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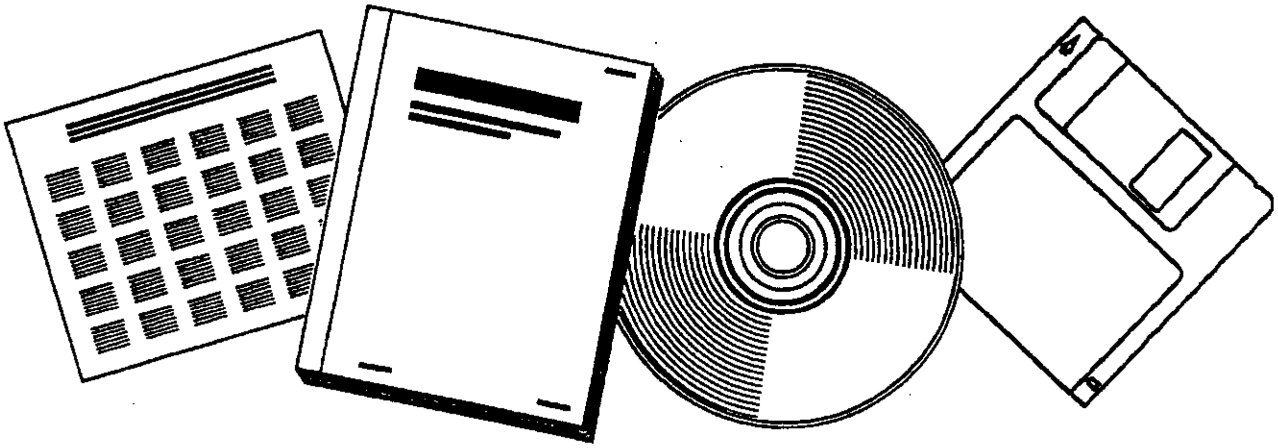
FISCHER-TROPSCH SLURRY PHASE PROCESS VARIATIONS. QUARTERLY REPORT, JANUARY 1, 1986-MARCH 31, 1986

MASSACHUSETTS INST. OF TECH., CAMBRIDGE

1986



DOE/PC/80015--2

DE86 009567

Fischer-Tropsch Slurry Phase Process Variations

Quarterly Report for Period
January 1, 1986 to March 31, 1986

Report No.: DOE/PC80015-2
Contract No.: DE-AC22-85PC80015

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Received by OSTI
APR 25 1986

Studies on activation of a reduced fused magnetite are summarized here:

Experimental

Catalyst composition, sampling procedures and details of the Mössbauer spectroscopy measurements are given in the October-December 1985 Quarterly Report. Two principal experiments were conducted, in which synthesis activity, selectivity, and the bulk catalyst composition were monitored for approximately the initial 200 hours on stream. One was performed at 248°C (run Fe22) and one at 232°C (run Fe27), with an intermediate period at 263°C. A third experiment (run Fe24) was conducted at 248°C for 22 hours to verify the reproducibility of the initial activity and selectivity results of run Fe22, but no catalyst samples were taken.

All studies were at 0.92 MPa, and a H_2/CO feed ratio of 0.93. The rate and selectivity data reported herein were obtained at a space velocity of 1500-1600 hr^{-1} (vol. dry synthesis gas at STP/ vol. catalyst/hr) for runs Fe22 and Fe24 and 1340 hr^{-1} for run Fe27. (Catalyst volume is that for a packed bed of catalyst before reduction.) The corresponding conversions are given in Table I.

Each experiment was conducted by first slurrying about 76-79 grams (unreduced basis) of freshly reduced catalyst of particle size of 170 to 270 mesh with about 420 grams of octacosane in the reactor. The reactor and contents were then brought to the desired temperature under nitrogen, before synthesis gas was introduced. Product gas samples and catalyst samples were initially taken about once every 45-60 minutes, which is the time required to run one gas sample on the GC. After the first 6-7 hours on stream the frequency of this product gas and catalyst sampling was decreased.

In run Fe22, these product gas and catalyst sampling procedures were conducted for the first 34 hours on stream. In addition, product liquid samples were also taken over three time periods, 0-7 hours on stream, 7-22 hours on stream, and 22-34 hours on stream. During the period from 34-200 hours, the space velocity was changed to cause the CO conversion to vary between 26% and 92%, for a series of studies irrelevant for present purposes. At 200 hours the original space velocity was restored and 18 hours later another product gas sample and another catalyst sample were taken.

In run Fe27, product gas and catalyst sampling procedures were conducted for the first 100 hours on stream. During the time period from 100-160 hours, the reactor temperature was increased to 263°C, after which reactor temperature was reset to 232°C, and after a 48-hour period, another product gas sample and another catalyst sample were taken.

Results

Phase Composition of Catalyst

Four phases of iron were identified in the catalyst, namely α-Fe, magnetite (Fe_3O_4), and two forms of iron carbide, χ-Fe_5C_2 (Hägg carbide) and ε'-$Fe_{2.2}C$. The Mössbauer parameters of these phases agree well with data in the literature, as shown in Table I of the Quarterly Report for October - December 1985.

Figures 1 and 2 show the Mössbauer spectra of the catalyst samples taken during runs Fe22 and Fe27, respectively. Figure 3 shows the corresponding phase compositions for both runs as a function of time. (Note the change in scale of the abscissa after 20 hours in this and subsequent figures.) Referring to the data in Figure 3 for run Fe22, it is seen that the initial catalyst sample was analyzed to be 100% α-Fe, indicating both complete reduction and good sampling technique. Within the first 34 hours on stream, 65% of the α-Fe had been converted to χ-Fe_5C_2; no magnetite was detected during this time period. The catalyst sample taken at 218 hours on stream showed an analysis of the bulk phase as 14% α-Fe, 77% χ-Fe_5C_2, and 7% Fe_3O_4. The magnetite was probably formed during some of the high conversion conditions that occurred between 34 and 200 hours, since at high conversions the gas composition is more oxidizing in character from the presence of CO_2 and H_2O.

The trend with time in the bulk phase composition of the catalyst for run Fe27 (T = 232°C) is shown in the lower portion of Figure 3. The first catalyst sample (t = 0 hours) was 83% α-Fe and 17% χ-Fe_5C_2. This was most likely due to the unintentional presence of synthesis gas in the reactor before start-up. After about 40 hours on stream, the bulk catalyst was 12% α-Fe, 71% χ-Fe_5C_2, and 16% $Fe_{2.2}C$. As with run Fe22 for about the same initial time period, no magnetite was present, but no $Fe_{2.2}C$ was detected in run Fe22. After 100 hours on stream, the temperature of the reactor was increased to 263°C for 60 hours. A slurry sample was taken at 160 hours but unfortunately it did not contain enough catalyst to be analyzed. The reactor temperature was then reset to 232°C and after a 40-hour period the catalyst contained 5% α-Fe, 75% χ-Fe_5C_2, and 20% $Fe_{2.2}C$, little changed from the composition at 100 hours.

Activity

Figure 4 displays the catalyst activity, defined as $-r_{H_2+CO}$ or $-r_{CO}$ as a function of time on stream for the three runs made. Run 24 was carried out for only 22 hours (November 1985 monthly report) but during this interval results are seen to be very similar to that of run Fe22, indicating that the catalyst sampling in run Fe22 did not disturb the system. The activity of the catalyst increased with time on stream for each run. In Table I are tabulated the initial and final CO and CO+H_2 conversions for the three runs.

Selectivity

The change in olefin/paraffin ratio with time for the C_2, C_3 and C_4 products is shown on Figure 5. In almost every case the olefin/paraffin ratio rose to a maximum, and then slowly decreased with time on stream. The C_2 olefin/paraffin ratio rose to a maximum of 3.1 at 232°C but never exceeded 1.0 at 240°C. This ratio is always unusually low for C_2 but notably here it was higher for C_3 than for C_4.

Methane selectivity is represented by the ratio of CH_4 to C_2+C_3 (Fig. 6). In all cases methane formation was favored on the freshly reduced catalyst. This selectivity decreased markedly during the first hour after which it reached a quasi steady-state. This was not significantly different between 232°C and 248°C.

α-Olefins are formed as primary products and isomerize to β-olefins by a secondary reaction. The change in the ratio of the C_4 β/α-olefins with time is shown on Figure 7. The ratio is much lower at 232°C than 248°C as is reasonable for a secondary reaction but activity for the isomerization reaction increases with time.

The ratio $r_{CO_2}/-r_{CO}$ shown on Fig. 8, compares the rate of the water gas shift to that of formation of organic products. At 248°C, the ratio rose to steady-state values after only 1 to 2 hours on stream. At 232°C, the ratio started low, rose through a maximum and then decreased to steady-state after about 15 hours.

The steady-state selectivities were not significantly different between 232°C and 248°C.

The change in the carbon number distribution (hydrocarbons plus oxygenates) with time on stream was studied for run Fe22 and is shown as a Flory plot on Fig. 9. Three material balances were performed, the first covered the initial 7 hours on stream, the second covered the next 15 hours on stream, and the third covered the next 12 hours on stream.

Some significant observations are as follows: First, as mentioned earlier, the methane selectivity was high for the earlier times on stream, (32 mole% methane) for 0-7 hours on stream as compared to 27 mole% for 7-22 and 22-34 hours on stream. Second, the C_2-C_7 product distributions were quite similar for the three time intervals. The value of α, as determined by the slope of the distribution of the C_3-C_7 products, increased only slightly over time, from a value of 0.62 from 0-7 hours to a value of 0.64 from 7-22 and 22-34 hours. Finally, the C_8-C_{14} fraction increased significantly with time, reflecting the effect of the accumulation and eventual saturation of heavier hydrocarbon products in the reactor.

In previous studies with this catalyst under these operating conditions in our apparatus the C_2 fraction isolated has usually corresponded to that predicted by the Flory distribution based on the C_3+ light products. The unusually low concentration here may well reflect incorporation of C_2 species into product by a secondary scavenging effect. This seems to occur on catalyst sites whose concentration decreases as the catalyst ages. We have observed secondary incorporation at higher pressures (e.g., 1.48 MPa) and it is accentuated at very high conversions where the depletion of CO, which is strongly adsorbed on the catalyst, allows increased opportunity for C_2 species to adsorb and react (Stenger and Satterfield, 1985). The scavenging effect causes a slight decrease in α and we note in Figure 7 that α increases slightly with time, the direction in which we would expect it to change if the scavenging effect were diminishing with time.

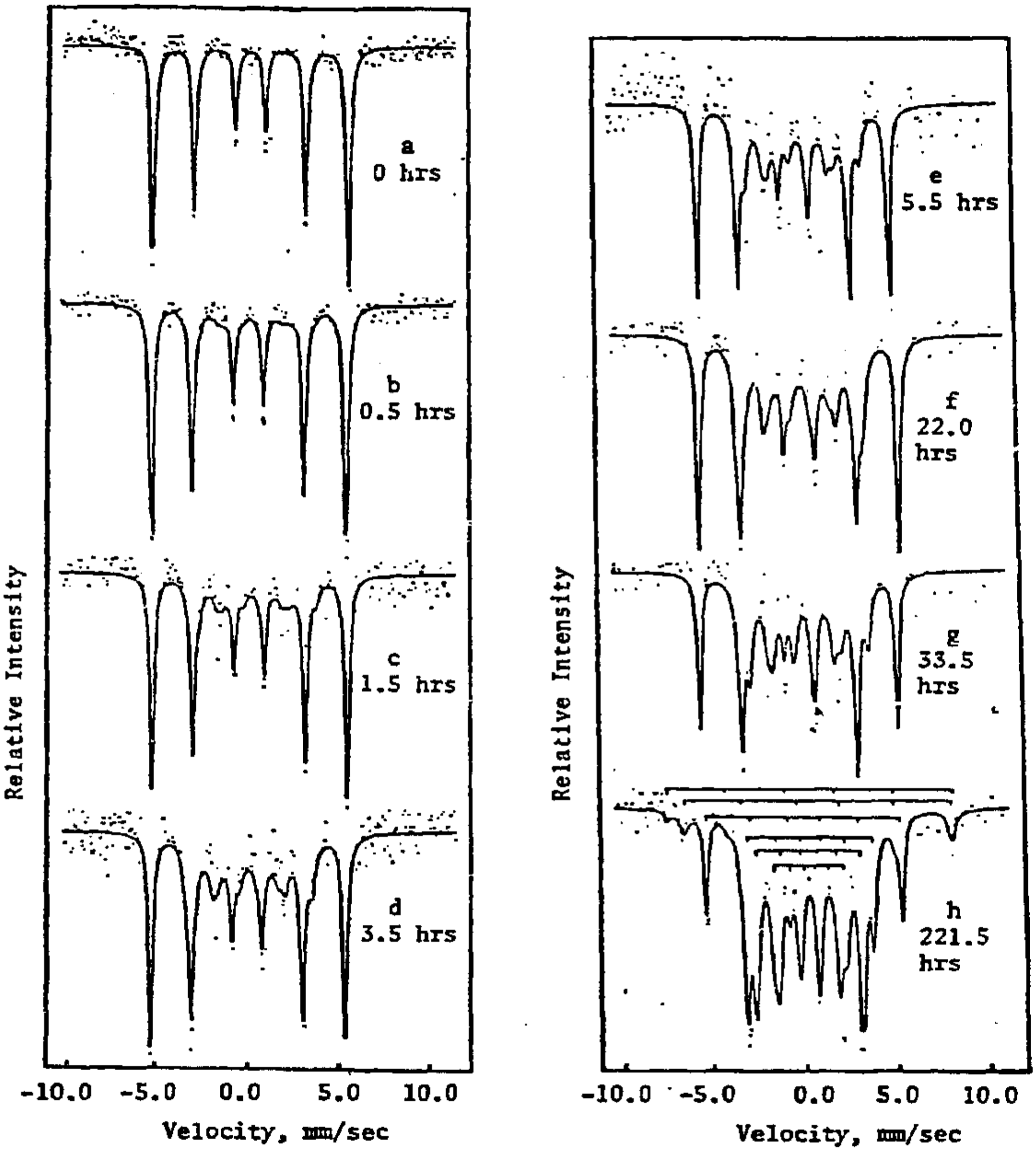

Figure 1 Mössbauer spectrum of run Fe22 (T = 248°C) catalyst samples after various periods of synthesis. The six identifications shown for the h spectrum represent, from top down, the Fe sites I and II in Fe_3O_4, α-Fe, and the Fe sites II, I and III in χ-Fe_5C_2.

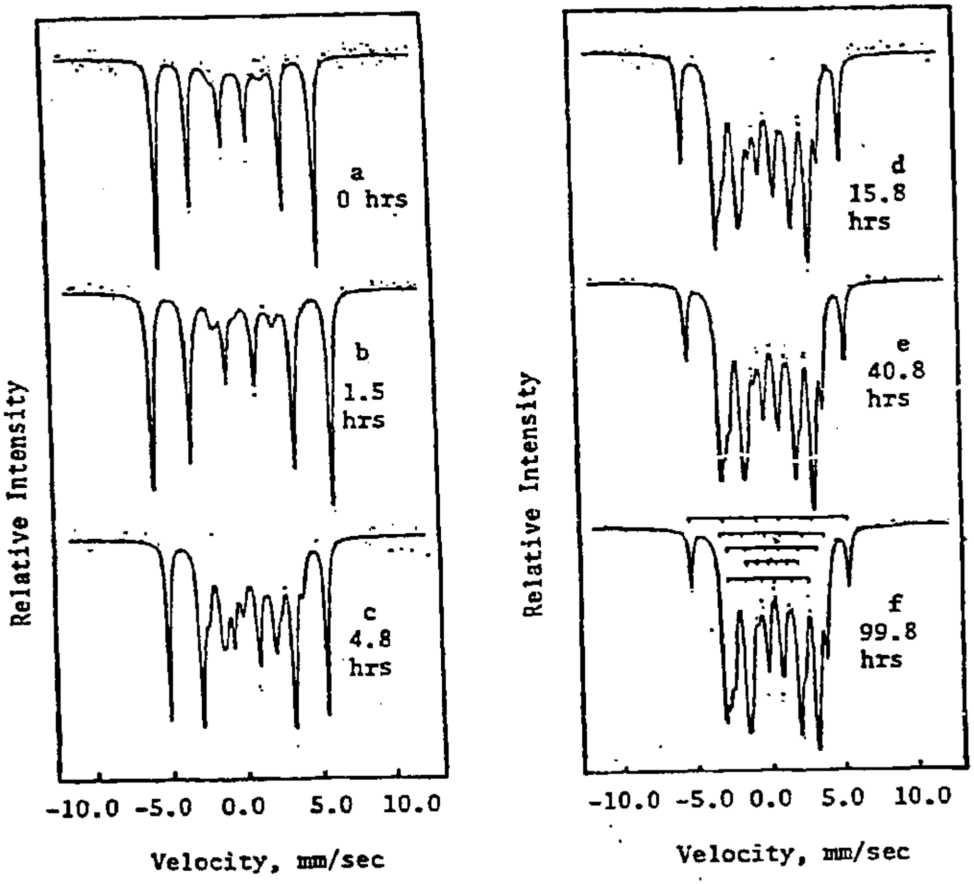

Figure 2 Mössbauer spectra of run Fe27 (T = 232°C) catalyst samples after various periods of synthesis. The five identifications shown for the f spectrum represent, from top down, α-Fe, the Fe sites II, I and III in χ-Fe_5C_2, and ε'-$Fe_{2.2}C$.

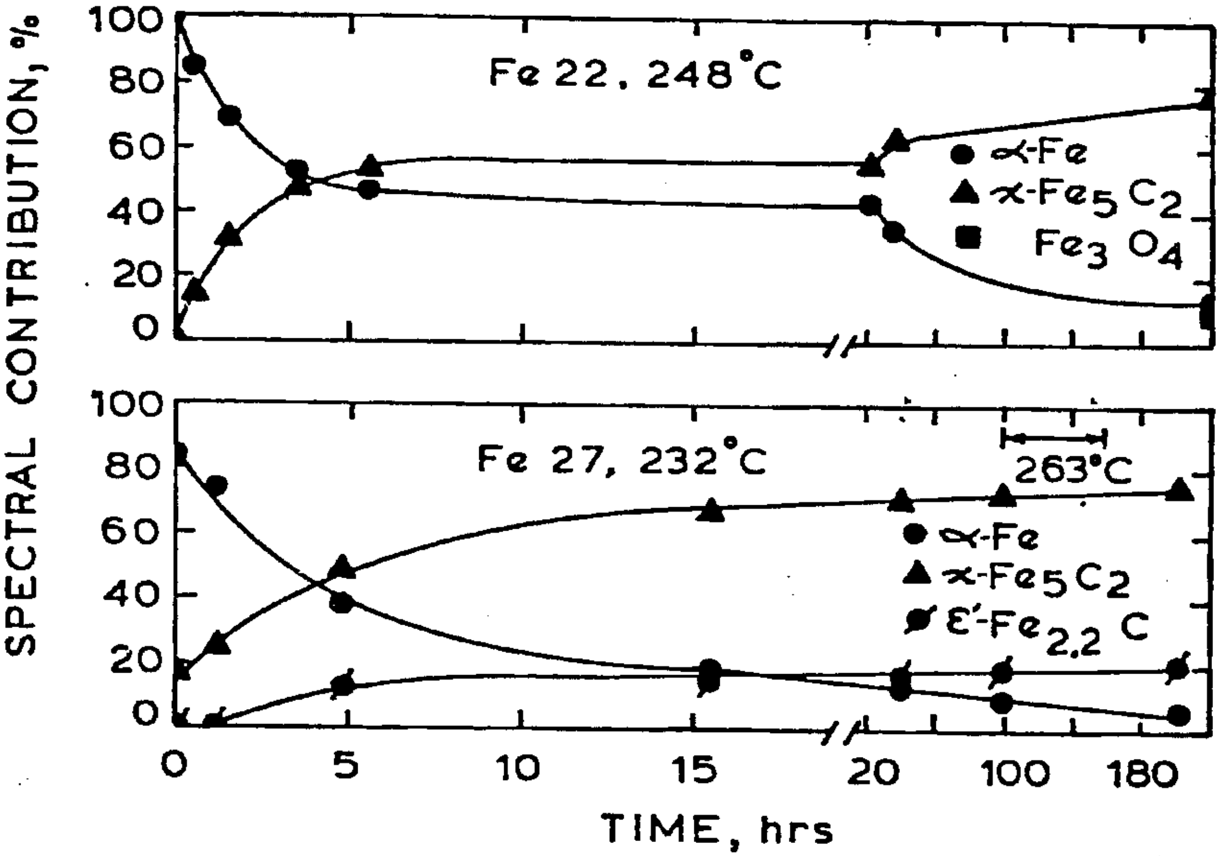

Figure 3 Iron carbide concentration in bulk catalyst increases at expense of metallic iron with time on stream.

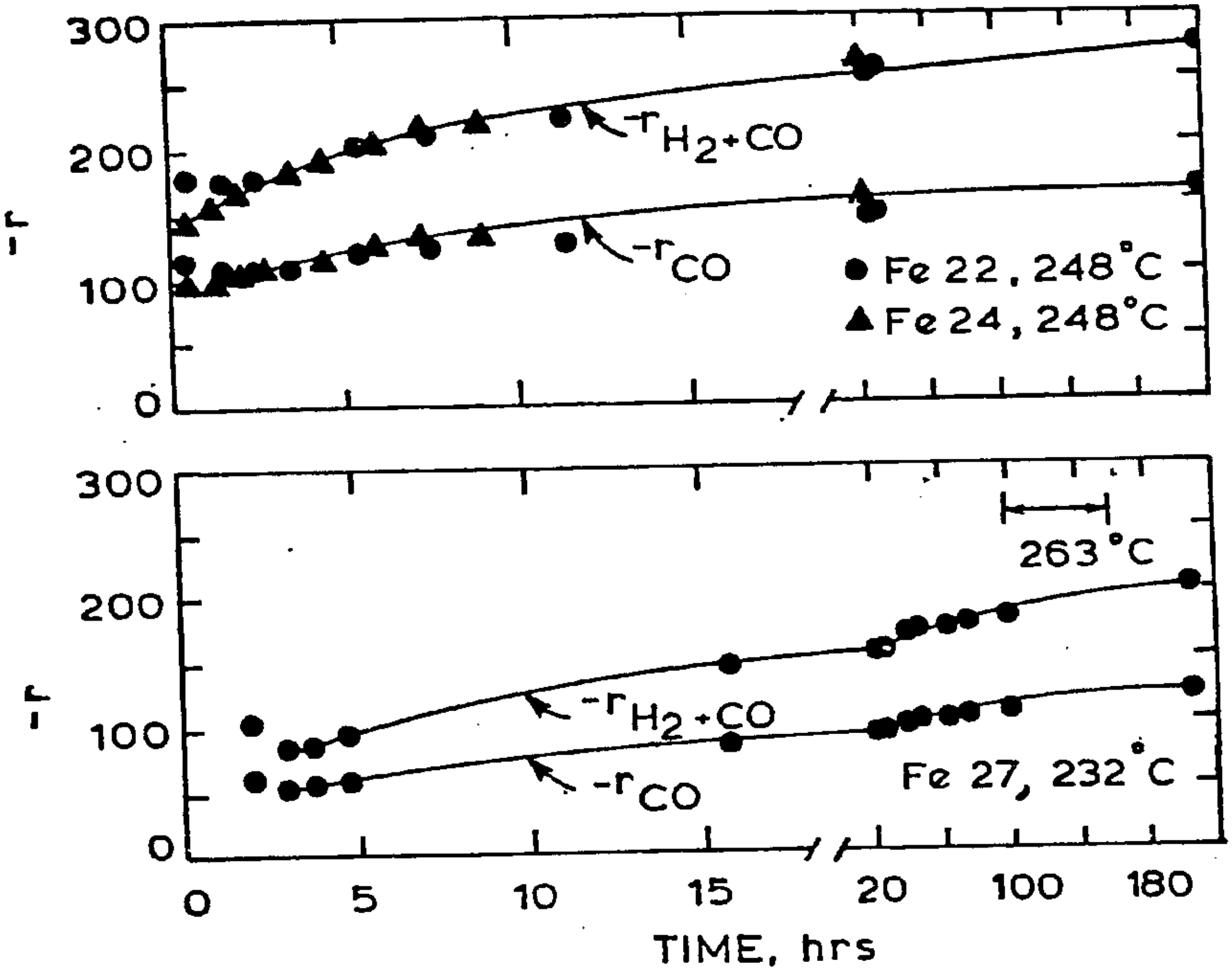

Figure 4 Catalyst activity increases with time on stream.

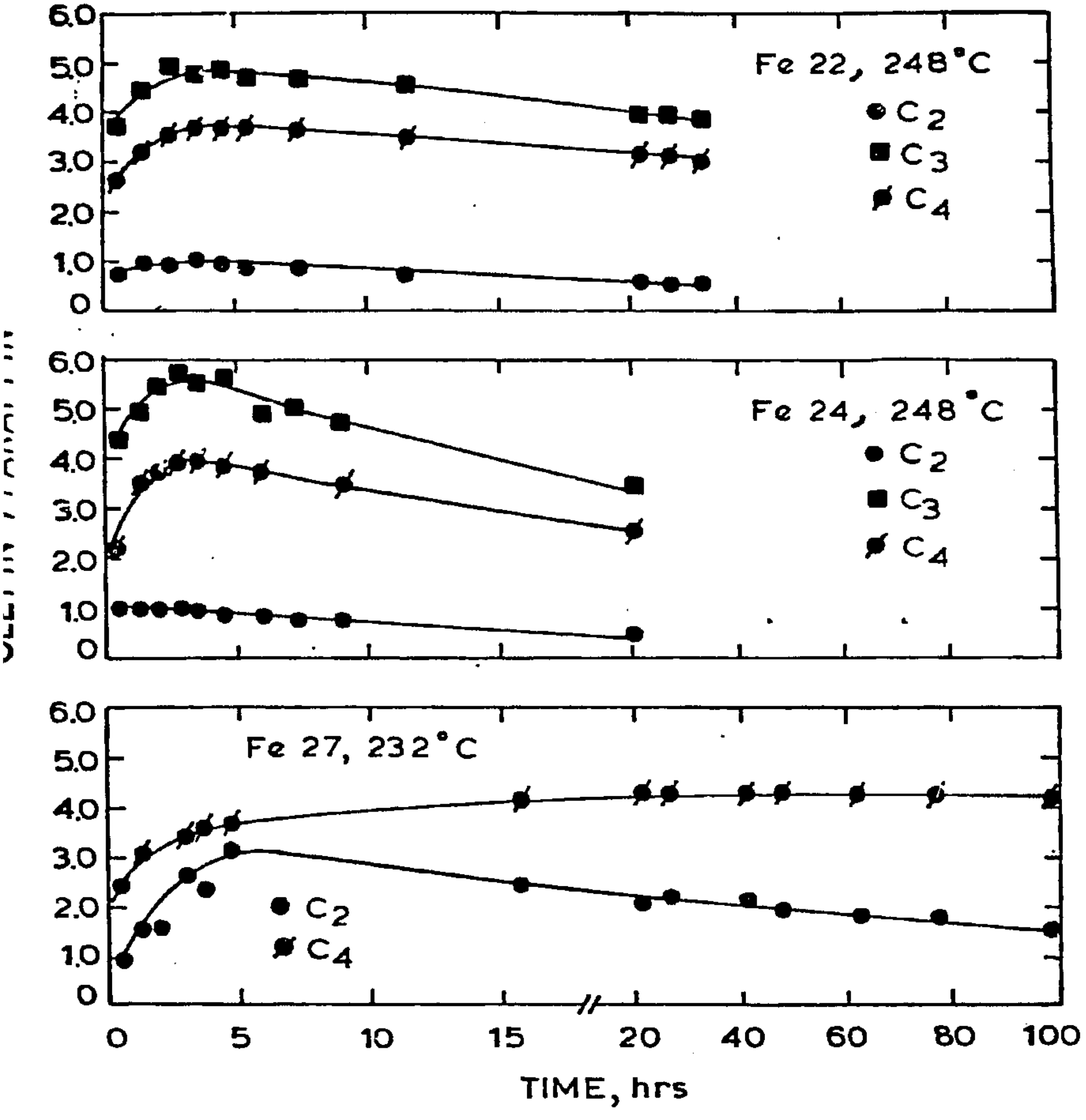

Figure 5 Olefin/paraffin ratio increases during first several hours of synthesis.

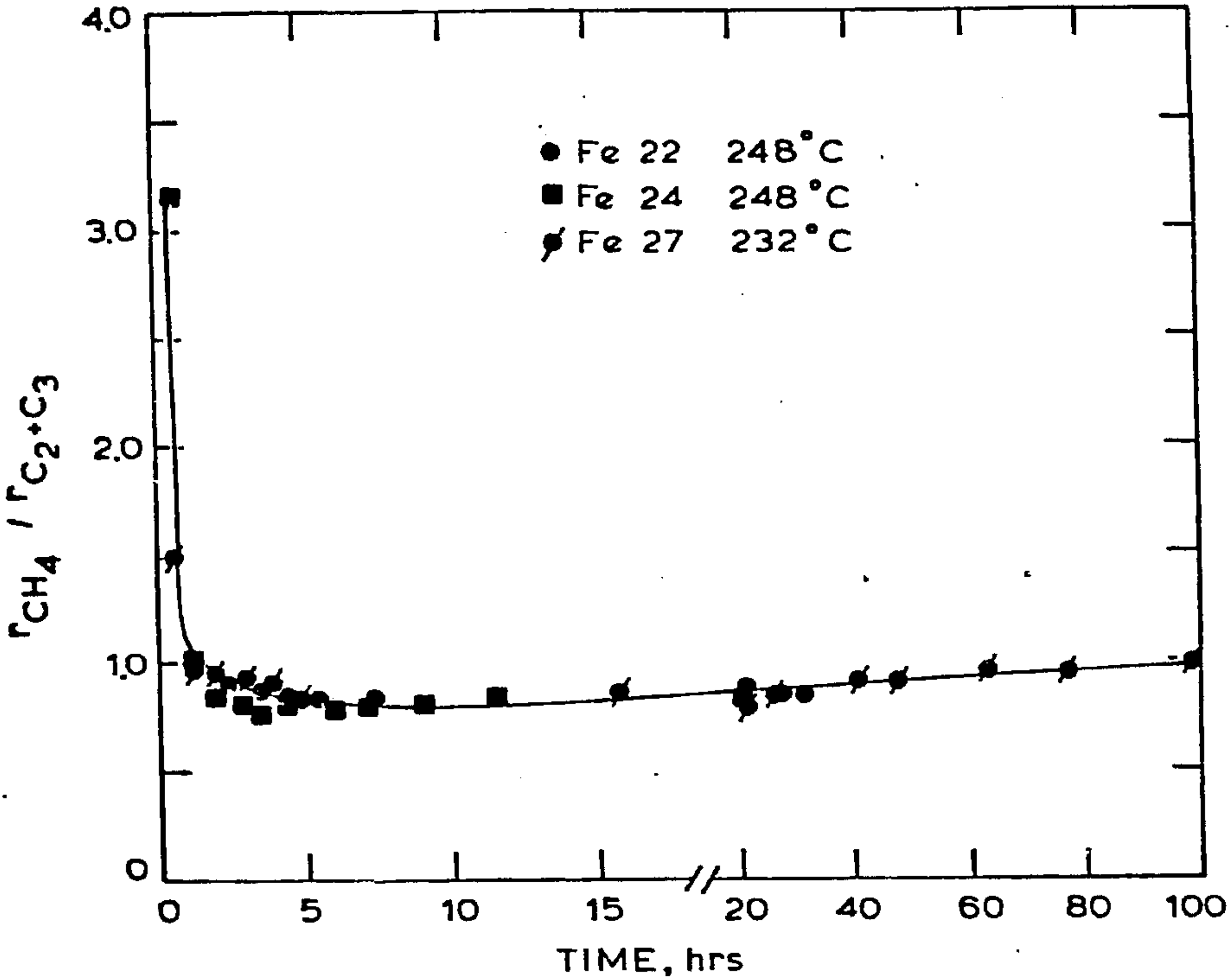

Figure 6 Methane selectivity decreases markedly during first hour of synthesis.

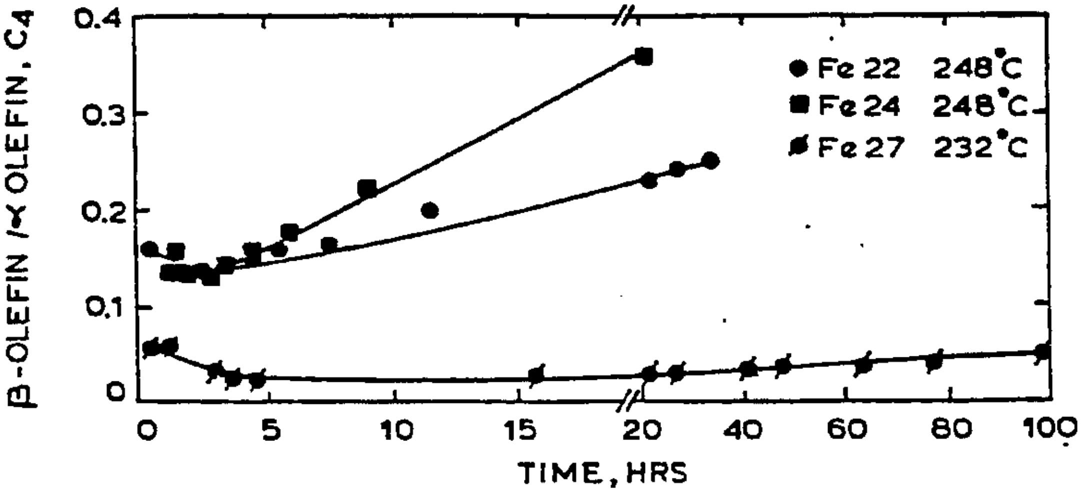

Figure 7 β-Olefin/α-olefin ratio slowly increases with time on stream.

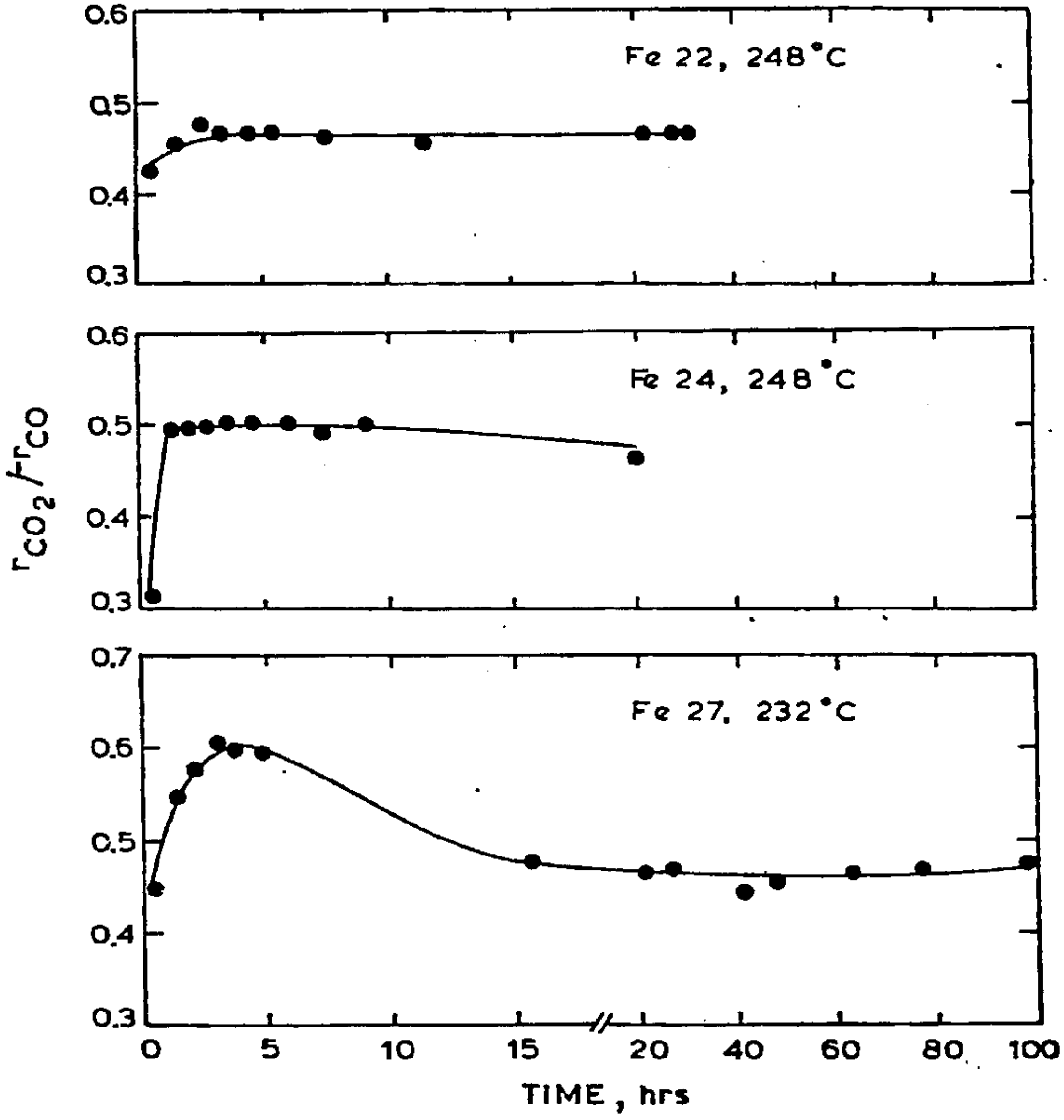

Figure 8 Water-gas-shift activity reaches steady-state within several hours at 248°C and within 15 hours at 232°C.

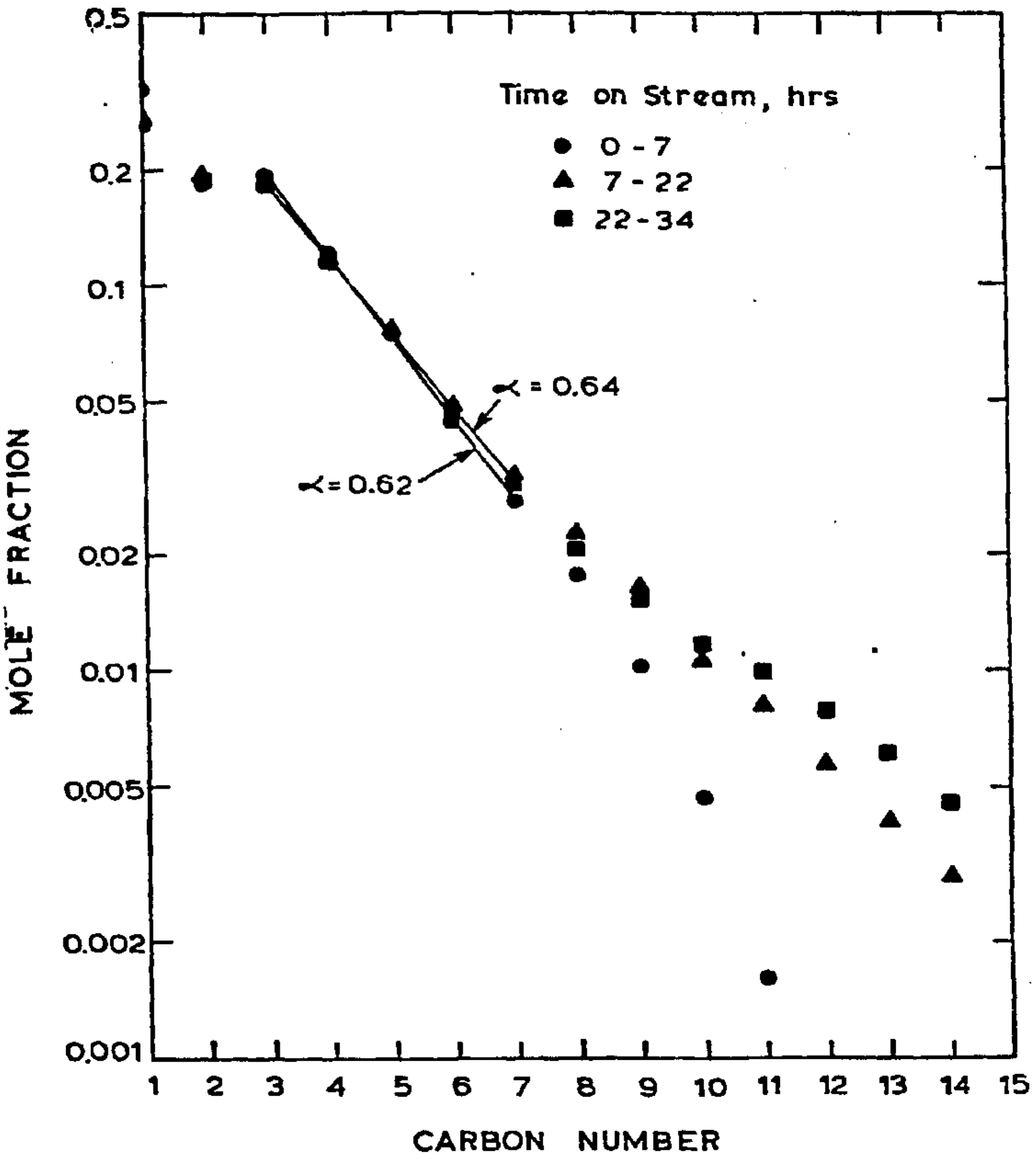

Figure 9 Flory distribution changes little with time on stream.