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Fischer–Tropsch Synthesis on a Precipitated Iron Catalyst

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The Fischer–Tropsch synthesis was carried out at various experimental conditions on an unpoisoned and sulfur-poisoned precipitated, alkali-promoted iron–copper catalyst. The sulfur, present in the fixed catalyst bed as a longitudinal concentration gradient, had little effect on conversion or product selectivity. However, for both poisoned and unpoisoned catalysts, there was a significant change in the CO conversion to CO_2 on going from a reaction temperature of 240 to 250°C. This suggests that there is a rapid change of our catalyst surface after 240°C: the surface changes from one that is effective for CO_2 formation to one that is not as effective. Finally, analysis of the condensed products led us to suggest that there are at least two types of sites for hydrocarbon chain formation, each with a slightly different value of the chain growth probability.

INTRODUCTION

Fischer and Tropsch produced the first measurable quantities of higher hydrocarbons, in 1923, by passing H_2 and CO over alkalized iron filings. Since this discovery, iron-based catalysts have proved to be a mainstay of the hydrocarbon synthesis process. In fact, about 40 years after the famous Schwarzheide tests (*1*) in which Fe-based catalysts were used, the only current commercial operation in Sasol, South Africa, still uses Fe-based catalysts. These catalysts can be poisoned by sulfur compounds present in the H_2 + CO feed gas obtained from coal gasification. At Sasol, for example, the Rectisol process is used to remove the sulfur before the synthesis step. Various past studies, recently reviewed in some detail (*2*), have shown that the interaction of sulfur compounds with Fischer–Tropsch (FT) iron catalysts is quite complex.

Two sets of investigations concerning the effect of S on Fe-based Fischer–Tropsch catalysts are of most interest to us: one by Rapoport and Muzovskaya (*3–5*) on alkalized precipitated Fe–Cu catalysts, and the other by Anderson and co-workers (*6–8*) on alkalized fused Fe catalysts.

The investigation by Rapoport and Muzovskaya indicated that when their catalyst was reduced in H_2 at 250°C it could be used with reactants containing 50 mg S/m^3 of inert-free synthesis gas for more than 2 months with little reduction in activity or change in selectivity (*3*). However, when the catalyst was reduced in H_2 at 500°C instead of 250°C, it rapidly deactivated in synthesis gas containing S (*5*). Rapoport and Muzovskaya noted that at the high reduction temperature the catalyst was reduced predominantly to metallic iron and therefore was easily poisoned. After reduction at 250°C, however, the catalyst contained predominantly iron oxides. They concluded that the presence of iron oxide was necessary to prevent rapid deactivation by S compounds during the FT synthesis.

The fused iron catalyst used by Anderson and co-workers (*6*) was reduced in H_2 at 450°C with 90% of the starting material being converted to metallic Fe. This catalyst deactivated rapidly in the presence of synthesis gas containing only 6.9 mg S/m^3 of gas. Carbiding or nitriding the reduced Fe catalyst (*7*) helped increase the resistance to S poisoning but did not prevent it. It should be noted that in the study by Ander-

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son and co-workers the catalyst was not uniformly poisoned but that there was a large longitudinal S concentration gradient on the catalyst in the tubular reactor (*8*).

This paper describes our investigation on an alkali-promoted precipitated Fe–Cu catalyst, similar to the one used by Rapoport and Muzovskaya, with and without the presence of sulfur. Sulfur, when used, was present as a longitudinal concentration gradient on the catalyst like in the work of Anderson *et al.* (*8*). Our objective was to learn, by obtaining detailed product analysis, how the presence of S would affect hydrocarbon selectivity. We wished to compare the results on the iron-based catalyst to those on the cobalt-based catalyst (*9*) which contained very similar longitudinal gradients and on which significant sulfur effects on condensed hydrocarbon distribution had been observed. The paper also attempts to address the dynamic nature of an iron catalyst surface during the FT synthesis.

EXPERIMENTAL

The apparatus, multiple reactor system, and analytical procedures have been described elsewhere (*9*).

The catalyst, 100 Fe : 21.8 Cu : 1 K_2CO_3, was specially prepared by Harshaw Chemical Company. A chloride solution was prepared to contain 75 parts Fe^{2+}, 25 parts Fe^{3+}, and 20 parts Cu^{2+}. The solution was heated to 70°C and then mixed with a hot, 90 to 100°C, solution of sodium carbonate. The mixing and the consequent precipitation was carried out as rapidly as possible and was limited only by the large quantities of foam generated. The final pH was approximately 7.5. The precipitate was filtered and washed with deionized water until the effluent had a chloride level slightly lower than tap water. The wet precipitate was then treated with a potassium carbonate solution. After drying, 60 to 120 mesh granules were prepared. The catalyst composition and preparation were similar to the precipitated iron catalyst described by Pichler (*1*).

The reactors were filled with 40 cm^3, 39.4 g, of the catalyst and flushed with He. Catalyst induction was then carried out at atmospheric pressure. First, the temperature of the catalyst was increased to 225°C under flowing H_2 and CO, $H_2 : CO = 1$, at a gas hourly space velocity (GHSV) of 100 V/V/h. The catalyst was treated under these conditions for 24 h. The induction temperature was then increased to 230°C, and the treatment was continued for 24 h. Finally, the temperature was raised to 235°C, and the treatment was ended after a final induction period of 24 h. The reactors were then flushed with He. This induction procedure is similar to that used before with similar catalysts (*1*, *10*). The effect of varying pretreatment on catalyst performance was not studied here.

The reactors containing catalysts which were not to be sulfided were closed off under positive He pressure. The other catalysts were sulfided at the final induction temperature of 235°C and atmospheric pressure. A 2 : 1 mixture of $H_2 : CO$ containing 150 ppm H_2S was used at a GHSV of approximately 400 V/V/h. No H_2S was detected coming out of the reactors during the sulfiding process. After the required amount of sulfiding was completed, H_2S was not added again to the catalyst at any time during experimentation.

Experiments were conducted simultaneously, with pure CO and H_2, on the sulfided and unsulfided catalysts at the same pressure, temperature, GHSV, and H_2/CO ratio. Each experiment was performed for 4 to 5 h. After each experiment, the catalysts were kept overnight in flowing He at the same temperature and pressure used in the experiment.

In this paper, results only with the catalyst containing the largest nominal S concentration will be compared to the unsulfided catalyst. Results with catalysts containing lesser loadings of S will not be reported as they do not contribute to or

TABLE 1

Longitudinal Sulfur Distribution in Catalyst Beds[a]

Section	S distribution (%S by wt)
1	13.50
2	5.27
3	0.77
4	0.15
5	0.04
6	0.04
7	0.04
8	0.02
9	0.06
10	0.01
11	0.01
12	0.02
13	0.03
14	0.01

[a] Nominal S level, as wt% of unreduced catalyst = 0.4%.

change the discussion in this paper; these results may be found in Madon *et al.* (*11*). The reproducibility of the results checked with two reactors containing unsulfided catalysts and working simultaneously was good and has been discussed in detail elsewhere (*11*).

The maximum nominal sulfur level obtained was 0.4 S wt% of the untreated catalyst; this corresponds to approximately 6 mg S/g Fe. As mentioned in the Introduction, the S was present as a longitudinal concentration gradient as in Anderson *et al.* (*8*) and Madon and Taylor (*9*). Therefore as a nominal S level does not give the complete information, a detailed longitudinal sulfur gradient analysis was performed (Table 1). After all the experiments had been completed, the catalyst to be analyzed was removed from the reactor in approximately equal sections. The inlet portion, approximately the first 28% of the bed, contains most of the sulfur though there is sulfur in the rest of the bed. The amount of sulfur in the unsulfided catalyst was found to be negligibly small throughout the bed, nominal sulfur content being 0.01 wt% S.

The synthesis reaction was carried out under integral experimental conditions in order to allow the product selectivity pattern to develop fully. However, as such operation often magnifies problems associated with transport phenomena, care was taken to minimize the effects of physical events on our studies. A detailed analysis of various transport artifacts is given in Madon *et al.* (*11*). The key design parameters to reduce the artifacts are (a) the catalyst powder size which has been kept below 0.2 mm to help eliminate internal diffusion and heat transfer problems, and (b) the reactor internal diameter which is 0.77 cm and thus prevents radial heat transfer problems. Longitudinal temperature gradients were checked with a "traveling" thermocouple. A hot spot was found approximately 5 to 10 cm below the catalyst bed inlet. When reaction temperatures were at or below 250°C, the spot temperature was 5 to 10°C above reaction temperature; at a reaction temperature of 260°C, the spot temperature was 15°C above reaction temperature; and at a reaction temperature of 270°C, the spot temperature rise was 25°C. The rest, about 95%, of the bed remained at the reaction temperature at all times. We feel that the appearance of a hot spot has not significantly masked our results.

RESULTS

As shown in Table 2, the activity, stated as percentage total conversion, is identical for the sulfided and unsulfided catalyst even though 28% of the sulfided catalyst has a

TABLE 2

Conversion of H_2 and CO

Expt. conditions[a]		H_2 + CO conv. (%)	
Temp (°C)	*P* (MPa)	S (wt%) = 0.4	0
241	1.0	66	66
230	1.0	47	46
242	0.5	47	47

[a] $H_2/CO \simeq 1.5$. GHSV $\simeq$ V/V/L.

significant amount of sulfur. One may argue that conversion values from the reactors are identical because the complete bed does not participate during reaction. And, therefore, even though the sulfided portion of the catalyst is inactive, there is sufficient remaining catalyst to give the appropriate conversion. This argument is valid for conversions of 99–100%. But for low conversions of 47% (Table 2), the above argument cannot be used to explain the observed identical conversions for sulfided and unsulfided catalysts. This lack of catalyst deactivation in the presence of a small amount of sulfur is real and agrees with the results of Rapoport and Muzovskaya (*3–5*). On the other hand, on fused reduced Fe catalysts, Anderson and co-workers (*7*, *8*) show that at approximately the same loading of sulfur per g of Fe as used by us, the catalyst activity decreases by more than 50%. And, as in our case, the S concentration on the fused iron catalyst is present as a longitudinal gradient.

Tables 3 and 4 show the effect of the H_2/CO ratio and space-velocity, respectively. A normalized selectivity is reported (percentage of reacted CO converted to the required product) to rule out effects due to variations in conversion. In both cases, there is virtually no effect of S on conversion or selectivity. Varying the H_2/CO ratio results in small changes in product selectivity as seen, for example, by the small decrease in CH_4 make at lower $H_2 : CO$. And there seems to be no real change in product selectivity on going from 100 to 250 V/V/h. However, there is a definite effect on the gaseous olefin/paraffin ratios: this ratio is increased when the H_2/CO ratio is decreased or the GHSV is increased. These results are expected; for as shown by Pichler *et al.* (*12*), the primary reaction in the FT synthesis is the formation of the α-olefin which is hydrogenated in a consecutive step to the corresponding paraffin. Thus the higher space velocity operation would favor increasing the primary α-olefinic products. What seems to be interesting, however, is that the olefin/paraffin ratio is not greatly affected by the presence of S. There is some small enhancement in $C_2H_4 : C_2H_6$ for the sulfided catalyst, but, in general, the effect of S is minimal. For the cobalt-based catalyst (*9*), depending on the experimental conditions, S helped enhance the olefin/paraffin ratio by almost a factor of 2. Sulfur thus seems to affect the olefin hydrogenation capacity more for the cobalt-based than for the iron-based catalyst.

TABLE 3

Effect of H_2/CO Ratio[a]

H_2/CO	1.61		1.03	
S nominal wt%	0.4	0	0.4	0
H_2 + CO conv (%)	80	81	88	87
Selectivity				
% CO conv. to				
CO_2	35.2	32.0	40.9	44.4
CH_4	6.2	6.7	4.7	4.5
C_5^+	39.4	39.5	43	38.3
Olefins in gaseous products				
C_2H_4/C_2H_6	0.19	0.12	0.35	0.27
C_3H_6/C_3H_8	3.23	2.69	4.33	4.62
C_4H_8/C_4H_{10}	2.50	2.05	3.58	3.80

[a] $T \simeq 250°C, P \simeq 1.0$ MPa, GHSV $\simeq$ 195 V/V/h.

TABLE 4

Effect of Space-Velocity[a]

GHSV, V/V/h	100		250	
S nominal wt%	0.4	0	0.4	0
H_2 + CO conv. (%)	74	70	66	65
Selectivity				
% CO conv. to				
CO_2	40.5	45.7	46.9	48.2
CH_4	3.9	3.4	3.0	2.8
C_5^+	42.6	38.2	39.1	38.7
Olefins in gaseous products				
C_2H_4/C_2H_6	0.10	0.09	0.81	0.49
C_3H_6/C_3H_8	2.68	2.70	4.48	4.34
C_4H_8/C_4H_{10}	2.17	1.85	3.56	3.58

[a] $T \simeq 240°C, P \simeq 1.0$ MPa, $H_2/CO = 1.5$.

Temperature, as shown in Fig. 1, has a

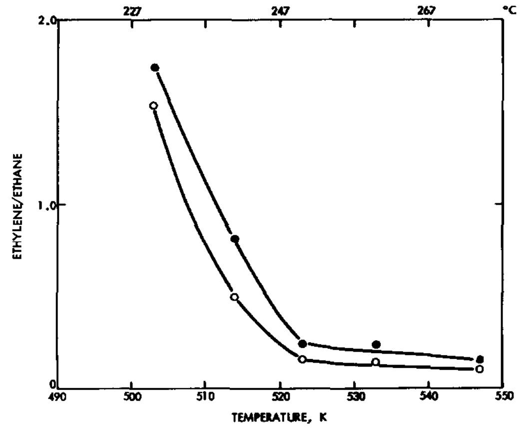

FIG. 1. Dependence of the ethylene/ethane ratio on temperature. $P \simeq 1.0$ MPa, GHSV $\simeq$ 250 V/V/h, $H_2/CO \simeq 1.5$. Open points, unsulfided catalyst; solid points, sulfided catalyst.

significant effect on the ethylene : ethane ratio. This ratio is greater than one at 230°C but falls rapidly as the temperature is increased; the value is less than 0.2 at 275°C. It should be noted that at all temperatures ethylene : ethane is slightly larger for the sulfided catalyst. In contrast to C_2, the propylene/propane and butene/butane ratios are relatively constant and independent of both temperature and the presence of S. The olefin/paraffin values are about 4 for C_3 and 3 for C_4. Madon and Taylor (*9*) and Schulz *et al.* (*13*) offer some explanations why ethylene/ethane ratios are usually small in normal FT synthesis: the values are very often less than one and almost always smaller than the corresponding C_3 and C_4 ratios. Our results at different space-velocities (Table 4) indicate ethylene rather than ethane to be the primary product. Therefore, though we cannot rule out the possibility in general, under our present conditions we do not feel that the C_2 fragment prefers to terminate as a paraffin rather than as an olefin. Perhaps ethylene can hydrogenate readily on different kinds of surfaces offered by the iron catalyst, whereas C_3H_6 and C_4H_8 need particular hydrogenation sites.

The effect of pressure, however, seems to be more significant than the effect of temperature on the gaseous olefin/paraffin ratios. Figure 2 shows that the ratios for C_2, C_3, and C_4 decrease with increasing pressure. This decrease is most dramatic for C_2; the ethylene/ethane ratio falls by a factor of 40 between 0.5 and 2.3 MPa. The hydrogenation of the primary α-olefin product becomes more effective at higher pressures. Though this could be predominantly kinetic, the possibility that this may be coupled to catalyst surface changes which effect more efficient hydrogenation cannot be ruled out. Again, like in the case of experiments done at various temperatures (Fig. 1), there is a small influence of S on the ethylene/ethane. There is no such S influence for the corresponding C_3 and C_4 ratios.

Figure 3 indicates the temperature dependence of CO_2 and CH_4 formation. Within a narrow temperature range, between 240 and 250°C, there is a sharp reduction in CO_2 selectivity and an increase in CH_4 selectivity. The C_2–C_4 selectivity, not shown in the figure, increased similarly,

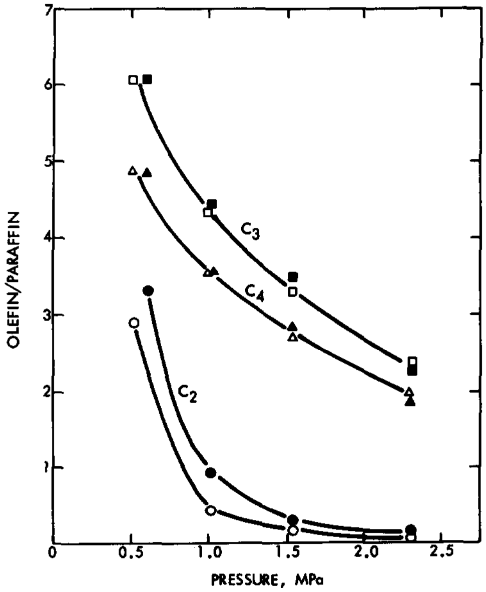

FIG. 2. Dependence of olefin/paraffin ratios on pressure. $T \simeq 240°C$, GHSV $\simeq$ 250 V/V/h, $H_2/CO \simeq 1.5$. Open points, unsulfided catalyst; solid points, sulfided catalyst.

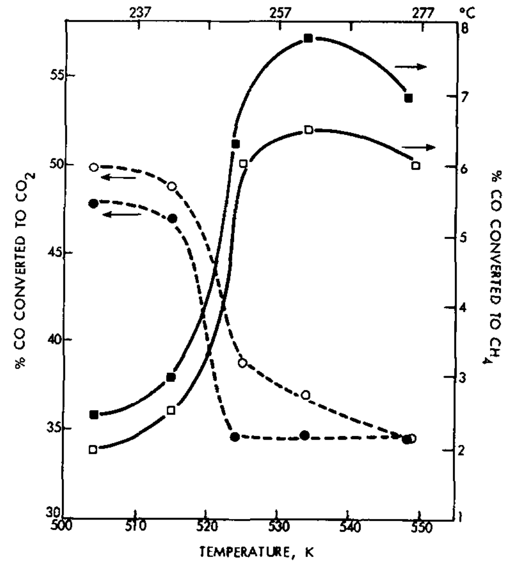

FIG. 3. Dependence of percentage reacted CO converted to CO_2 and CH_4 on temperature. $P \approx 1.0$ MPa, GHSV $\approx$ 250 V/V/h, $H_2/CO \approx 1.5$. Open points, unsulfided catalyst; solid points, sulfided catalyst.

whereas the C_5^+ selectivity remained constant. However, it should be noted that the selectivity is stated as percentage CO converted to particular products. Hence, the decrease in CO consumption to CO_2 has to show up as an increased CO consumption to hydrocarbons; it is interesting that this increase shows up in the light hydrocarbons whereas the condensed C_5^+ product selectivity remains relatively unchanged.

Just as CO_2 formation decreases with increasing temperature, a similar but not as large a decrease in CO_2 formation takes place with increasing pressure: the percentage reacted CO converted to CO_2 decreases from 55% at 0.5 MPa to 41% at 2.3 MPa, the temperature being 240°C and $H_2 : CO = 1.5$.

Comparison of Iron-Based and Cobalt-Based Catalysts

Both catalysts were promoted with alkali and studied with similar longitudinal S gradients. The effect of S was more pronounced with the cobalt catalyst (*9*). With cobalt, not only was the olefin/paraffin ratio affected but large differences were observed in the condensed product distributions: the presence of S enhanced the formation of heavier hydrocarbons. Under similar conditions, the effect of S on our iron catalysts was negligible. In neither case did S severely reduce the activity of the catalyst.

Table 5 compares the performance of unsulfided catalysts at similar pressures and $H_2 : CO$ ratio. Except for the fact that a large amount of CO_2 is formed on the iron catalyst, the selectivities, on a CO_2-free basis, are quite close. One point concerns the C_2 make: it is quite high on the iron catalyst and much lower on the cobalt catalyst. We will pursue this point in another paper. The gaseous olefin/paraffin ratios show that under FT conditions cobalt

TABLE 5

Comparison of Precipitated Iron-Based and Cobalt-Based Catalysts[a]

	Fe-based	Co-based
Reaction temperature (°C)	240	195
GHSV (V/V/h)	244	208
H_2 conversion (%)	45	90
CO conversion (%)	94	67
CO converted to hydrocarbons (%)	49	65
H_2 usage ratio	0.41	0.67
Selectivity, % CO converted to		
CO_2	48.2	2.9
CH_4	2.8(5.4)[b]	4.7(4.8)
C_2	3.5(6.8)	1.8(1.9)
$C_3 + C_4$	6.8(13.1)	10.4(10.7)
C_5^+	38.7(74.7)	80.2(82.6)
Olefins in gaseous products		
C_2H_4/C_2H_6	0.49	~0
C_3H_6/C_3H_8	4.34	2.23
C_4H_8/C_4H_{10}	3.58	1.36

[a] CO: ThO_2 : kieselguhr : K_2CO_3, $P = 1.1$ MPa, $H_2/CO = 1.53$; Fe : Cu : K_2CO_3, $P = 1.0$ MPa, $H_2/CO = 1.46$.

[b] Numbers in parentheses represent values on CO_2-free basis.

is a much better hydrogenation catalyst than iron.

For the iron catalyst, the amount of CO converted is large, but a significant portion is used to produce CO_2 rather than hydrocarbons. The H_2 usage ratio defined as the ratio of moles of H_2 converted to the total moles of H_2 and CO converted indicates that for cobalt

$$CO + 2H_2 \rightarrow -CH_2- + H_2O \quad (1)$$

is the main reaction. For iron, the usage ratio is lower indicating that less H_2 and/or more CO is being consumed. Thus if on iron Eq. (1) takes place as the primary reaction and some water–gas shift (WGS) takes place as a secondary reaction

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

then the reactions together would give a H_2 usage ratio less than 0.67. A primary reaction

$$2CO + H_2 \rightarrow -CH_2- + CO_2 \quad (3)$$

would also account for a low H_2 usage ratio of 0.33. However, the usage ratio in most of our experiments on iron fluctuated between 0.4 and 0.55. Furthermore, we did observe H_2O as a product. Knowing the conversion of CO to various products, we calculated (*11*) the hydrogen consumption using Eqs. (1) and (2). The calculated values matched the experimentally observed value of hydrogen consumed remarkably well. No such agreement was obtained if Eq. (3) was assumed to be the main reaction or if all CO_2 was assumed to occur via the Boudouard reaction [$2CO \rightarrow CO_2 + C$]. One may indeed argue that Eqs. (1) and (3) can occur together to give both H_2O and CO_2, and that Eq. (4) is therefore not necessary to account for CO_2. Though it is difficult to disprove this, our work and the experiments of Dry *et al.* (*14*) indicate WGS to be a very probable secondary reaction during iron FT catalysis and that under steady-state operation Eq. (3) is not important. These conclusions substantiate the suggestions of Anderson and coworkers (*15, 16*), Dry *et al.* (*14*), and Kölbel *et al.* (*17, 18*) that on iron catalysts Eqs. (1) and (2) are the main reactions.

DISCUSSION

The rapid reduction in CO_2 make, as shown in Fig. 3, suggests that between 240 and 250°C there is either a mechanistic change and/or a change in the catalytic surface. We believe that the latter reason is more important and that if a mechanistic change occurs it is due to the catalytic surface having undergone transformation.

Recently Jacobs and Ollis (*19*), working at atmospheric pressure on a similarly prepared catalyst as ours, obtained the same result as described above for CO_2 formation. More importantly they showed that both the reaction rate and selectivity for CO_2 formation declined rapidly at about 250°C not only for the FT reaction but also for the WGS reaction; i.e., the CO_2 formation trend during WGS mimicked that during FT synthesis. Jacobs and Ollis performed X-ray diffraction on catalysts used for FT synthesis for 12 h at 240 and 260°C. The catalyst used at 240°C gave a pattern that was predominantly Fe_3O_4 and some iron–carbon solution; carbides were not observed. At 260°C, however, the X-ray pattern corresponded predominantly to the χ and ϵ iron carbides.

Our X-ray work on a fresh catalyst sample that was inducted in 1:1 H_2:CO at 240°C overnight at atmospheric pressure showed Fe_3O_4, Cu, and some α-Fe. In the FT synthesis tests, our final six experiments were carried out at temperatures $\leq$240°C; X-ray diffraction patterns on this used catalyst showed Fe_3O_4 and Cu but no α-Fe or iron carbides (*20*).

A key experiment by Jacobs and Ollis was performed on a catalyst similar to that discussed so far but not promoted by alkali. In this case the CO_2 formation rate and selectivity did not decrease after 240°C but kept increasing for both the WGS and FT reactions. X-Ray diffraction on such an unpromoted catalyst at both 240 and 260°C showed no signs of iron carbides; the pattern was predominantly Fe_3O_4 and at the higher temperature the pattern due to the iron-carbon solution increased.

It is well known (*21*) that during hydrocarbon synthesis iron-based catalysts make CO_2 as the principal oxygenated product whereas Ni, Co, and Ru-based catalysts make H_2O. However, as indicated in the previous section, H_2O is a primary product on iron-based catalysts and CO_2 is formed via a secondary reaction: the water–gas shift.

Though, of course, X-ray results do not give information regarding the state of the catalyst surface, our work and that of Jacobs and Ollis strongly suggests that the reason why CO_2 is obtained so readily on Fe-based catalysts is because the catalyst, at least in part, offers a very active surface, magnetite, for WGS: magnetite being a well known active material for the shift reaction (*22*). During our experiments at or below 240°C, we speculate that the catalyst surface has a significant amount of Fe_3O_4; thus enabling substantial amounts of CO_2 to be formed. It is very likely that shift occurs via the Temkin regenerative mechanism (*23*) in which the adsorbed reactant CO combines with the surface oxygen [O] of magnetite to give CO_2

$$CO_{ad} + [O] \rightarrow CO_2 + [\ ]$$

and the primary FT product water regenerates the surface

$$H_2O_{ad} + [\ ] \rightarrow H_2 + [O]$$

This mechanism on magnetite has been confirmed by Boreskov *et al.* (*24*) and most recently substantiated by Dumesic and coworkers (*25*).

In our case, at reaction temperatures above 240°C, we postulate that iron carbides are rapidly formed leading to the observed rapid decrease in CO_2 formation. Two limiting possibilities therefore exist for the decreased CO_2 production above 240°C. First, the amount of surface Fe_3O_4 present is decreased, and the fewer available sites for WGS result in less CO_2 formation. Second, the surface contains no Fe_3O_4 and is completely carbided: this too would result in less CO_2 formation as the rate of WGS is less on iron carbide than on Fe_3O_4 (*16, 17*). The WGS mechanism on the carbide would, of course, not be of the regenerative type but may follow the adsorption scheme postulated by Oki *et al.* (*26*).

Early investigations at the U.S. Bureau of Mines (*16, 27*) showed that magnetite was an integral and often substantial part of an iron-based FT catalyst. McCartney *et al.* (*27*) found that catalysts, similar to the one used by us, after induction or use in the synthesis reaction, gave electron diffraction patterns of magnetite though X-ray patterns suggested that carbides were also present. The authors suggested that the catalyst surface is predominantly magnetite and that the oxided state of the catalyst surface is maintained due to the presence of product H_2O and CO_2 during reaction. Later Shultz *et al.* (*16*) confirmed the fact that H_2O plays a very important role in determining the surface state of the iron-based catalyst. They found that even on an iron catalyst that was carbided before being used magnetite formed during the synthesis reaction. And the rate of magnetite formation increased with higher conversions of H_2 + CO, i.e., with greater H_2O make. Shultz *et al.* (*16*) postulated that water would directly oxidize Fe_2C to give magnetite, H_2, and C or CH_4. They stated that during their investigation with iron-based catalysts the H_2O/H_2 ratio was always large enough for oxidation of the catalytic surface; indeed such oxidation was possible at CO + H_2 conversions greater than only about 5% (*16*). On the other hand, the CO_2/CO ratio was probably large enough for oxidation only at conversions greater than 80% (*16*).

Thus the partial pressure of H_2, CO, CO_2, and H_2O, the experimental conditions and extent of reaction, and, as shown by Jacobs and Ollis (*19*), the presence of a promoter can all affect the state of an iron catalyst surface during FT synthesis. This complex situation may be schematically represented as follows:

$$\begin{tikzcd} Fe_3O_4 \arrow[r, shift left] \arrow[rr, bend right, shift right] & Fe \arrow[l, shift left] \arrow[r, shift left] & \text{Carbide } (\epsilon', \epsilon, \chi) \arrow[l, shift left] \arrow[ll, bend left, shift left] \end{tikzcd}$$

Often at the start of the synthesis reaction, a reduced fused iron catalyst may be predominantly in the metallic state. However, past investigations of used traditional FT iron-based catalysts, either fused or precipitated, have not found metallic Fe to be a major component to the same extent that Fe_3O_4 and/or carbides are major components.

McCartney *et al.* (27) found that on their iron-based catalysts the catalytic activity and selectivity remained essentially constant over the experimental period in which both the catalyst surface and bulk were being converted to Fe_3O_4. Interestingly, nitrided iron catalysts whose surface contained nitrides and carbonitrides showed marked differences in activity and selectivity (27) when compared with inducted, reduced, or carbided iron catalysts; all of the latter being much more similar to each other. In our case, over the whole range of temperature studied the amount of reacted CO converted to C_5+ hydrocarbons remained quite constant. Jacobs and Ollis (19) even on their unalkalized catalyst, in which X-ray patterns of carbides were not observed, found that reaction did take place; interestingly the rate of methanation on promoted and unpromoted catalyst was close, whereas the overall rate of CO reacted was much higher for the promoted catalyst.

It seems that there is synthesis activity whether the iron catalyst is more in the "oxided" state or the "carbided" state. This suggests that either most, if not all, forms of iron are active for the FT synthesis, or that some type of active site can exist in the presence of both oxides and carbides. Indeed, though the catalyst bulk is an identifiable oxide and/or carbide, the surface under reaction conditions may be a combination of iron, carbon, and oxygen whose mole ratios are quite different from those in the bulk. Thus it is tempting to speculate that the active site may be composed of clusters of active metallic iron. The performance and stability of this active Fe may be influenced by whether it is present on top of and/or next to a carbide or oxide phase.

For CO_2 formation, these speculative suggestions may be coupled with the scheme shown above. When conditions favor the limit $Fe_3O_4 \leftrightharpoons Fe$, more CO_2 is produced due to the large presence of magnetite; when conditions favor the limit $Fe \rightleftharpoons$ carbides, CO_2 production falls because magnetite is not present and WGS takes place more slowly on the carbide (16, 17).

Similarly, the state of the iron surface may control the extent and rate of catalyst deactivation by sulfur. As stated in the Introduction (5) and as shown in the Results section, a partially oxided iron surface is more resistant to S poisoning than a well reduced, metallic iron surface. Anderson *et al.* (7) showed that a carbided or nitrided iron surface was also more resistant to S poisoning than a reduced iron surface. Though the physical state, surface area and pore size distribution, of a catalyst can affect deactivation, we believe the chemical state of the iron surface is a more determinative factor.

Recently, studies on clean and preoxidized iron surfaces led Dwyer and Somorjai (28) to speculate that a small concentration of highly active clean iron sites may be responsible for FT activity. Similarly, Matsumoto and Bennett (29) state that in the presence of adsorbed hydrogen bulk carburization does not affect the surface which remains metallic and active for synthesis.

Recent investigations on supported iron catalysts carried out at differential conditions in conjunction with Mössbauer Spectroscopy by Raupp and Delgass (30, 31) and by Amelse *et al.* (32) have brought to light some interesting features of the synthesis reaction. However, an iron surface, when reaction conversions are low, may not reflect an iron surface at high conversions in the presence of higher H_2O and CO_2 formation. As stated elsewhere in the discussion, H_2O and to a lesser extent CO_2 play an important role in defining the steady-state surface where synthesis and WGS take place. We suggest that when differential FT studies are carried out on iron catalysts at least some experiments be performed in which H_2O and/or CO_2 are added to the reactants so that realistic values of H_2O/H_2 and CO_2/CO are achieved over the catalyst. This would further enhance the use of differential studies on iron catalysts to explain FT synthesis. We also suggest that CO_2 formation during synthesis may be used as a probe in helping to understand the catalytic surface during FT synthesis and consequently the effect on the surface due to particle size, support, and promoter. It is intriguing, for example, that Raupp and Delgass (*31*) report that excessive amounts of CO_2 were formed on their iron on magnesia catalyst.

Condensed Product Distributions

Figure 4 shows that the condensed product distributions for the sulfided and unsulfided catalyst are very similar. For the latter catalyst, there is a small variation around C_{32} from an otherwise smooth plot. We can offer no explanation for this. The chromatograph was checked for linearity of response factors by means of calibration standards containing *n*-paraffins of carbon number $n > 30$. We also note that there is some loss of light products. Thus these distributions are useful in giving trends rather than accurate yields. Even though the light products have been lost, we can analyze the data to give some useful information.

Friedel and Anderson (33) used the following equation to analyze chain growth in FT synthesis:

$$\phi_n = \phi_x \alpha^{n-x}, \qquad n \geq x \qquad (4)$$

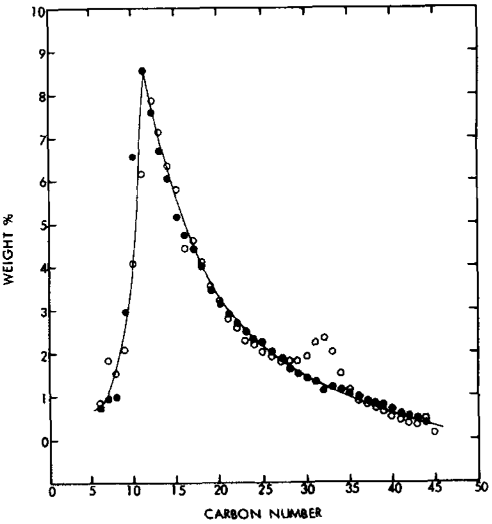

FIG. 4. Distribution of condensed products. $T \simeq 240°C$, $P = 1.0$ MPa, GHSV $\simeq 250$ V/V/h, $H_2/CO \simeq 1.5$. Open points, unsulfided catalyst; solid points, sulfided catalyst.

where ϕ is the moles of product of carbon number n or x, and α is the probability of chain growth. This equation is Markovian. And it may be used to fit data even if reliable data are available only after a certain carbon number. If one normalizes for carbon numbers $\geq x$, Eq. (4) reduces to

Weight fraction $[W_n]$

$$= \frac{n\alpha^{n-x}(1-\alpha)^2}{1+(x-1)(1-\alpha)}, \qquad n \geq x. \qquad (5)$$

At $x = 1$, Eq. (5) is the Flory equation which has been used recently (*34–37*) to analyze FT data. On plotting ln W_n/n versus n, data fitting Eq. (5) should give a straight line with slope α.

With the data given in Fig. 4, we obtain the result shown in Fig. 5. The data do not fall on a single straight line. There is a distinct break, and the data may be represented by two lines. Breaks in similar plots have been shown by Anderson (*16*), albeit at lower carbon numbers, when plotting results of Fe-based catalysts studied at the Schwarzheide tests. Hall *et al.* (*38*) have suggested that beside stepwise growth with

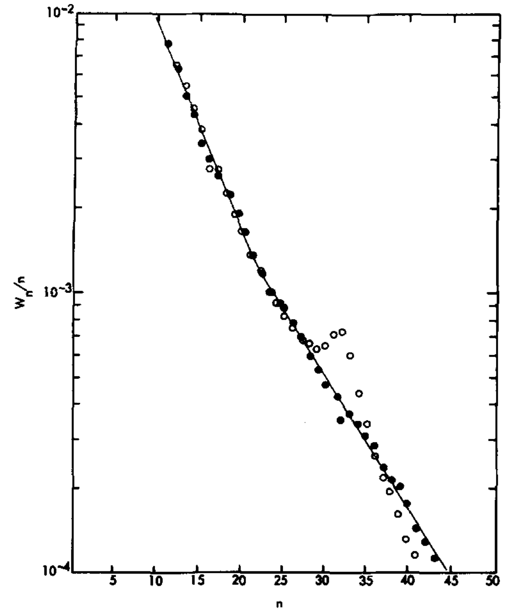

FIG. 5. Plot of ln W_n/n versus carbon number n. Experimental conditions as in Fig. 4. Open points, unsulfided catalyst; solid points, sulfided catalyst.

single carbon intermediates multiple build-in of growing chains could occur during synthesis. This could affect the growth rate of heavy hydrocarbons. Alternatively, we suggest that chain growth takes place on at least two types of sites, each having a slightly different chain growth probability α.

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