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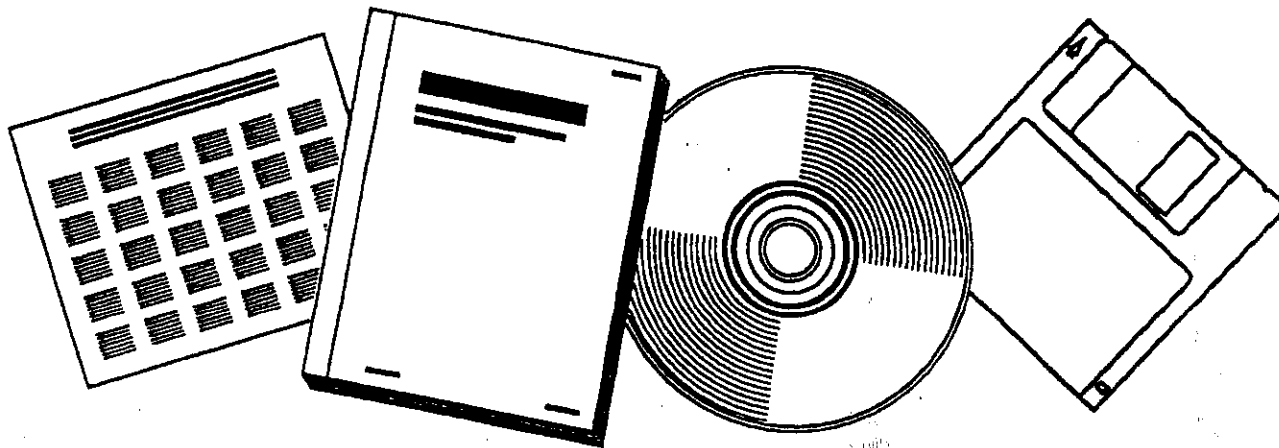
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**FISCHER-TROPSCH SLURRY PHASE PROCESS  
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### Summary

Our studies under Task 5, Activation Procedure Research are summarized in the form of a self-standing report which is attached. This is also being submitted for publication.

Under Task 4, Reaction Conditions, a series of runs is being conducted over the range of 232 to 310°C at a constant pressure of 1.48 MPa to see how product distribution changes with temperature and also  $\alpha_1$  and  $\alpha_2$ . It is difficult to determine  $\alpha_2$  with accuracy since runs must be made for a considerable length of time to accumulate sufficient product for accurate analysis.

Our results to date indicate that  $\alpha_1$  is not significantly affected by temperature but  $\alpha_2$ , based on the C<sub>9</sub>-C<sub>13</sub> overhead fraction, drops significantly. Hence at high temperatures the entire product might easily be ascribed to a single value of  $\alpha$  except for very accurate data.

### Construction of New Apparatus

Some of the runs required to achieve the goals of the present contract must be of substantial duration to collect truly representative product. To improve our research productivity we are presently starting to construct, with approval of our project monitor, a second stirred autoclave apparatus. We presently possess the autoclave and ancillary apparatus. We are now in the process of acquiring the necessary temperature controller, mass flow controller, computer system, etc., required for the complete installation.

Initial Behaviour of a  
Reduced Fused-Magnetite Catalyst  
in the Fischer-Tropsch Synthesis

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Abstract

In studies at 232°C and 248°C and 0.92 MPa, during the first 20 hours on stream, both Fischer-Tropsch synthesis activity and CO consumption increased to quasi-steady-state values. The bulk catalyst, initially  $\alpha$ -Fe, was converted to a mixture of  $\alpha$ -Fe and iron carbides, as determined by Mössbauer spectroscopy. During the first few hours, methane selectivity decreased markedly while the olefin/paraffin ratio increased. No change was observed in the C<sub>2</sub>-C<sub>8</sub> product distribution with time on stream.

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When an industrial iron-based Fischer-Tropsch catalyst is first put on stream some 20 to 40 hours may elapse before its activity and selectivity approach steady-state conditions and during this time the phases present in the catalyst usually change markedly. Numerous studies have been published of correlations between the phases present in an iron catalyst and its reaction behaviour as summarized, for example, in the recent paper by Dwyer and Hardenberg (1984).

Consensus remains elusive, however, in part because of the considerable number of variables that affect phase composition, and the fact that many of the forms of iron catalysts that have been studied in the laboratory are significantly different than those used industrially. In particular industrial catalysts used to date invariably contain potassium, an important promoter that has major effects on activity, product distribution and catalyst life, but many laboratory studies have focused on forms of pure iron, either in bulk form or

supported. Moreover, many laboratory studies have been carried out at atmospheric pressure whereas pressures of the order of 2 MPa are more characteristic of industrial practice.

The present study used a fused triply-promoted magnetite catalyst, sold for use in ammonia synthesis, which is very similar to one of the kinds of iron catalyst used industrially at SASOL in South Africa. It was completely reduced initially. Reaction was carried out in semi-continuous fashion in a well-stirred 1-liter autoclave. We were particularly concerned with studying the activity and selectivity of this catalyst as it approached steady-state behaviour and determining if this correlated with the phases present in the catalyst as determined by Mössbauer spectroscopy.

### Experimental

Catalyst composition, sampling procedures, and details of the Mössbauer spectroscopy measurements are given in the accompanying paper (Satterfield, et al., 1985). 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<sub>2</sub>/CO feed ratio of 0.93. The rate and selectivity data reported herein were obtained at a space velocity of 1500-1600 hr<sup>-1</sup> (vol. dry synthesis gas at STP/

vol. catalyst/hr) for runs Fe22 and Fe24 and  $1340 \text{ hr}^{-1}$  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 slurring 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  $263^{\circ}\text{C}$ , after which reactor temperature was reset to  $232^{\circ}\text{C}$ , 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  $\alpha$ -Fe, magnetite ( $\text{Fe}_3\text{O}_4$ ), and two forms of iron carbide,  $\chi$ - $\text{Fe}_5\text{C}_2$  (Hägg carbide) and  $\epsilon'$ - $\text{Fe}_{2.2}\text{C}$ . The Mössbauer parameters of these phases agree well with data in the literature, as shown in Table 1 of the accompanying paper (Satterfield, et al., 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%  $\alpha$ -Fe, indicating both complete reduction and good sampling technique. Within the first 34 hours on stream, 65% of the  $\alpha$ -Fe had been converted to  $\chi$ - $\text{Fe}_5\text{C}_2$ ; 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%  $\alpha$ -Fe, 77%  $\chi$ - $\text{Fe}_5\text{C}_2$ , and 7%  $\text{Fe}_3\text{O}_4$ . 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  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

The trend with time in the bulk phase composition of the catalyst for run Fe27 ( $T = 232^\circ\text{C}$ ) is shown in the lower portion of Figure 3. The first catalyst sample ( $t = 0$  hours) was 83%  $\alpha$ -Fe and 17%  $\chi$ - $\text{Fe}_5\text{C}_2$ . 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%  $\alpha$ -Fe, 71%  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>, and 16% Fe<sub>2.2</sub>C. As with run Fe22 for about the same initial time period, no magnetite was present, but no Fe<sub>2.2</sub>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 48 hour period the catalyst contained 5%  $\alpha$ -Fe, 75%  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>, and 20% Fe<sub>2.2</sub>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. Run 24 was carried out for only 22 hours 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<sub>2</sub> conversions for the three runs.

#### Selectivity

The change in olefin/paraffin ratio with time for the C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> 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<sub>2</sub> 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<sub>2</sub> but notably here it was higher for C<sub>3</sub> than C<sub>4</sub>.

Methane selectivity is represented by the ratio of  $\text{CH}_4$  to  $\text{C}_2+\text{C}_3$  (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.

$\alpha$ -Olefins are formed as primary products and isomerize to  $\beta$ -olefins by a secondary reaction. The change in the ratio of the  $\text{C}_4$   $\beta/\alpha$ -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  $r_{\text{CO}_2}/-r_{\text{CO}}$  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<sub>2</sub>-C<sub>7</sub> product distributions were quite similar for the three time intervals. The value of  $\alpha$ , as determined by the slope of the distribution of the C<sub>3</sub>-C<sub>7</sub> 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<sub>8</sub>-C<sub>14</sub> 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<sub>2</sub> fraction isolated has usually corresponded to that predicted by the Flory distribution based on the C<sub>3</sub>+ light products. The unusually low concentration here may well reflect incorporation of C<sub>2</sub> 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<sub>2</sub> species to adsorb and react (Stenger and Satterfield, 1985). The scavenging effect causes a slight decrease in  $\alpha$  and we note in Figure 7 that  $\alpha$  increases slightly with time, the direction in which we would expect it to change if the scavenging effect were diminishing with time.

## DISCUSSION

### Phase Composition - Thermodynamics

During synthesis  $\alpha$ -iron is converted to a mixture of three iron phases,  $\alpha$ -iron, magnetite, and some form of iron carbide.

The equations and equilibrium constants for the reactions as reported by Anderson (1984, pp. 19, 22) are:

	<u>K</u>	<u>400°K</u>	<u>500°K</u>	<u>600°K</u>	<u>700°K</u>	
$3/4 \text{ Fe} + \text{H}_2\text{O} = 1/4 \text{ Fe}_3\text{O}_4 + \text{H}_2$	$P_{\text{H}_2} / P_{\text{H}_2\text{O}}$	590	70	18	--	(1)
$5/2 \text{ Fe} + 2 \text{ CO} = 1/2 \text{ Fe}_5\text{C}_2^a + \text{CO}_2$	$P_{\text{CO}_2} / P_{\text{CO}}^2$	--	$1.2 \times 10^7$	$3.0 \times 10^4$	--	(2)

(pressure in atmospheres)

(Anderson represents Hägg carbide as  $\text{Fe}_2\text{C}$ . Other researchers report the stoichiometry of Hägg carbide as  $\text{Fe}_5\text{C}_2$ .)

For representative gas compositions in normal Fischer-Tropsch synthesis, magnetite and carbide thermodynamically are favored relative to  $\alpha$  iron. However,  $\alpha$ -iron was detected in this study in catalyst samples used at 232°C (Fe27) and at 248°C (Fe22) after a significant amount of time on-stream (approximately 200 hours). Studies of CO hydrogenation by Anderson, et al. (1951) and Loktev, et al. (1973) on potassium promoted fused-iron catalysts also reported pure iron to exist in aged catalysts.

Dry (1981) has suggested that the presence of metallic iron in aged catalysts indicated that a layer of inert oxide has blanketed the metal. Our results at 232°C conflict with this suggestion since no oxides were found in the catalyst. Diffusional limitations of carbon in iron are unlikely as was pointed out by Tau, et al. (1984), especially when considering the long time scale of our experiments. Tau, et al., went on to argue that the rate-controlling process in the carburization of iron at 270°C must be associated with the surface of the catalyst. Another possibility suggested by our results is that formation of iron carbide at the outer surface of the iron crystallites prevents

the further diffusion of carbon into the  $\alpha$ -Fe. However, we are not aware of any studies of the diffusion of carbon through iron carbide.

#### Phase Composition - Oxide Formation

After 34 hours in run Fe22 at 248°C, the ratio  $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$  was 0.088 which from a thermodynamic point of view should cause magnetite to form from metallic iron. This was not observed except for the sample taken at 184 hours. During the preceding period, however, space-time had been lowered for several 8-hour intervals to cause CO conversion to exceed 90%. This would cause higher partial pressures of water to form in the reactor which would increase the driving force for formation of magnetite.

No magnetite was observed at 232°C, even though other studies (Huff and Satterfield, 1984) indicate that the water vapor partial pressure at this temperature can be substantially greater than that set by the equilibrium of the water gas shift.

The fact that magnetite was observed only after conditions of high conversion suggests that at lower conversions, iron carbide is the thermodynamically favored phase. Anderson (1984, p. 46) discusses the equilibrium between iron carbides and  $\text{Fe}_3\text{O}_4$ . Iron carbides react with water apparently largely to form elemental C, plus  $\text{H}_2$  and  $\text{Fe}_3\text{O}_4$ , although  $\text{CH}_4$  formation is also possible. At high conversions then  $\text{Fe}_3\text{O}_4$  becomes thermodynamically favored over iron carbides.

Oxide formation during Fischer-Tropsch synthesis over potassium promoted, fused-iron catalysts was observed to occur at a low rate by Anderson, et al. (1951), Loktev, et al. (1973), and Dry (1981). As time-on-stream increased the amount of magnetite also increased. In all three studies the sizes of the catalyst

particles were large (e.g., 6- to 8-mesh in Anderson's study). The large sizes most likely caused diffusional limitations in the catalyst, resulting in an increased partial pressure of  $H_2O$  in the interior of the particles. Thus, while the outer regions of the catalyst were being converted to carbide, the inner regions, being subjected to a more oxidizing environment, were being converted to magnetite.

From the above argument, one would suspect then that with small catalyst particles, in which inner-particle diffusional effects were negligible, this "inside-out" oxidation process would not occur. This would explain then why magnetite did not readily form on the fine catalyst used here. In support of this reasoning, Dry reported that magnetite was not found in very fine iron catalyst particles.

#### Phase Composition - Carbide Formation

Numerous studies have reported on the nature of the iron carbide phase formed during the Fischer-Tropsch synthesis. Anderson et al. (1951), Dry (1981), Matsumoto and Bennett (1978), and Matsumoto (1984) all reported that during Fischer-Tropsch synthesis on potassium-promoted fused-iron catalysts the carbide formed is Hägg carbide. The studies of Dry, Matsumoto and Bennett, and Matsumoto were conducted at temperatures in excess of  $250^\circ C$ . Anderson et al. conducted their study at  $235^\circ C$  for the initial 46 hours of synthesis and then at temperatures equal to or exceeding  $257^\circ C$  for the remaining 2000 hours. Dry also noted the initial formation of an unstable pseudo-cementite phase (ps  $Fe_3C$ ) that disappeared after a few hours on-stream and, after several days, the formation of Eckstrom-Adcock carbide ( $Fe_7C_3$ ). The Eckstrom-

Adcock carbide concentration slowly increased with time.

Niemantsverdriet et al. (1980) used Mössbauer spectroscopy and X-ray diffraction to identify the formation of 4 different carbide phases during Fischer-Tropsch synthesis at 1 atm, using a gas composition of  $\text{CO}:\text{H}_2:\text{He} = 1:1:3$ , and an unpromoted, unsupported metallic iron catalyst. An unidentified carbide phase ( $\text{Fe}_x\text{C}$ ) was formed at 433 and 463° and during the early stages in time-dependent experiments at 513°K. The carbides  $\epsilon'$ - $\text{Fe}_{2.2}\text{C}$  and  $\chi$ - $\text{Fe}_5\text{C}_2$  appeared in the catalyst from temperatures of 463 up to 523°K. Cementite,  $\theta$ - $\text{Fe}_3\text{C}$ , was formed at 623 and 723°K. At 723°K cementite was the only carbide phase present.

Amelse et al. (1978) working with a 4.94 wt%  $\text{Fe}/\text{SiO}_2$  catalyst at 523-528°K and 3  $\text{H}_2:\text{CO}$ , used Mössbauer spectroscopy to show that  $\epsilon'$  carbide was the only carbide formed.

Fischer-Tropsch studies by Raupp and Delgass (1979) using a  $\text{Fe}/\text{SiO}_2$  catalyst at 523°K and 3.3  $\text{H}_2/\text{CO}$  and using Mössbauer spectroscopy showed that small iron particles favor the formation of  $\epsilon'$ - $\text{Fe}_{2.2}\text{C}$  and  $\epsilon$ - $\text{Fe}_2\text{C}$  while larger particles favor the formation of  $\chi$ - $\text{Fe}_5\text{C}_2$ . They suggest that the  $\epsilon'$  and  $\epsilon$  carbides are normally unstable but under certain conditions (i.e. small iron particle size) the silica support may serve to stabilize them in the bulk iron.

Bianchi et al. (1983) used Mössbauer spectroscopy to show that a reduced  $\text{Fe}/\text{Al}_2\text{O}_3$  catalyst formed a mixture of  $\chi$ - $\text{Fe}_5\text{C}_2$  and  $\epsilon'$ - $\text{Fe}_{2.2}\text{C}$  at 1 atm, 285°C, and 9  $\text{H}_2/\text{CO}$ . Tau et al. (1984) performed studies under conditions similar to Bianchi et al. using both  $\text{Fe}/\text{Al}_2\text{O}_3$  and  $\text{Fe}/\text{SiO}_2$  catalysts. They also found  $\chi$  and  $\epsilon'$

to be the two carbides formed and that  $\epsilon'$  formation was favored at long reaction times.

The results shown in Figure 1 together with the results summarized above seem to indicate that  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> and, to a lesser extent,  $\epsilon'$ -Fe<sub>2.2</sub>C are the predominant carbides formed during normal Fischer-Tropsch synthesis. Of the studies cited above, only the study by Raupp and Delgass reported the formation of  $\epsilon$ -Fe<sub>2</sub>C carbide. Niemantsverdriet et al. later presented arguments to suggest that the  $\epsilon$ -Fe<sub>2</sub>C carbide detected by Raupp and Delgass should have been ascribed to  $\epsilon'$ -Fe<sub>2.2</sub>C.

Whether or not  $\epsilon'$ -Fe<sub>2.2</sub>C forms at all seems to depend on the temperature and on the nature of the iron catalyst (i.e., supported, promoted, etc.). In our studies,  $\epsilon'$ -Fe<sub>2.2</sub>C was formed at 232°C but not at 248°C. In the other studies using potassium-promoted, fused-iron catalysts (Anderson et al., 1951; Dry, 1981, Matsumoto and Bennett, 1978, and Matsumoto, 1984), in which the reaction temperatures were in excess of 232°C,  $\epsilon'$ -Fe<sub>2.2</sub>C was not detected. This effect of temperature on the carbide phase composition also occurs with unpromoted catalysts, both supported and unsupported, as reported by Niemantsverdriet and van der Krann (1981) and Tau et al. (1984).

The interconversion of carbide phases in fused catalysts was discussed by Loktev et al. (1972) based on studies of alcohol synthesis at 200 atm from CO and H<sub>2</sub>. As proposed by Loktev et al.,  $\epsilon$ - and  $\epsilon'$ -phases are formed simultaneously at low temperatures (115°C), only the  $\epsilon$ -phase is formed at 150-185°C and only the  $\chi$ -phase at 220-400°C, and only cementite is formed at 450°C and above.



The temperature at which the  $\epsilon'$  or  $\epsilon$ -phase is transformed to the  $\chi$ -phase under Fischer-Tropsch conditions is a matter of dispute. Our studies suggest that the transformation occurs between 232 and 248°C. Niemantsverdriet et al. (1980) reported on the formation of  $\epsilon$ -Fe<sub>2.2</sub>C as high as 350°C. Amelse et al. (1978) detected  $\epsilon'$ -Fe<sub>2.2</sub>C at 225°C and further confirmed the thermal stability of the  $\epsilon'$ -phase by showing the  $\epsilon'$ -phase to be stable at 400°C. As suggested by Niemantsverdriet et al., the stabilization of the  $\epsilon'$ -phase at high temperatures is most likely due to the nature of the catalyst (e.g., promoted or supported).

#### Correlation of Activity to Bulk Phase Composition

In this study, during the initial time period of synthesis, both the synthesis activity and the bulk iron-carbide content of the catalyst started low and increased to a quasi-steady-state value (see Figures 3-4) after about 20 hours. This result is in agreement with other studies conducted with iron catalysts (Niemantsverdriet et al., 1980; Amelse et al., 1978; Raupp and Delgass, 1979; Bianchi et al., 1983). Three models proposed to explain such behaviour of the iron catalyst have been summarized by Niemantsverdriet and van der Kraan (1981). They term these the slow activation model, the carbide model, and the competition model.

These will not be discussed here except to say that our results are consistent with the carbide model. In this model the catalyst is taken to have an iron carbide bulk structure which influences the nature, and thus the activity, of the catalyst surface. The carburization of the bulk contributes to the development of the active surface. This model is favored by Amelse et al.

(1978), Matsumoto (1984), and Raupp and Delgass (1979). The latter reported synthesis activity to increase almost linearly with the extent of carburization, but this may not be generally true. Why catalytic activity should increase with extent of carburization is uncertain and it is not clear whether effects of this sort are primarily a change in the chemical nature of the surface or an increase in surface area.

On iron and other metals carbon is often formed as filaments, the head of which contains a small particle of the metal or metal carbide. With iron the effect was apparently first observed by Fischer in his early work on synthesis and it is described in some detail by Shultz et al. (1961), who refer to it as "carbon-expanded iron". The mechanism of formation is unclear but in any event it can lead to a large increase in surface area of an initially low-area catalyst and hence a large increase in activity on a mass basis.

#### Water-Gas-Shift Selectivity

Figure 8 shows the ratio of water-gas-shift rate to synthesis rate ( $r_{\text{CO}_2}/-r_{\text{CO}}$ ) at 248°C to start low and quickly rise to a steady-state value after 1-2 hours. At 232°C it starts low, quickly rises to a maximum and then decreases to essentially the same steady-state value after 15-hours. As seen in Figure 1, bulk magnetite was not detected at either 232°C or 248°C during the short time period when the water-gas-shift selectivity attained a steady-state value. The rates of each of the two reactions may well differ from one another with respect to degree of conversion, reaction conditions and nature of the catalyst. For example, Matsumoto and Bennett (1978), working with a K-promoted, fused magnetite catalyst at 250°C, 1 atm and with a (H<sub>2</sub>/CO) feed ratio

of 9 reported that  $\text{CO}_2$  was the principal by-product at high conversions but  $\text{H}_2\text{O}$  was more abundant at low conversions.

#### Fischer-Tropsch Product Selectivity

During the first few hours on-stream, the olefin/paraffin ratio increases and the selectivity to form methane drops markedly (Figures 5 and 6).

These effects during the early stages of synthesis can most likely be attributed to the higher hydrogenating ability of the iron catalyst in its completely reduced state relative to its carbided state; the reduced catalyst favors the formation of methane and paraffins. Subsequently the synthesis rate increases,  $\text{CH}_4$  selectivity slowly increases, O/P ratio drops and secondary isomerization of olefins increase but all these effects occur quite slowly.

The initial high methane selectivity over a reduced iron surface is in agreement with other studies (Amelse, et al, 1978; Raupp and Delgass, 1979). Initial olefin selectivity results are difficult to compare since significant shifts in the trends occur over the first few hours of reaction. In time-dependent studies, using unpromoted, unsupported iron catalysts, Krebs et al. (1981) report that the  $\alpha$ -olefin/paraffin ratio initially decreases and after a short time (<25 minutes) increases. Amelse et al. (1978) and Raupp and Delgass (1979) using supported iron catalysts report that the  $\alpha$ -olefin/paraffin ratio decreased with the extent of carbiding.

The apparent absence of a shift in the  $\text{C}_2+$  product distribution in this study with time on-stream could be because all significant changes occurred rapidly and were not observed when averaged over

the initial 7 hours of synthesis. Krebs et al. reported that during the first three hours of synthesis, the chain growth probability, as determined from the  $C_1$ - $C_5$  product distribution, decreased from 0.46 to 0.39. However Schulz et al. report a slow steady increase in the chain growth probability over as much as 50 hours, working with a precipitated iron (FeMn?) catalyst at 250°C and 10 bar. Shultz et al. (1955) did not observe a significant difference in selectivity between reduced and carbided iron.

#### Summary

In studies at 232°C and 248°C and 0.92 MPa, during the first 20 hours on stream, both Fischer-Tropsch synthesis activity and CO consumption increased to quasi-steady-state values. During this time the bulk catalyst, initially  $\alpha$ -Fe, was converted to a mixture of  $\alpha$ -Fe and iron carbides, as determined by Mössbauer spectroscopy. At 248°C, the carbide formed was  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>. At 232°C,  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> and to a lesser extent  $\epsilon'$ -Fe<sub>2.2</sub>C formed. At neither temperature was magnetite formed. During the first few hours, methane selectivity decreased markedly while the olefin/paraffin ratio increased. Subsequently, methane selectivity increased, olefin/paraffin ratio decreased, and  $\beta$ -olefin/ $\alpha$ -olefin ratio increased, but all these effects occurred quite slowly. No change was observed in the  $C_2$ - $C_8$  product distribution with time on stream.

The water-gas-shift selectivity attained steady-state within the first several hours at 248°C and within about 15 hours at 232°C.

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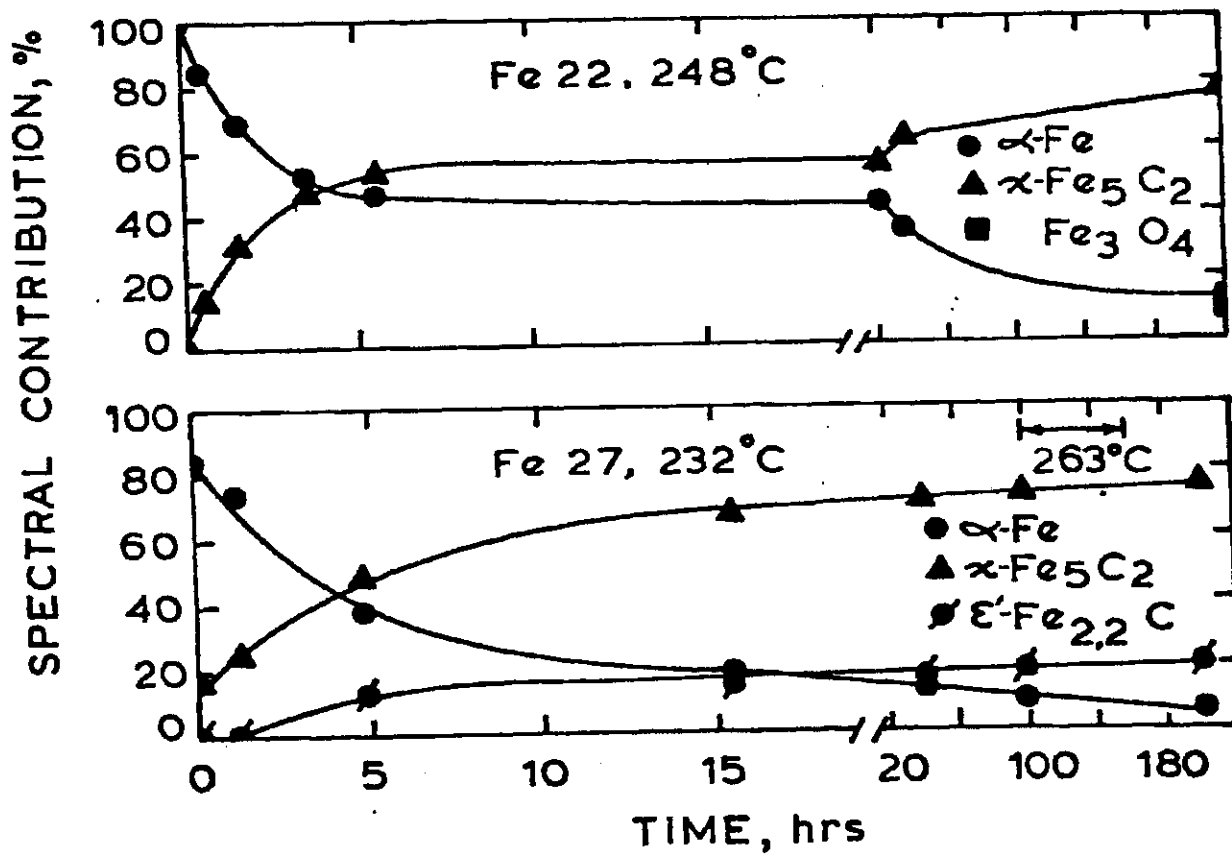
Table I Fractional Conversions

<u>RUN</u>	<u>T(°C)</u>	<u>x<sub>CO</sub></u>		<u>x<sub>CO+H<sub>2</sub></sub></u>	
		<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>
FE22	248	50	65	42	56
FE24	248	47	75	37	65
FE27	232	30	58	24	50

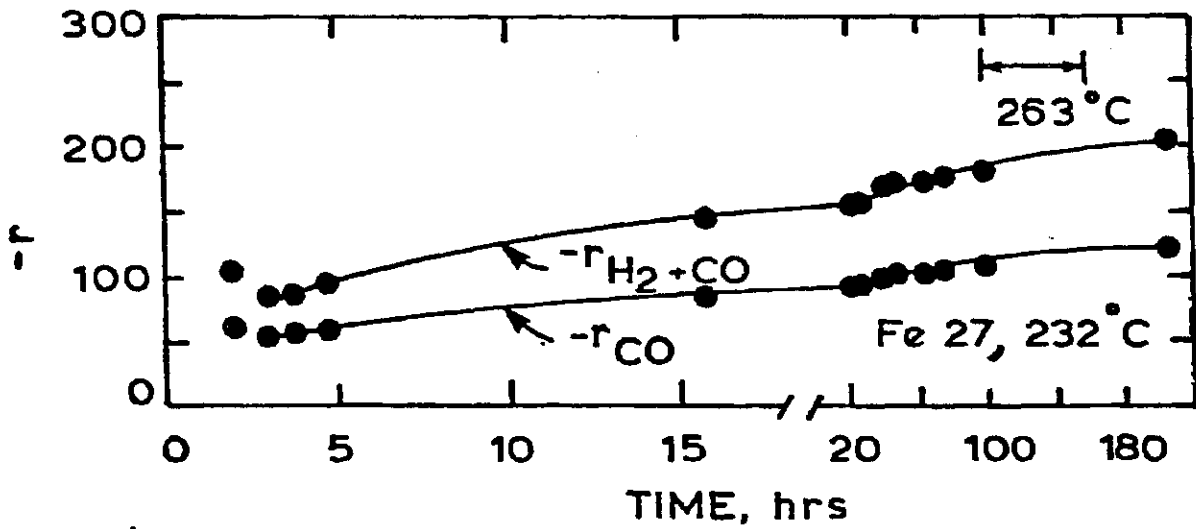
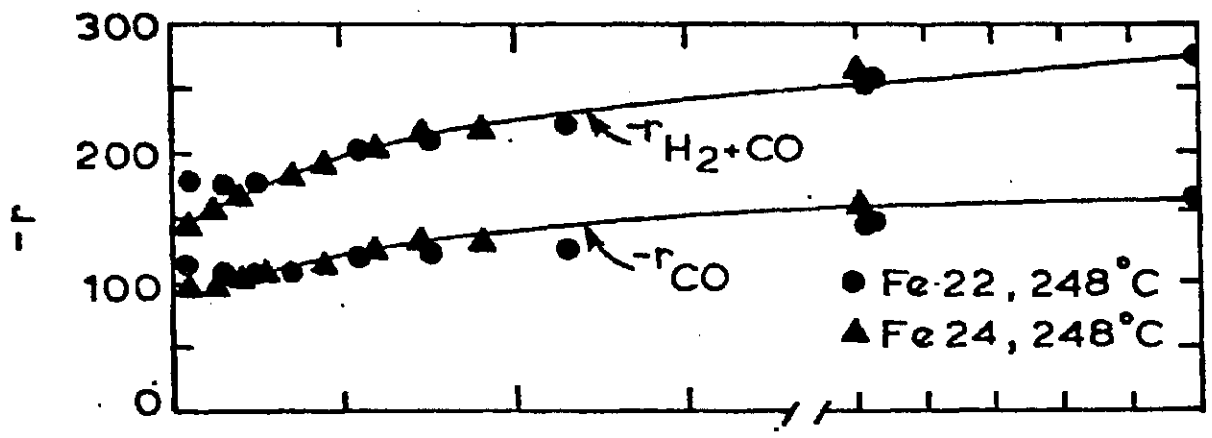


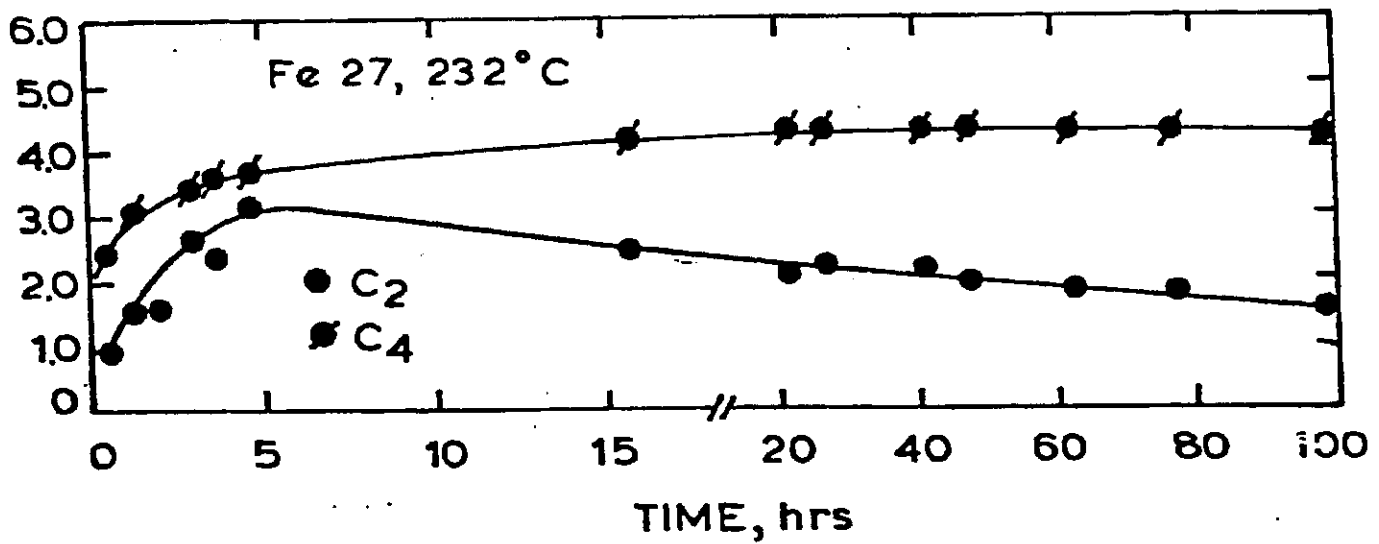
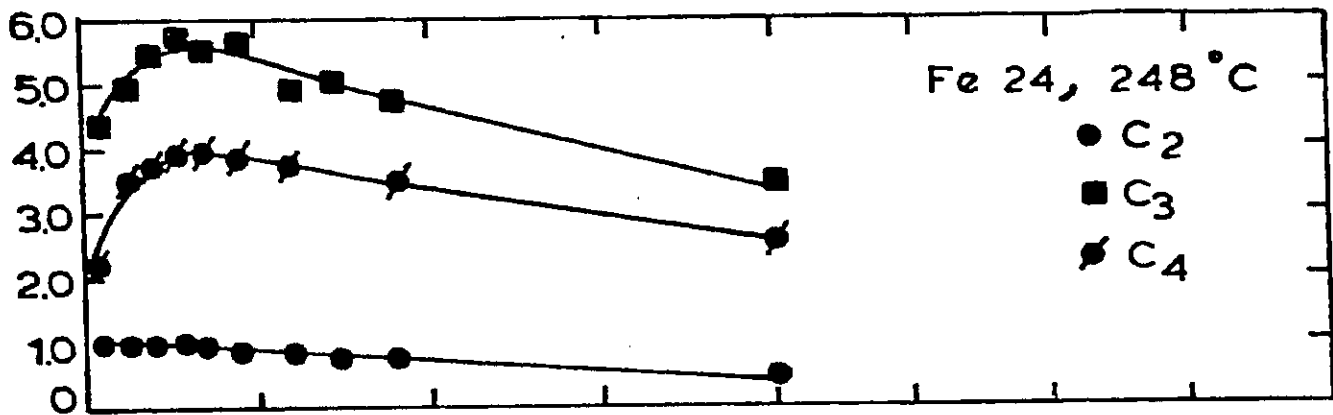
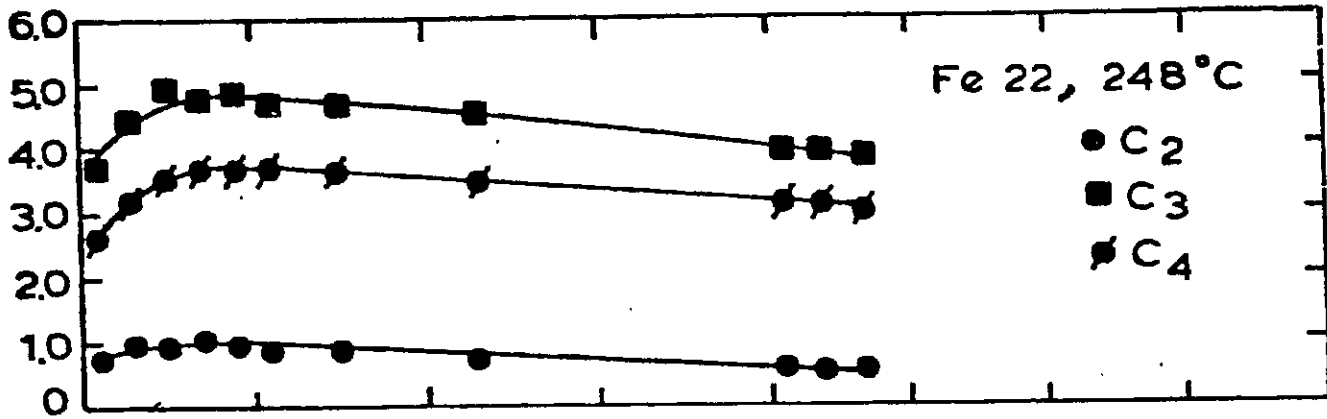
### Figure Captions

- Figure 1 Mossbauer spectrum of run Fe22 ( $T = 248^{\circ}\text{C}$ ) catalyst samples after various periods of synthesis. The six identifications shown for the  $\underline{h}$  spectrum represent, from top down, the Fe sites I and II in  $\text{Fe}_3\text{O}_4$ ,  $\alpha\text{-Fe}$ , and the Fe sites II, I and III in  $\chi\text{-Fe}_5\text{C}_2$ .
- Figure 2 Mossbauer spectra of run Fe27 ( $T = 232^{\circ}\text{C}$ ) catalyst samples after various periods of synthesis. The five identifications shown for the  $\underline{f}$  spectrum represent, from top down,  $\alpha\text{-Fe}$ , the Fe sites II, I and III in  $\chi\text{-Fe}_5\text{C}_2$ , and  $\epsilon'\text{-Fe}_{2.2}\text{C}$ .
- 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  $\beta\text{-Olefin}/\alpha\text{-olefin}$  ratio slowly increases with time on stream.
- Figure 8 Water-gas-shift activity reaches steady-state within several hours at  $248^{\circ}\text{C}$  and within 15 hours at  $232^{\circ}\text{C}$ .
- Figure 9 Flory distribution changes little with time on stream.

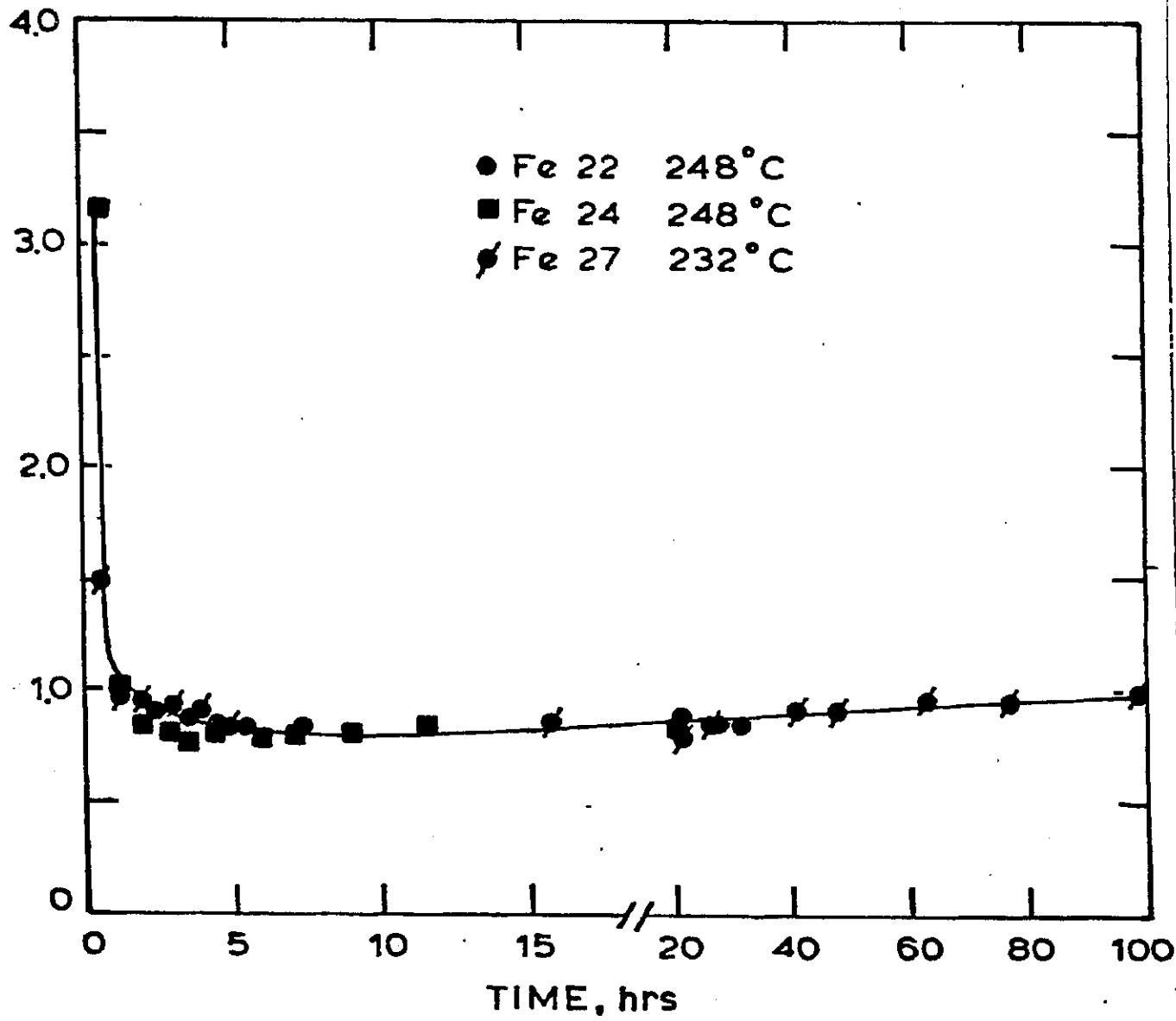


(3)

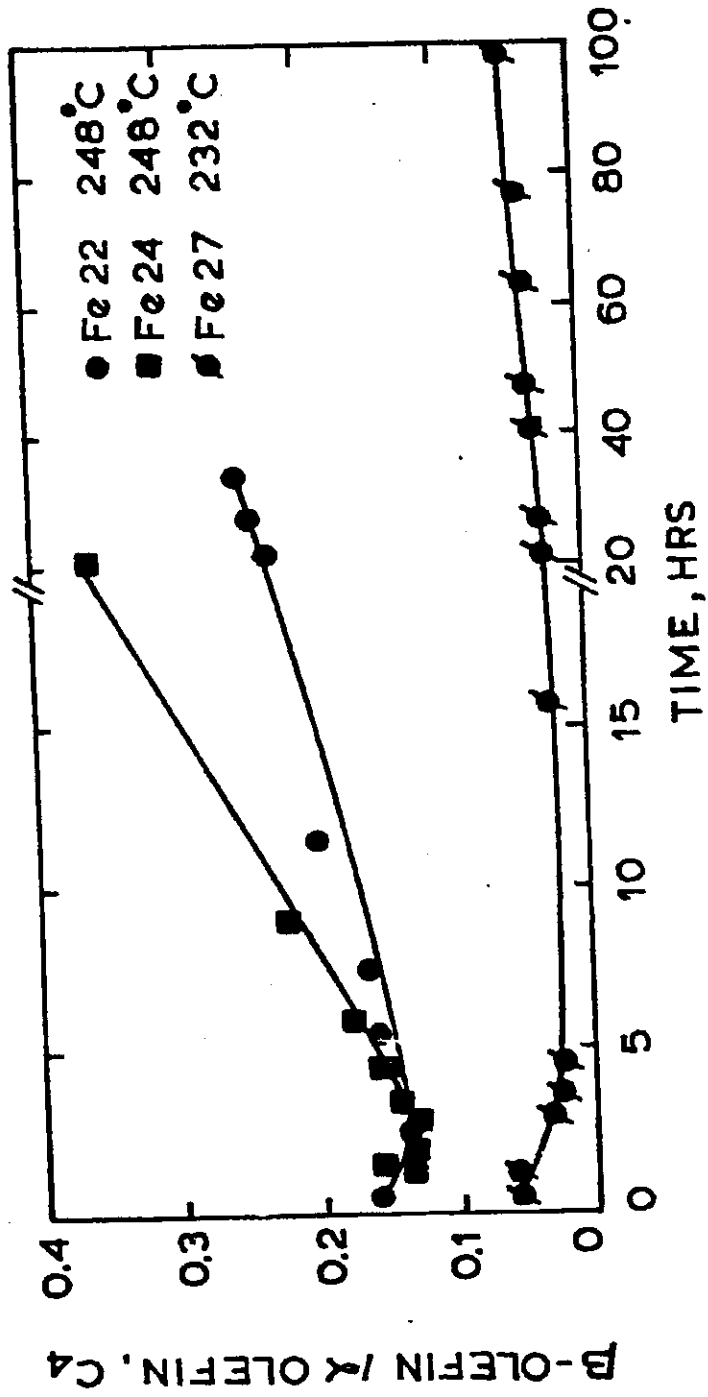




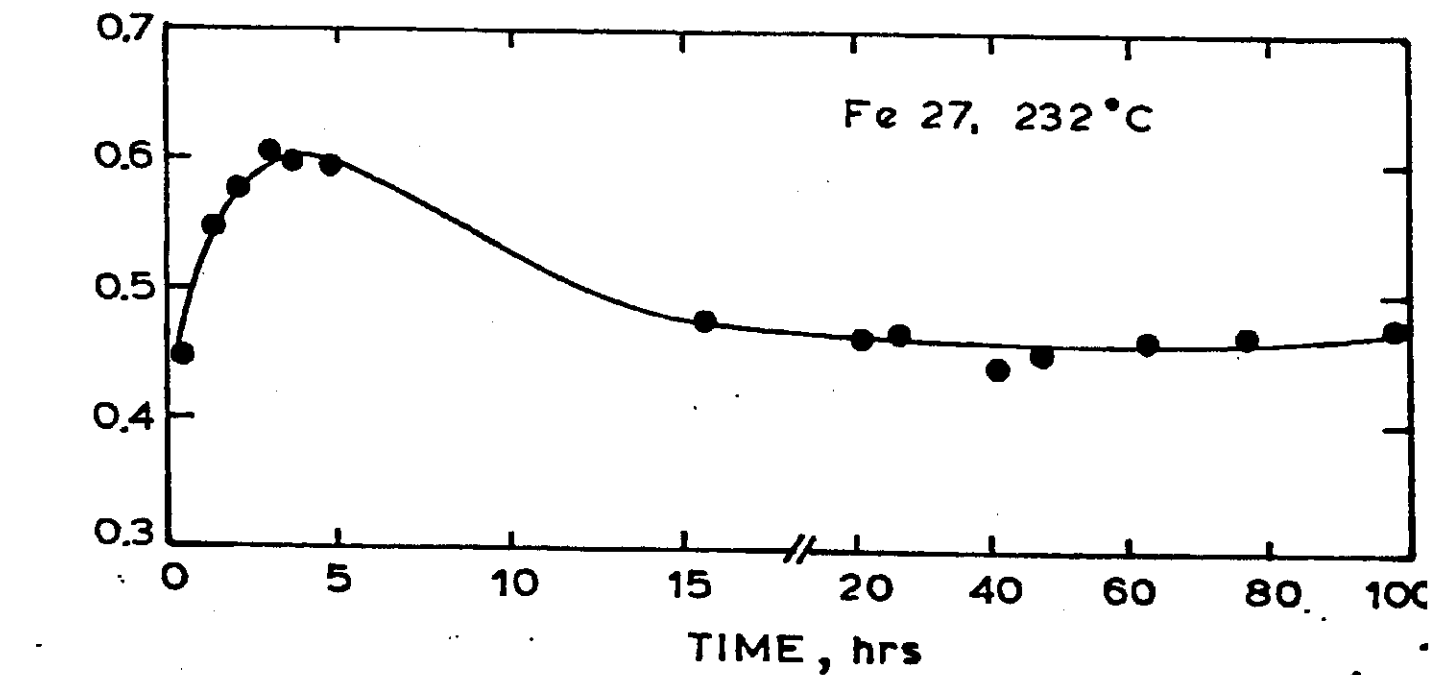
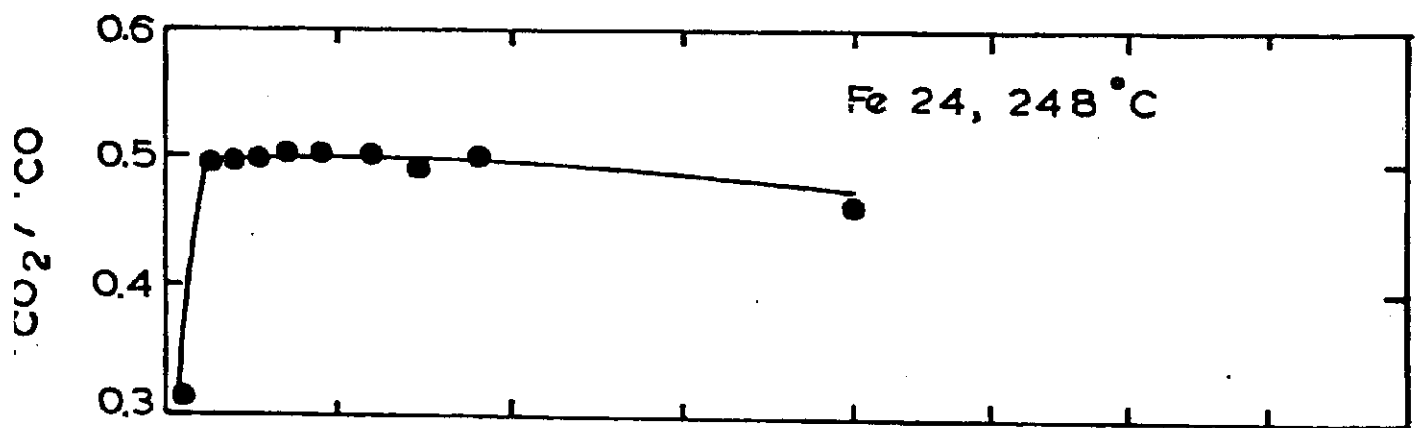
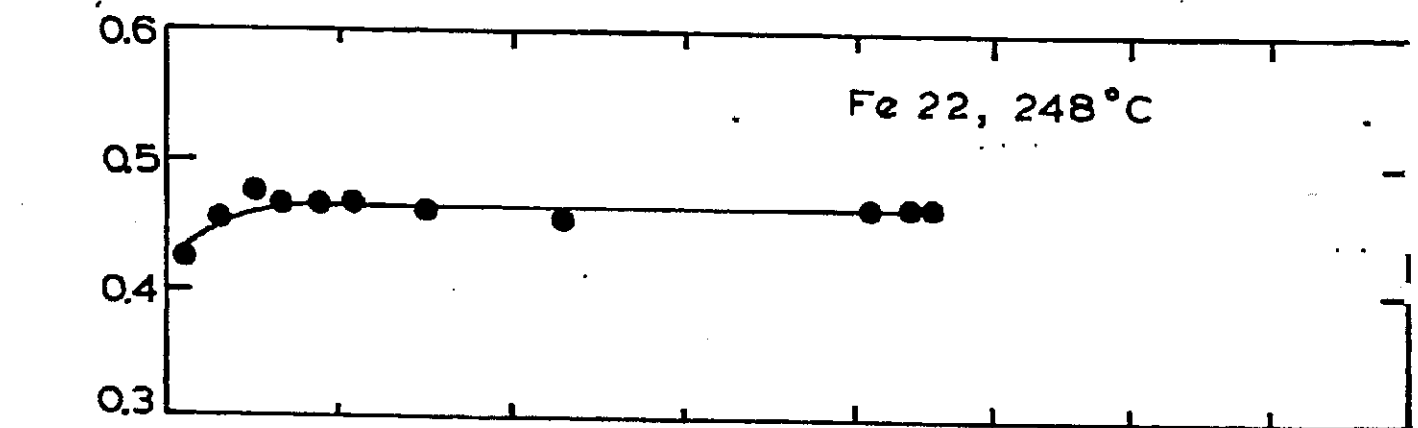
(5)



(6)



7



8

