmospheres. The SF plots of this work (33) are shown in Figure 4.6.6.
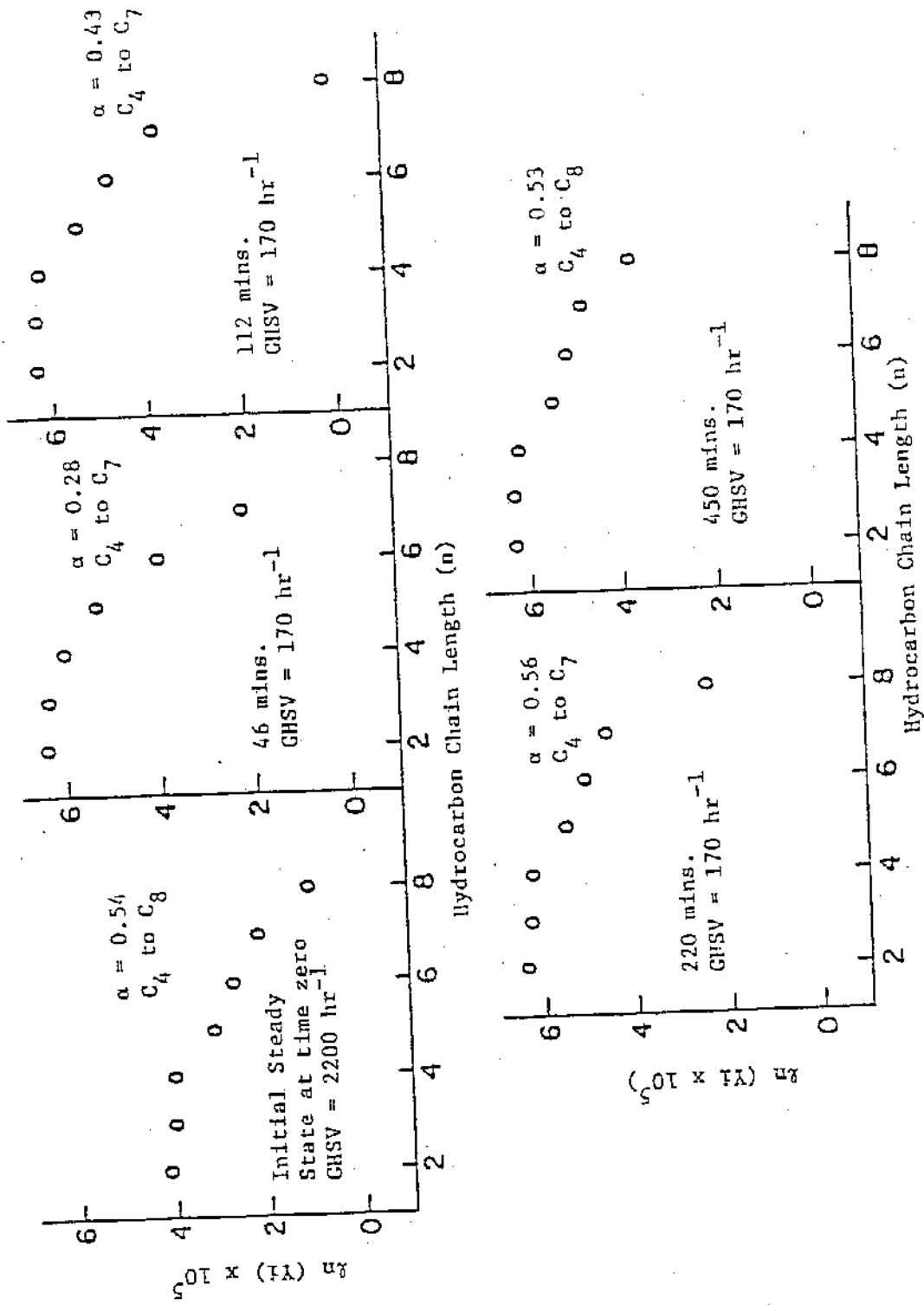
Figure 4.6.5 Transient response of $C_{n>2}$ hydrocarbon products using SF parameterization for Leh Fe catalyst at 7.8 atmospheres and 250°C using the 1/1 CO/H_2 feed.
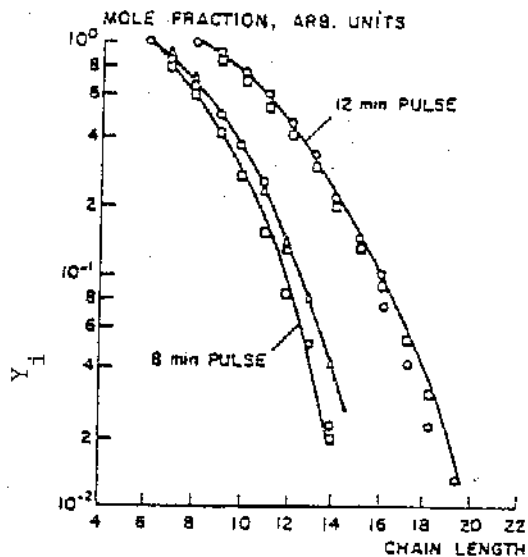
Figure 4.6.6 Transient response in the hydrocarbon product distribution for a Ru/Al_2O_3 catalyst. From reference (3,4).

The transient behavior of the product distribution produced by varying feed gas pulses is similar to that observed in the case of a step change in the gas hourly space velocity (GHSV). Both experimental procedures can create surface concentrations of reaction intermediates which are not at steady state values. The trend towards higher α values with increasing CO/H_2 pulse duration is consistent with the longer times required to build up multicarbon surface intermediates.

Dautzenberg et al. (33) assume that all the propagation rate constants (k_i for $i = 6$ to 18) are constant and time independent. They further assume that the reaction intermediate P^*, formed by the adsorbed reactants exist at a steady state concentration throughout the transient period. Such assumptions are required for the quantitative calculations of the various rate constants (33) but are not necessary for the compatability of the observed transients with the proposed reaction scheme of equation 4.6.1. Dautzenberg et al. (33) found that the overall reaction rate is comparable to the propagation rate k^*_i ($i = 6$ to 18) which is the limiting step in the production of hydrocarbon chains. A summary discussion on the various reaction rates involved in the overall synthesis is given in section 6.3.

4.6.4 Transient Studies Using the 1/3 CO/H_2 Feed

Figure 4.6.7 presents the product yields of methane and the low molecular weight olefins as a function of time for a transient experiment conducted at 14 atmospheres using the 1/3 CO/H_2 feed. The catalyst carburized and allowed to reach steady state at a GHSV of $850hr^{-1}$ corresponding to a CO conversion of approximately 1.8%. After 145
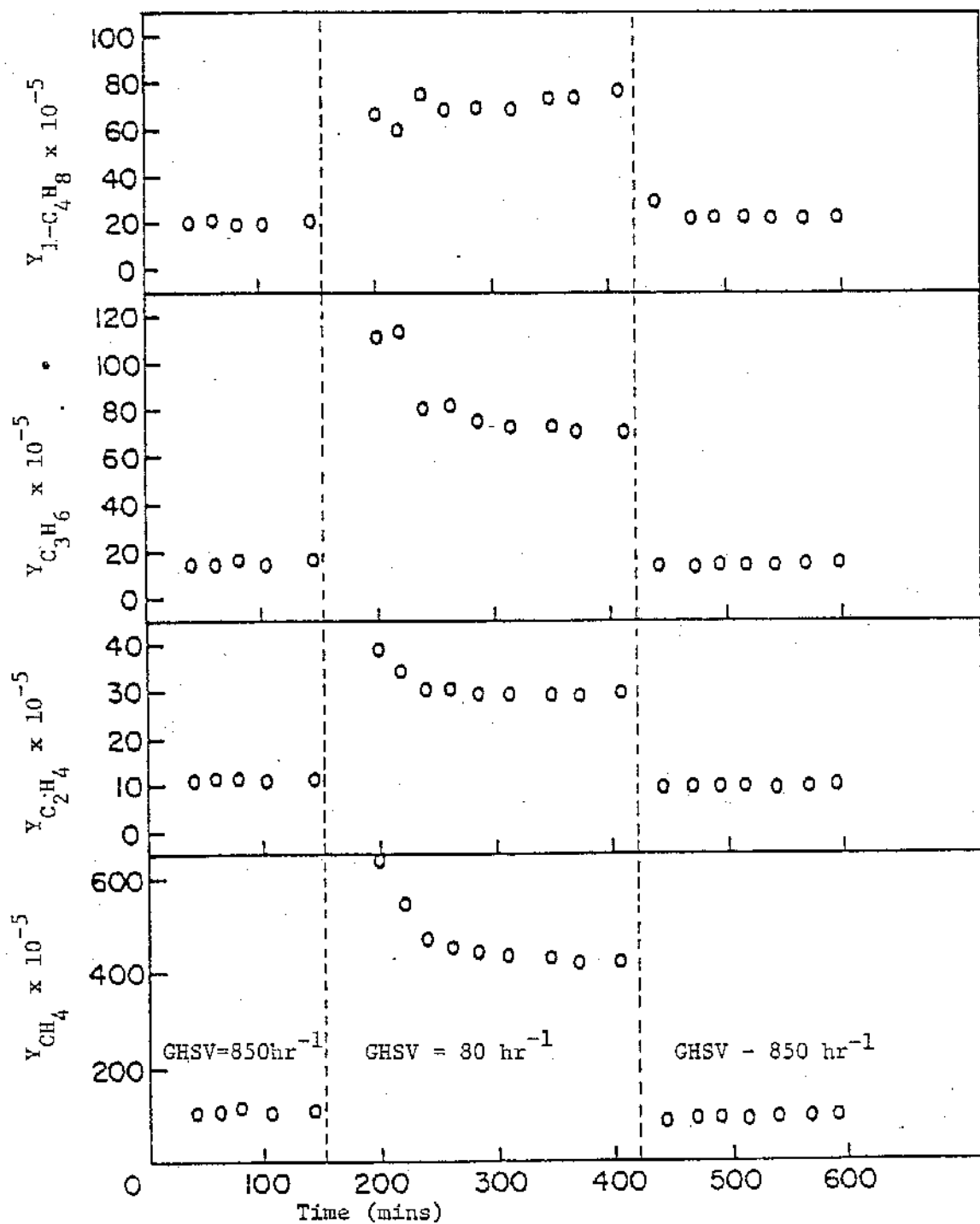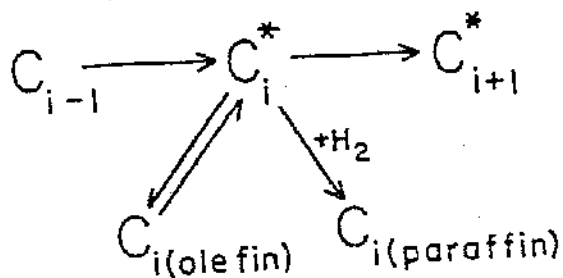
Figure 4.6.7 Products Yields (Yi) for CH_4, C_2H_4, C_3H_6 and $1-C_4H_8$ as a function of time during transient experiment for the Fe catalyst at 14 atmospheres and 250°C. Feed mixture is $1/3$ CO/H_2.

minutes the feed flow rate was decreased to a value corresponding to 8% conversion (GHSV = 60). In this case the transient responses of the low molecular weight product yields are significantly different than those obtained with the 1/1 feed (Compare Figures 4.6.7 with 6.4.1). With the 1/3 feed, the methane, ethylene, and propylene product yields undergo an initial increase when the GHSV is decreased, followed by a decrease in the yields as the product distribution approaches the new steady state. Similar behavior is observed for ethane and propane at these conditions.

The product yields of the high molecular weight olefins are presented as a function of time in Figure 4.6.8. The sequential increase in product yield with increasing carbon chain length is again observed. However under these conditions it appears that the C_5 and C_6 α-olefin yields go through a maximum during the transient period similar to that observed for the low molecular weight products. Similar behavior is observed for the corresponding paraffin yields.

A maximum in the olefin yield transient response can be expected if there is a significant amount of hydrogenation of the absorbed intermediate. One can envision a reaction sequence containing the reaction scheme depicted in equation 4.6.1 and a reaction path involving the hydrogenation of the intermediate involved with chain growth, C_i^*. This mechanism is shown below
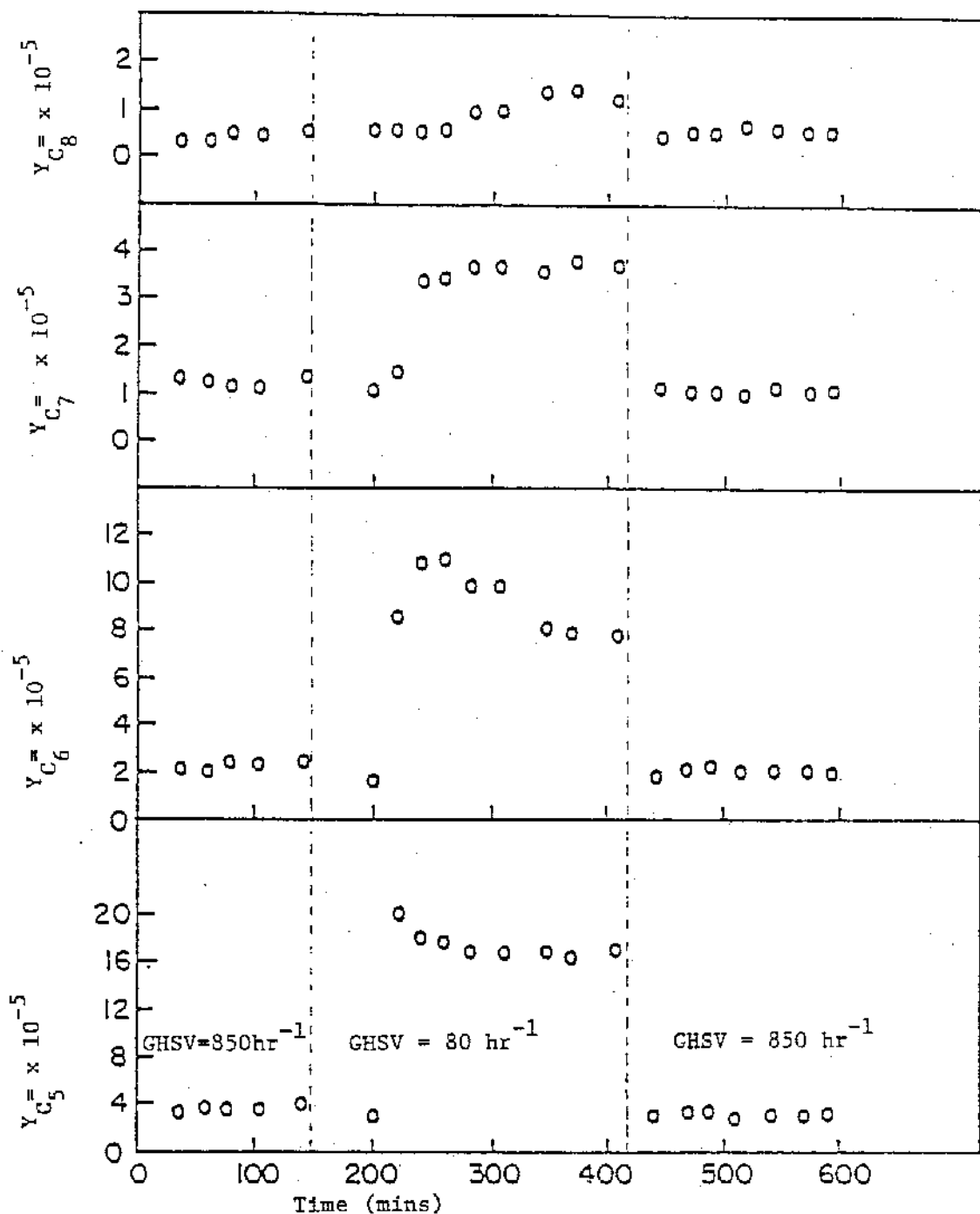
$$C_{i-1} \longrightarrow C_i^* \longrightarrow C_{i+1}^*$$

4.6.5

$$C_{i(olefin)} \qquad \overset{+H_2}{\longrightarrow} C_{i(paraffin)}$$

Figure 4.68 α olefin yields (Yi) for C_5 through C_8 as a function of time during transient experiment for the Fe catalyst at 14 atmospheres and 250°C using 1/3 CO/H_2 feed.