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COMPARISON OF IRON FISCHER-TROPSCH CATALYSTS USING ON-LINE GAS CHROMATOGRAPHY

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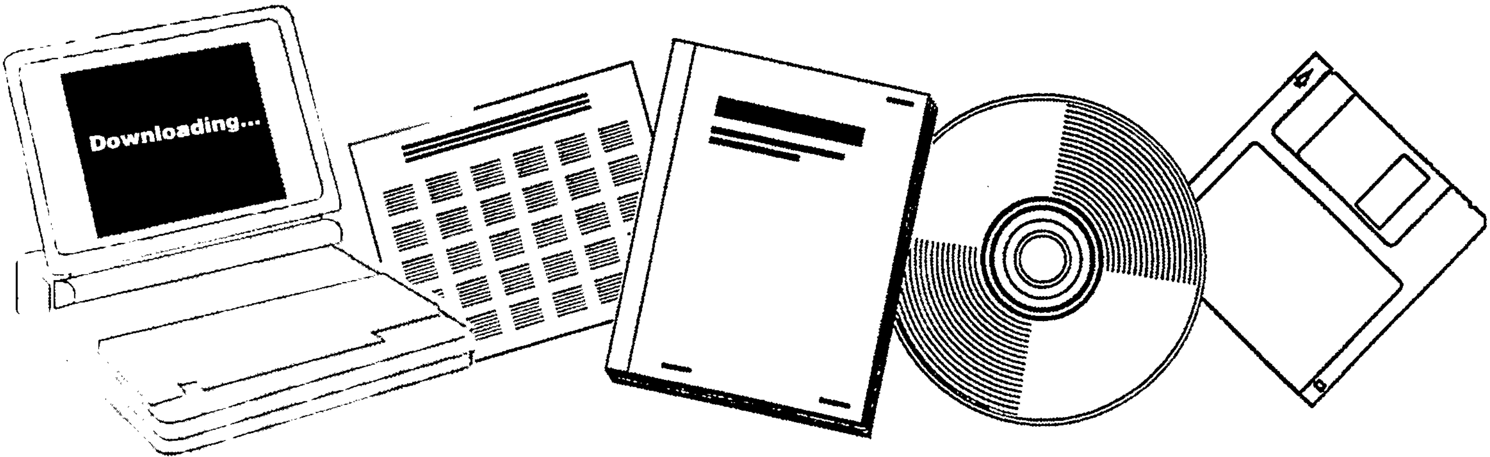

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A COMPARISON OF IRON FISCHER-TROPSCH CATALYSTS USING ON-LINE GAS CHROMATOGRAPHY

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Iron-based Fischer-Tropsch (F-T) catalysts could well play an important role in the conversion of lean syngas mixtures ($H_2/CO < 1$) to liquid fuels in a liquid phase reactor. While a tremendous amount of data concerning catalyst performance has been accumulated over the past 50 years, seldom have Fischer-Tropsch catalysts been tested under identical reaction conditions; therefore a meaningful comparison of catalyst activity and selectivity could not be made. Such data are important in order to select a catalyst that will yield a given product slate. In particular, attention will be given to determining which catalyst would be most effective in maximizing gasoline selectivity in a slurry reactor.

The problems encountered in testing catalysts used for syngas conversion are well documented and will be described only briefly here. The highly exothermic nature of the reaction precludes the use of large volumes of catalyst for converting large volumes of syngas in an adiabatic vapor phase reactor. Berty reactors or reactors with external recycle capability can be operated so as to achieve nearly isothermal operation, but these reactors are expensive and labor intensive and therefore not well suited for screening a large number of catalysts. Meaningful conversion-selectivity data can be obtained using adiabatic microreactors, where the magnitude of the temperature exotherm can be minimized by dilution of the syngas with an inert gas, dilution of the catalyst bed, and working at low percent conversion of syngas. While these microreactors are found in most catalyst laboratories, one problem associated with their use in converting syngas to liquid products is the fact that periods as long as 24 hours are required to accumulate a few mL of liquid product. Quantitative recovery of such a small amount of product is difficult. Exacerbating the recovery problem is the fact that light gases dissolved in the liquid product are flashed off whenever liquid samples are taken. Recovery of these gases when working on the microreactor scale is nearly impossible. Even if 100% product recovery could be effected, a significant change in conversion or selectivity over the period of the run can easily render meaningless the calculation of conversion and selectivity.

These product recovery problems can be largely circumvented by the use of an on-line gas chromatographic analysis. A schematic of the combined reactor - G.C. (gas chromatograph) is shown in Figure 1. The reactor was a 0.0095-m diameter stainless steel tube mounted vertically above the G.C. and connected to the sample valves of the G.C. by a heated transfer line. This line and the sample valve compartment were maintained at the same temperature as the reactor to insure that condensation of the F-T product did not occur. A detailed drawing of the sample valve compartment is shown in Figure 2. The gas chromatograph was a Hewlett-Packard* 5750A equipped with dual flame ionization detectors (FID) and dual thermal conductivity detectors (TCD). The product gas from the reactor passed through the first sample valve and then to an ice trap where the aqueous product and C_{5+} hydrocarbons were condensed. The unreacted syngas, CO_2, and C_1-C_4 hydrocarbons then entered the second sample valve and from this valve proceeded to the back pressure regulator. Column 1 was a 6.1-m x 0.0032-m 10% SP 2100 on 100/120 Supelcoport which was effective in resolving the C_1-C_{20} product according to carbon number. Column 2 was a 1.83-m x 0.0032-m 100/120 Carbosieve

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*Use of brand names facilitates understanding and does not necessarily imply endorsement by the U. S. Department of Energy.

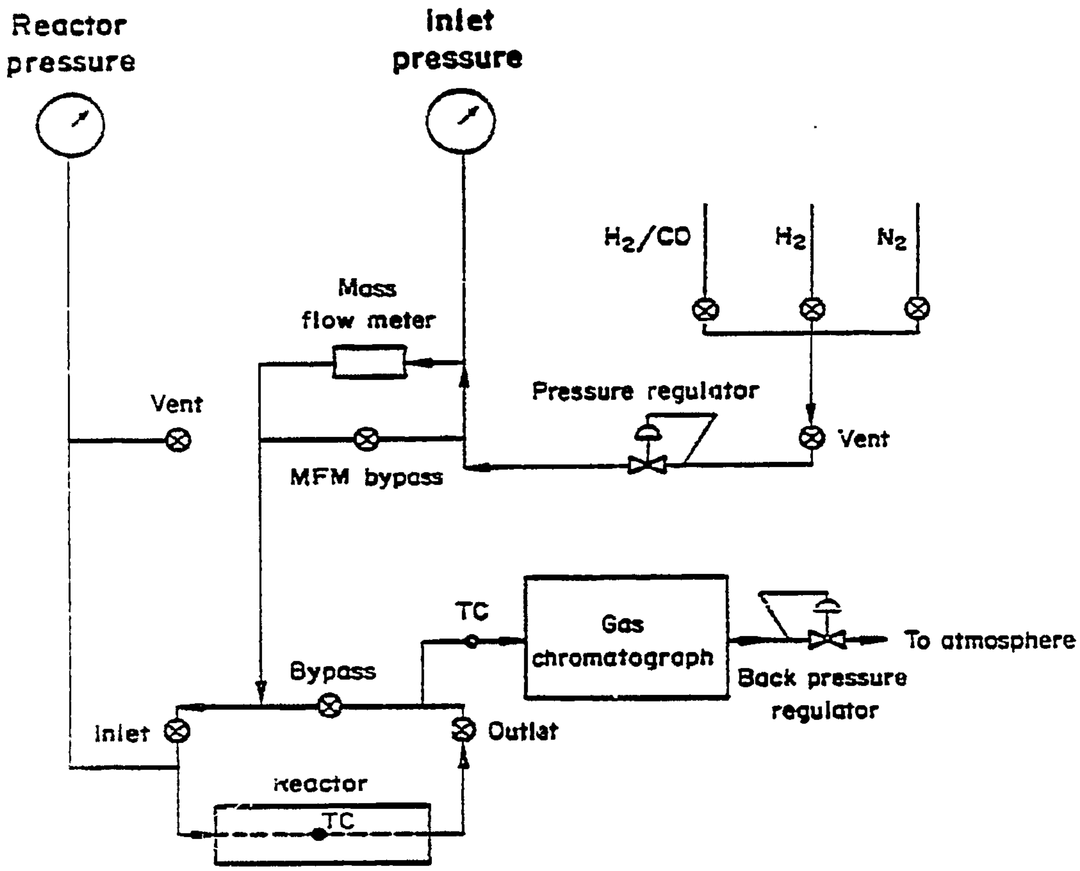

Figure 1 - Micro reactor and Gas chromatograph.

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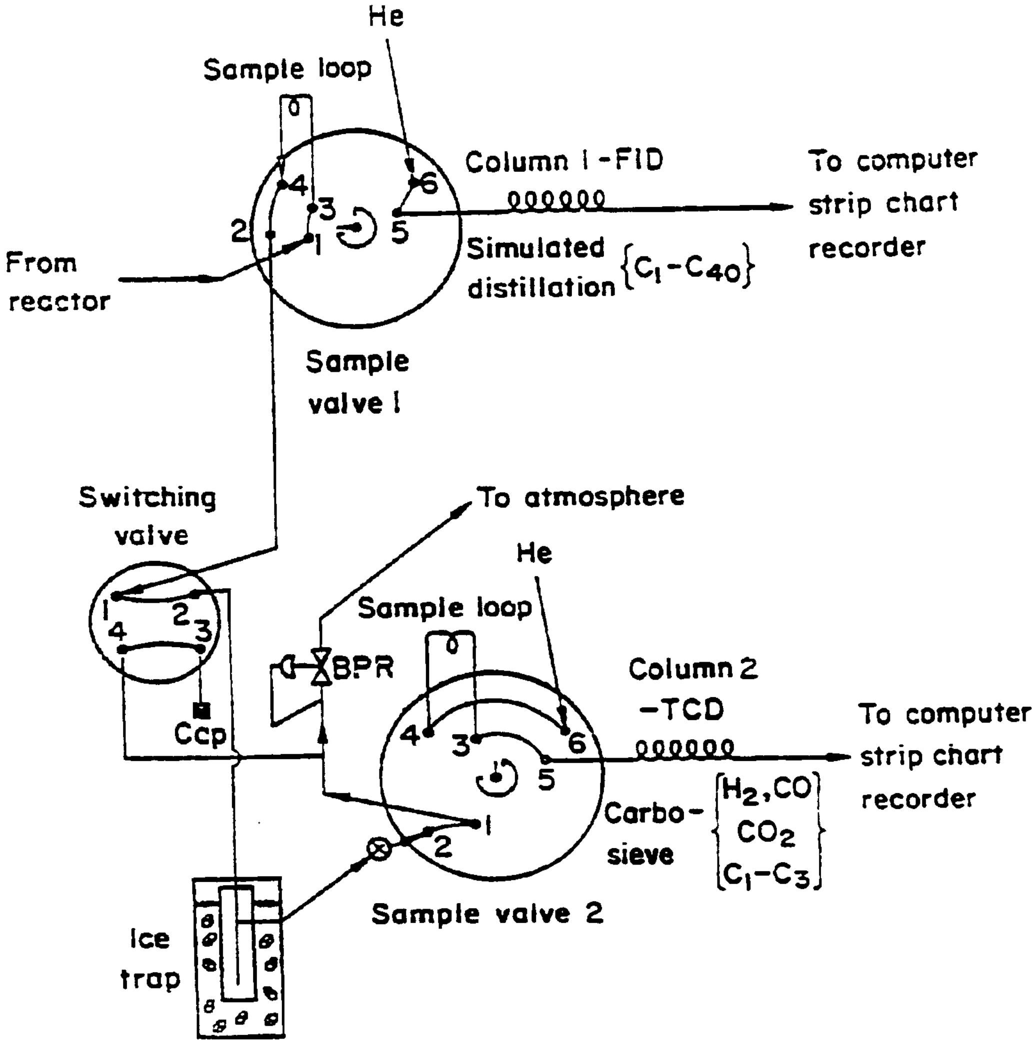

Figure 2 - Sample valve compartment.

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5 column useful for separating the light gases. The oven was temperature-programmed from 223°K (2-minute hold) to 623°K at a rate of 8°K/min. Typical chromatograms are shown in Figure 3. The top chromatographic profile was obtained using column 2 and a TCD. The negative peak is due to H_2, followed by the O_2, N_2, CO, CH_4, C_2H_4, and C_2H_6 peaks. At the same time the FID signal is shown with the peaks of a given carbon number clustered together. The clustering of these peaks greatly facilitates analysis of the data since resolution and identification of each isomer peak was rendered unnecessary for the purposes of this study. The retention times are shown in Tables 1 and 2.

TABLE 1
RETENTION TIMES FOR COMPOUNDS DETECTED BY TCD

Compound	Time (min)
H_2	1.63
CO	15.65
CH_4	22.21
H_2O	23.26
CO_2	26.58
C_2H_4	37.95
C_2H_6	41.06

The on-line G.C. technique has a number of limitations. It is useful for analyzing a product that consists of only paraffinic and/or olefinic hydrocarbons. Oxygenates and aromatics are not resolved from the paraffins and olefins on the SP2100 column and since their F.I.D. response factors differ significantly

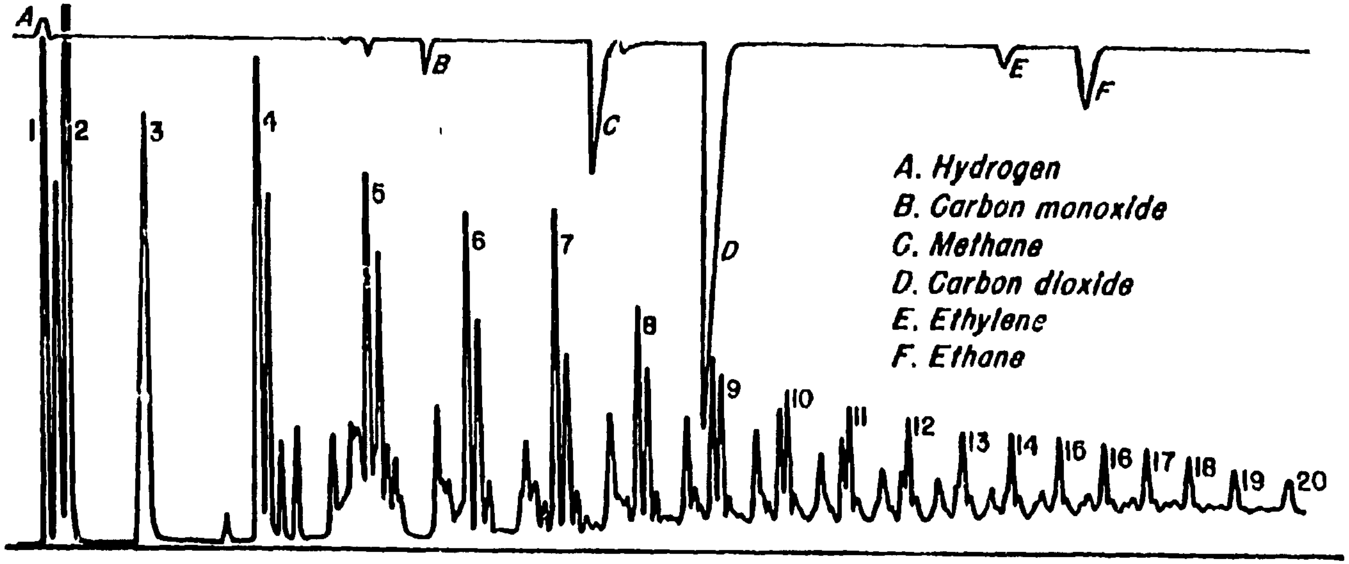

Figure 3 - Gas chromatogram of Fischer - Tropsch Product. Peaks numbered 1-20 represent C_1-C_{20} hydrocarbons as detected by FID. Peaks labeled *A-F* were detected on the TCD.

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TABLE II
RETENTION TIMES FOR COMPOUNDS DETECTED BY FID

Compound	Time (min)
CH_4	1.62
C_2H_4	1.97
C_2H_6	2.37
C_3H_6	5.06
C_3H_8	5.31
C_4*	8.31-11.01
C_5*	12.05-15.00
C_6*	16.41-18.46
C_7*	18.79-21.80
C_8*	22.55-25.60
C_9*	26.03-28.12
C_{10}*	28.73-30.65
C_{11}*	31.25-33.02
C_{12}*	33.61-34.88
C_{13}*	35.25-36.93
C_{14}*	37.79-38.85
C_{15}*	39.50-40.64
C_{16}*	41.22-42.84
C_{17}*	43.13-43.92
C_{18}*	44.38-45.49
C_{19}*	45.96-47.25
C_{20}*	47.74-49.27

*Retention times for C_n (n=4-20) fractions are given for all C_n compounds.

from those of aliphatic hydrocarbons, a significant yield of either oxygenates or aromatics leads to erroneous results in determining product distribution. As far as aliphatic hydrocarbons are concerned, twelve compounds ranging from methane to octadecane were found to have nearly identical F.I.D. response factors (on a weight percent basis). The second problem with this type of G.C. analysis is that if reactor pressure is, for example, 2068 kPa, then the pressure of the product gas in the sample valves is also 2068 kPa. As a result, when the sample is injected into the carrier gas stream which is at 345 kPa, considerable expansion of the injected sample occurred, resulting in peak broadening and poorer resolution. Runs have been made at pressures as high as 2758 kPa, but at that pressure the peak broadening makes it difficult to resolve methane from ethylene and ethane using the SP2100 column. Resolution of these peaks is critical because the methane peak is used to relate the CO and CO_2 peaks from the TCD with the C_{2+} peaks from the FID.

Having determined the weight fractions for the various carbon numbers, the Anderson-Schulz-Flory (A-S-F) equation was used to determine if the selectivity data could be reconciled to a polymerization type reaction as suggested by Anderson et. al.,(1) Henrici- Olive and Olive,(2) and others.

$$\log W_n/n = n \log p + \log \frac{(1-p)^2}{p}$$

where W_n = weight fraction of carbon number n

p = probability of polymerization

From a plot of $\log W_n/n$ vs. n, the slope = log p, and the intercept on the ordinate $= \log \frac{(1-p)^2}{p}$. Having calculated p, one can then calculate the degree of polymerization, D, where $D = \frac{1}{1-p}$.

TABLE 3
FUSED IRON CATALYST COMPOSITION AND ACTIVATION CONDITIONS

	Temperature, °K	Time(min)	Gas	Space Velocity (liters hr^{-1} g^{-1})
Reduction	723	120	H_2	7.2
Induction	523	60	$H_2/CO=1$	7.2
Synthesis	573		$H_2/CO=3$	7.2

The following data were obtained using the on-line G.C. technique with a fused iron catalyst, C-73-2, available from United Catalysts. The catalyst composition and conditions for reduction, induction, and synthesis are given in Table 3. Reduction and induction were carried out at 101 kPa; synthesis pressure was 2068 kPa. The A-S-F plot is shown in Figure 4. There is some curvature at the high carbon numbers, which is due to a baseline shift resulting from column bleed from the SP2100 column. Experimental artifacts of this sort can easily mislead the casual observer to the conclusion that a meaningful deviation from the A-S-F distribution has been found. In general, however, deviation of the point for C_2 is not uncommon when studying iron catalysts and probably results from the facile incorporation of ethylene into the growing carbon chain.

The on-line microreactor technique has been used to determine the conversion and selectivity of a number of iron-containing Fischer-Tropsch catalysts. The study was carried out with the objective of finding a catalyst that would maximize gasoline selectivity as well as unsaturates while at the same time minimizing C_1-C_2 formation and carbon deposition. Since the long term objective is to use the microreactor technique to select catalysts for use in a slurry phase reactor,

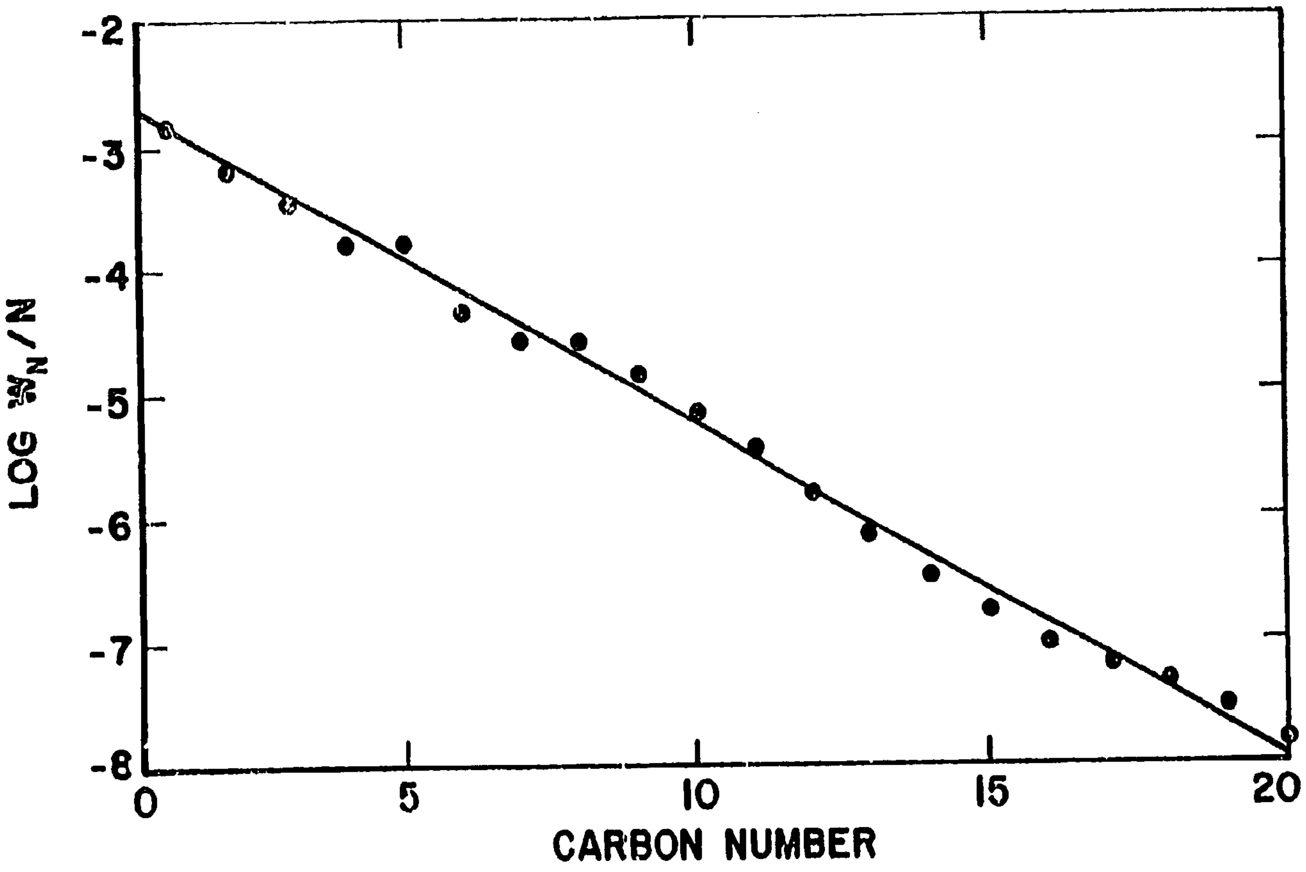

Figure 4 - Anderson - Schulz - Flory Plot of C-73-2 Fused Iron Catalyst (T=573°K, H_2/CO=3).

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a lean syngas ($H_2/CO = 1$) was used. The recent growing interest in the slurry phase reactor arises predominantly from economic considerations. So-called second generation gasifiers, such as the Texaco, Shell-Koppers, and BGC-Lurgi gasifiers, are more efficient than earlier gasifiers and produce a H_2-lean syngas with a $H_2/CO \approx 0.6$. Iron Fischer-Tropsch catalysts, if used with such a lean gas, will deactivate readily in a fixed-bed, gas-solid reactor due to carbon deposition on the catalyst surface. As a result, an expensive water-gas shift step is required to increase the H_2/CO ratio to 2 or higher. Slurry reactors, however, because of their more effective heat removal and elimination of hot spots can be used with a lean syngas. Thus, by eliminating the need for a water-gas-shift step through the use of a slurry reactor, the improved thermal efficiency of the second-generation gasifiers results in greater efficiency for the overall process involving conversion of coal to hydrocarbon fuels. According to R.M. Parson's study in 1977,(3) it was estimated that up to 6% cost reduction would result for a coal-based slurry phase F-T plant, as compared to a coal-based gas phase F-T plant. However in order to make a complete economic comparison, it is necessary to establish the conversion-selectivity data for the F-T catalysts.

The composition and manner of catalyst preparation are as follows:

A. Fused iron - United Catalysts C-73-2

Wt.% Fe- 67.1 Al_2O_3-3.02
CaO- 1.82 K_2O- 0.60
MgO- 0.17

B. Precipitated iron. Prepared by adding a 10% Na_2CO_3 solution to a 10% $Fe(NO_3)_3 \cdot 9H_2O$ solution, both at 353°K, until a pH of 7 was reached. After heating the resulting slurry to boiling, the slurry was filtered and washed with deionized water. The soda content was less than 0.1%.

C. Potassium-promoted precipitated iron. Prepared as above, but a 10% K_2CO_3 solution was added to the moist filter cake. The K content was 1.1%.

D. Precipitated iron-cobalt (potassium-promoted). Prepared in a manner similar to that described for B and C (%Fe-36.8, %Co-13, %K-5.1).

E. Precipitated iron-manganese. This catalyst was provided by Professor Deckwer, Hannover University, W. Germany. This Kolbel-type catalyst was prepared by mixing a $Fe(NO_3)_3 \cdot 9H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ solution at a temperature of 368°K and at a pH of 7. The Mn/Fe ratio was 9.

In order to maximize catalyst performance, thermogravimetric studies were carried out to determine the effect of the following variables:

1. Reduction temperature and gas composition
2. Carbiding temperature and gas composition
3. Effect of reduction temperature on carbiding rate

A Perkin-Elmer TGS-2 analyzer system was used to determine the weight changes observed as a result of the reduction and carbiding reactions. All thermogravimetric and microreactor studies were carried out with a (-200 ÷ 325) mesh particle size.

A. Fused iron. The reduction in H_2 of this catalyst at different temperatures is shown in Figure 5. Not only is the reduction temperature important from the standpoint of the time difference required for reduction but also because of its effect on the rate of carbiding, as indicated in Figure 6. The difference in carbiding rates is probably due to the difference in the exposed metal surface area of the catalysts, although a crystallite size dependence (after normalizing the rate for metal surface area) cannot be ruled out. Microreactor studies were carried out by reducing the catalyst at $723^{o}K$ in H_2, followed by carbiding with syngas ($H_2/CO = 1$) at $523^{o}K$ at 101.3 kPa.

B,C,D. Precipitated iron catalysts. It is apparent from Figure 7 that the reduction of the cobalt-containing catalysts proceeds most rapidly, as would be expected in view of the greater ease in reducing oxides of Co. The potassium-promoted iron catalyst reduces less rapidly than the unpromoted iron catalyst, B. This is consistent with observations by other workers, particularly Dry,(3) who have shown that while potassium increases carbiding rates, the rate of H_2 reduction decreases. The difference in carbiding rates is shown in Figure 8. While the difference between the potassium promoted and unpromoted catalysts is small, the addition of Co

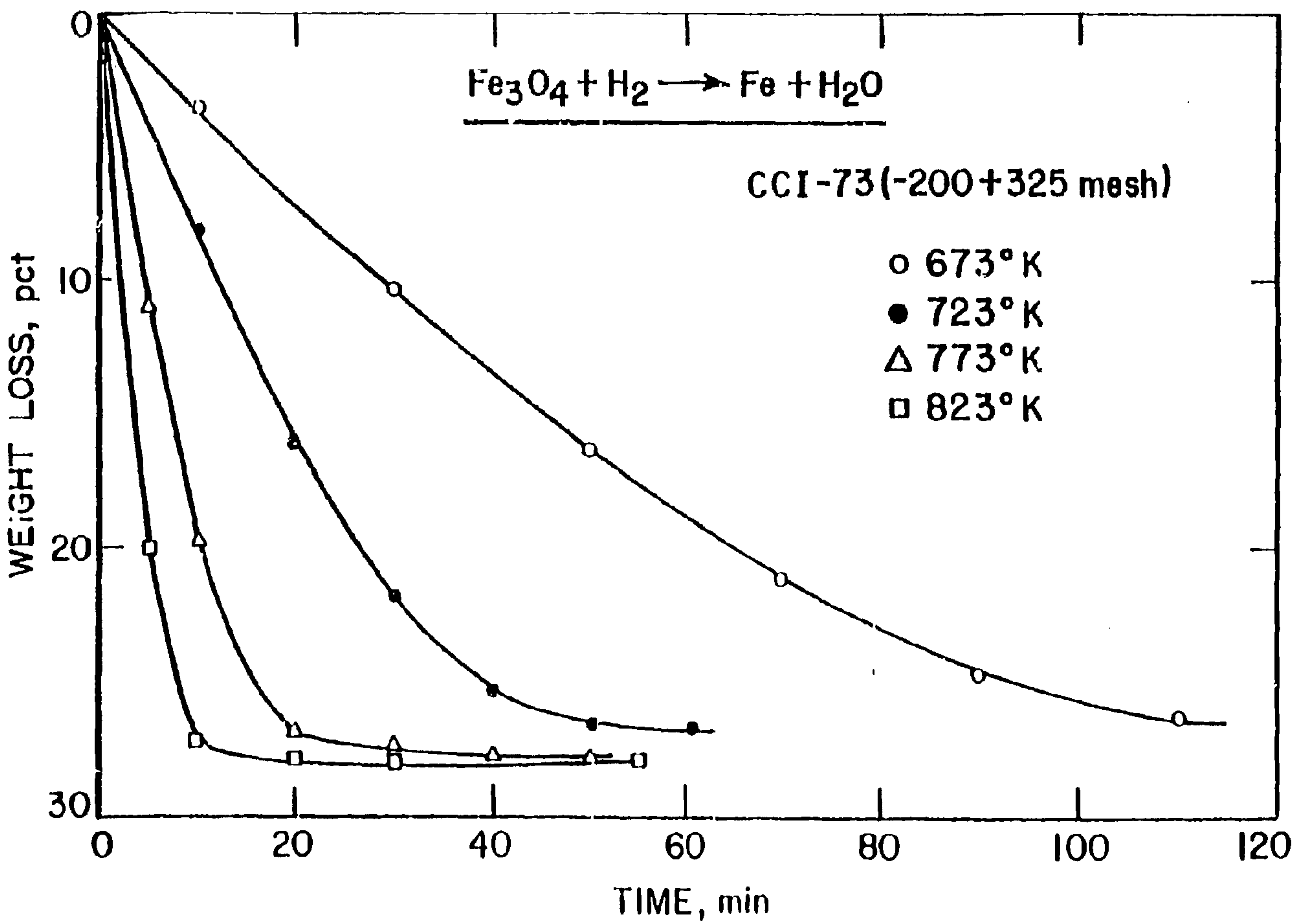

Figure 5 - Reduction of 200/325 mesh Fused Iron Catalyst as a function of temperature.

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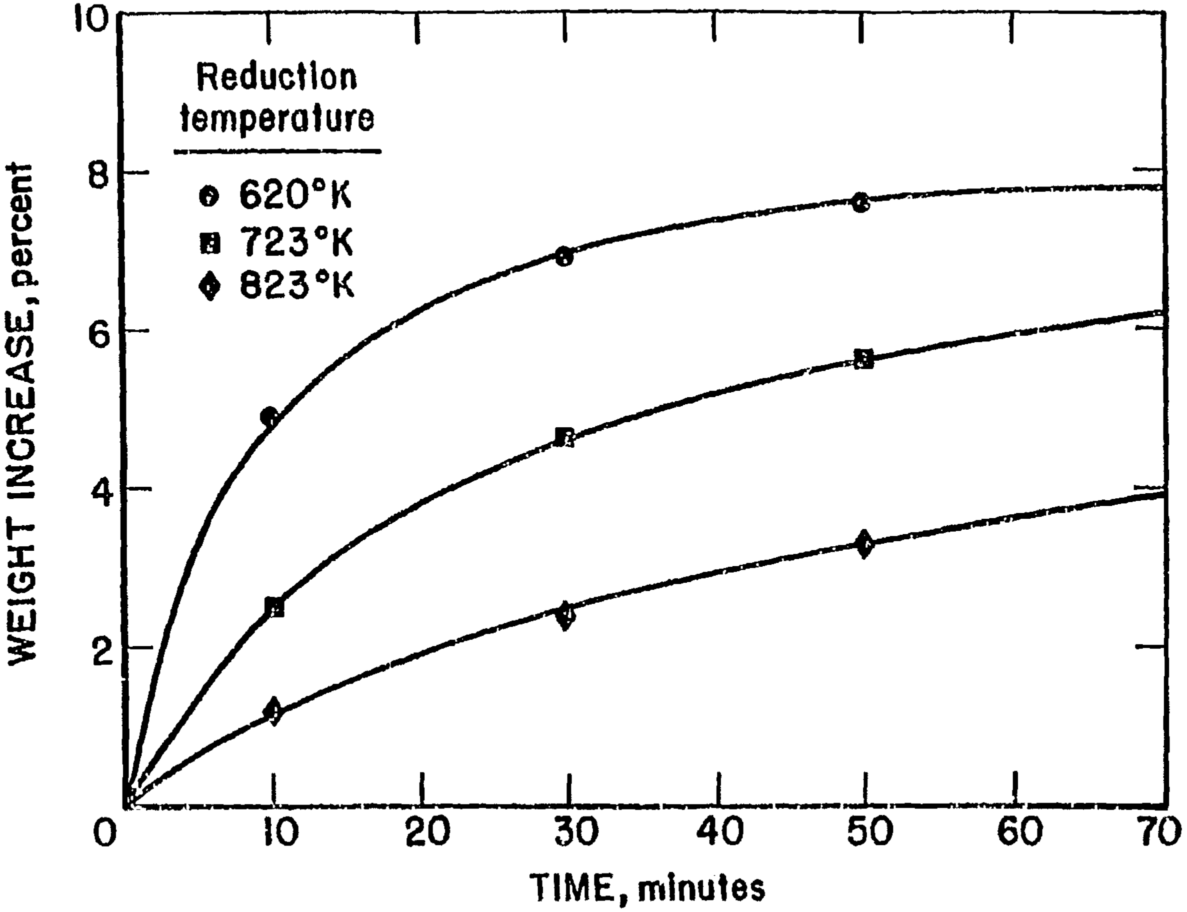

Figure 6 - Carbiding of Fused Iron Catalyst in Syn Gas (1/1) at 493°K.

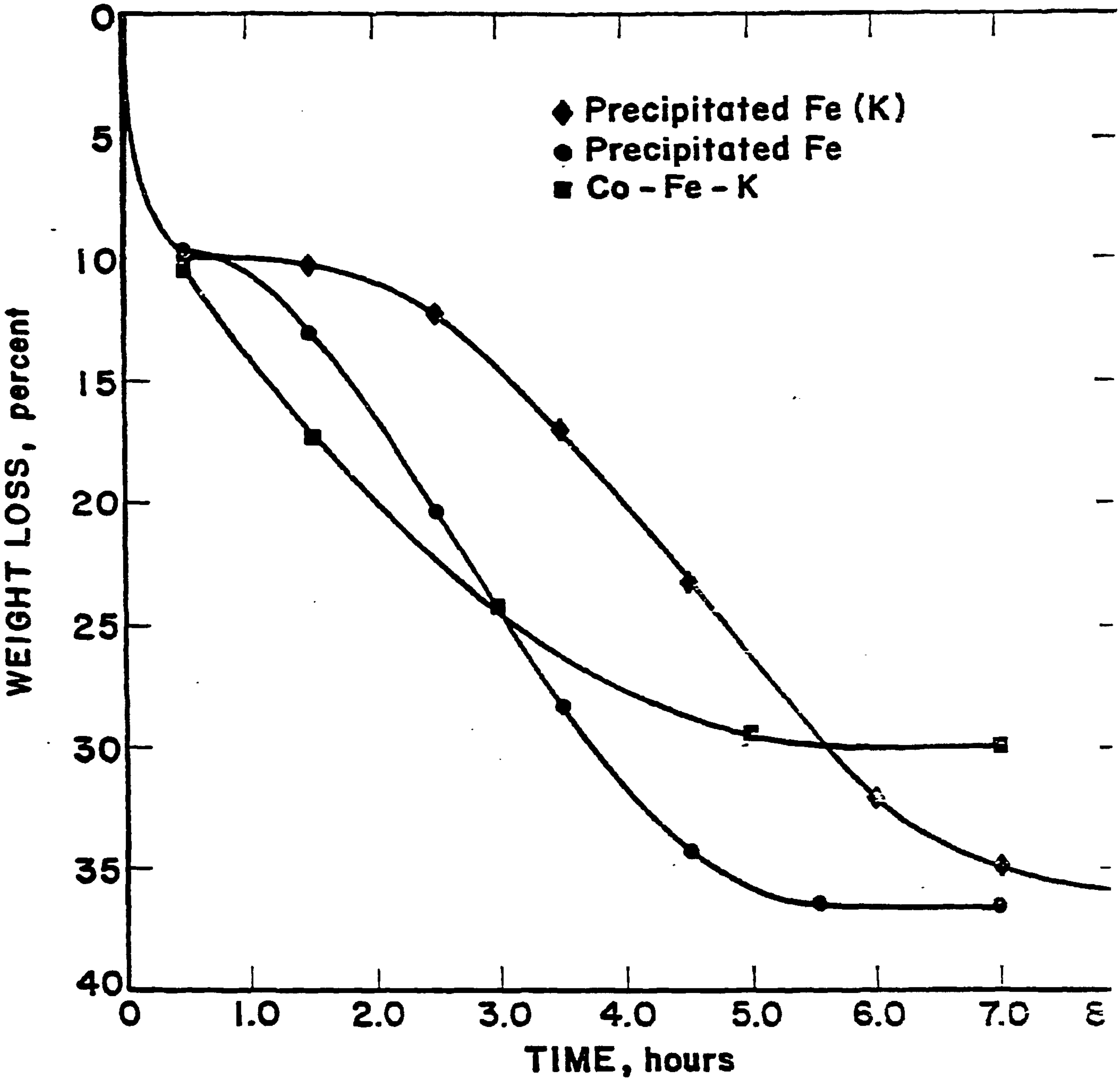

Figure 7 - Reduction of Precipitated Iron Catalysts in H_2 at 523° K.

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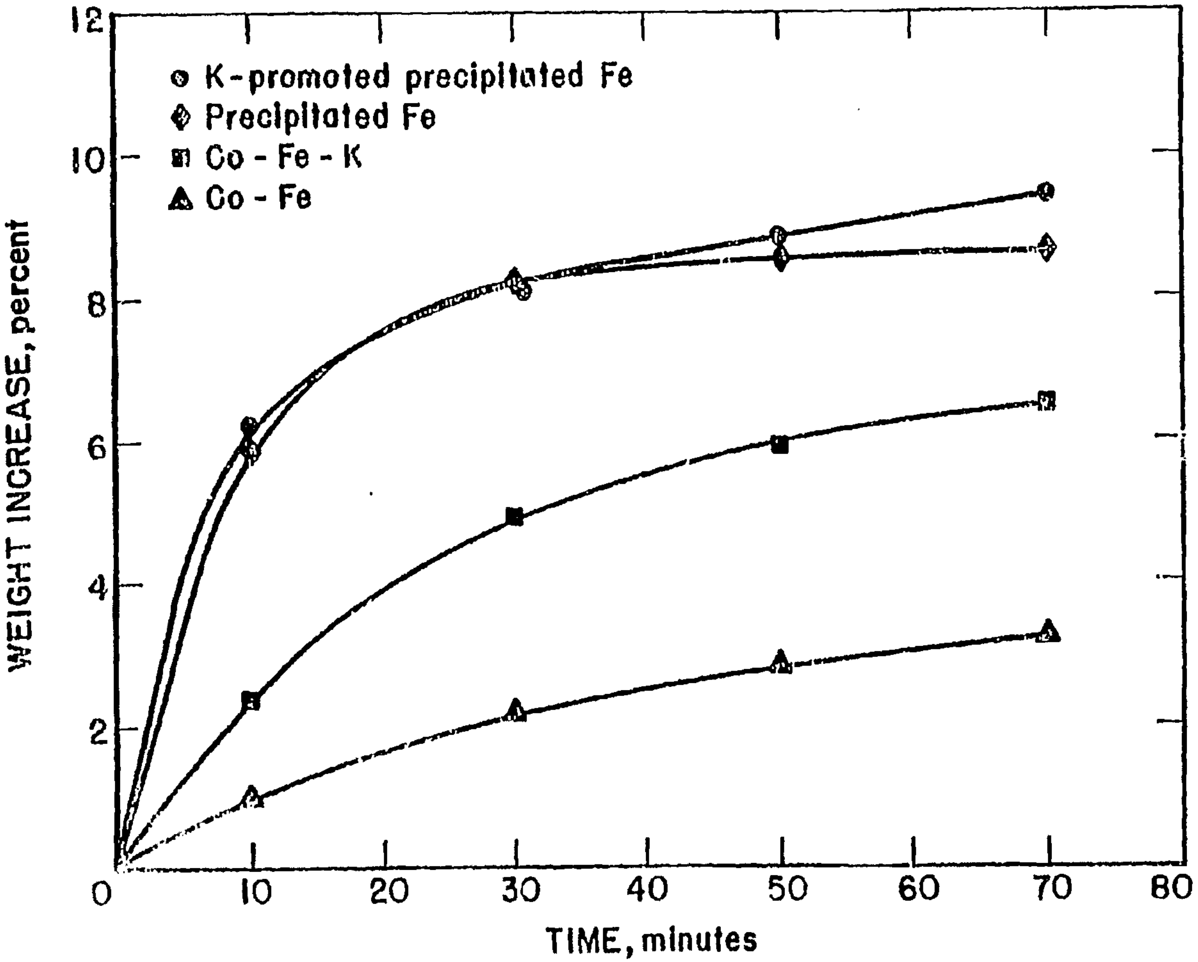

Figure 8 - Carbiding of Iron Catalysts with 1/1 Syn Gas at 493°K.

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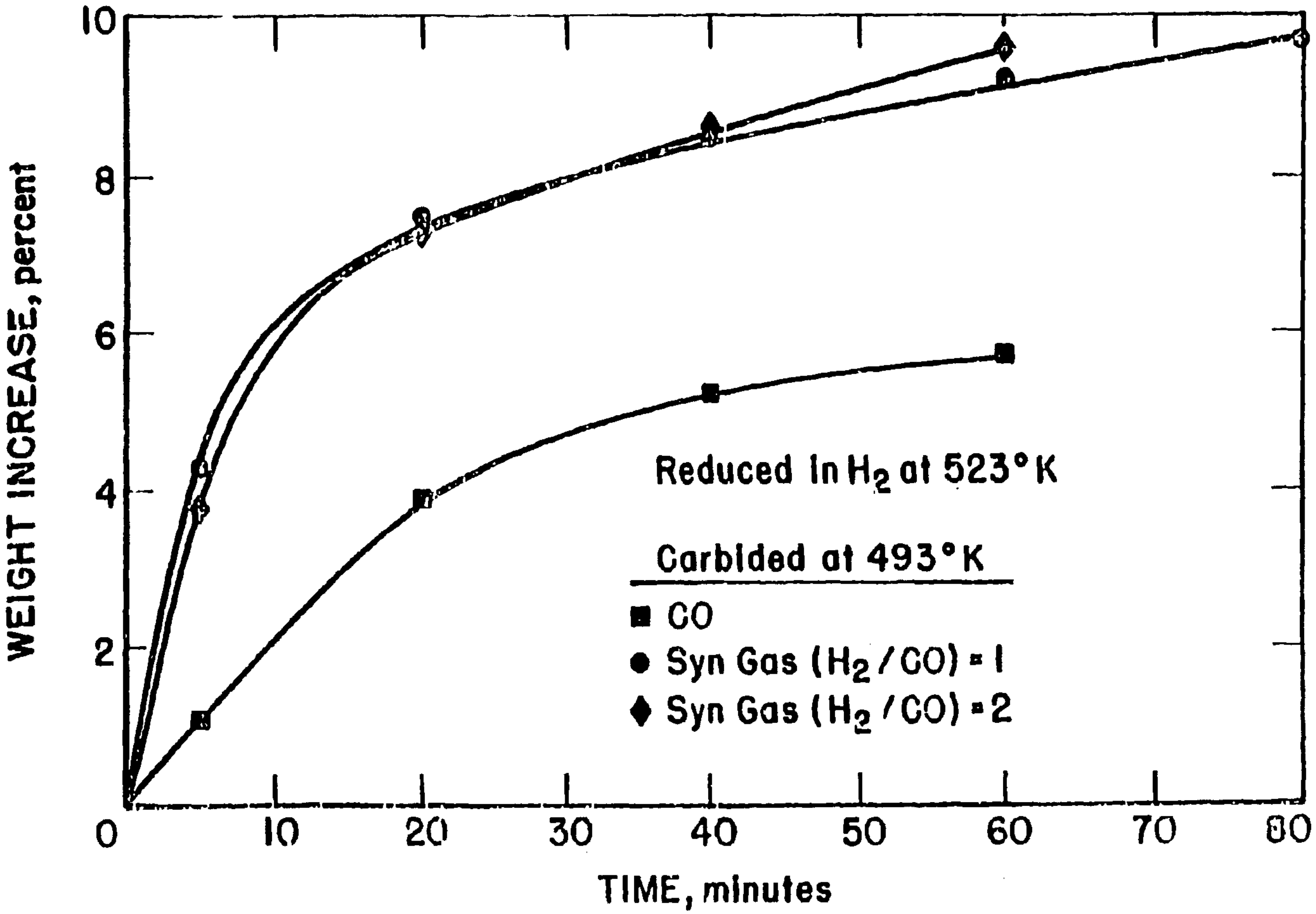

Figure 9 - Carbiding of K-promoted Precipitated Iron Catalyst.

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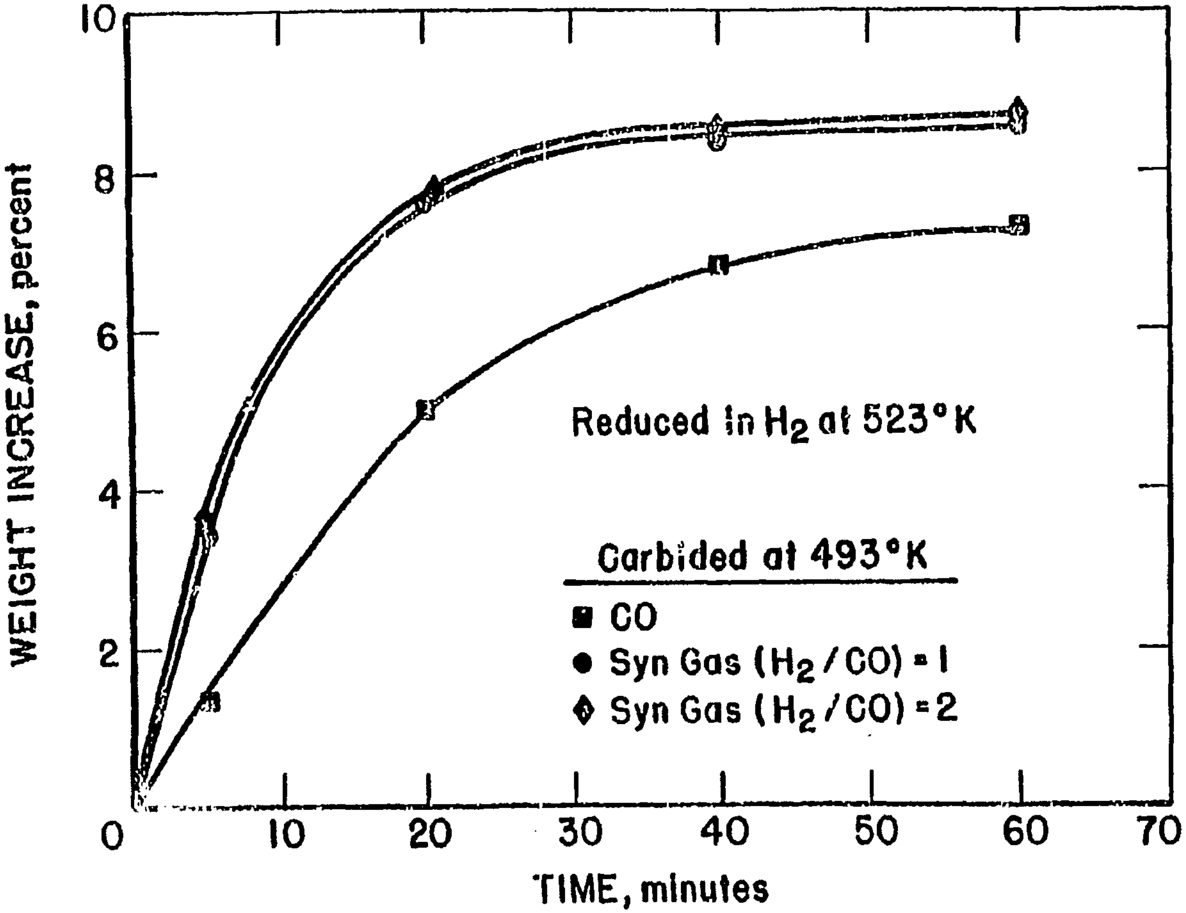

Figure 10 - Carbiding of Precipitated Iron Catalyst.

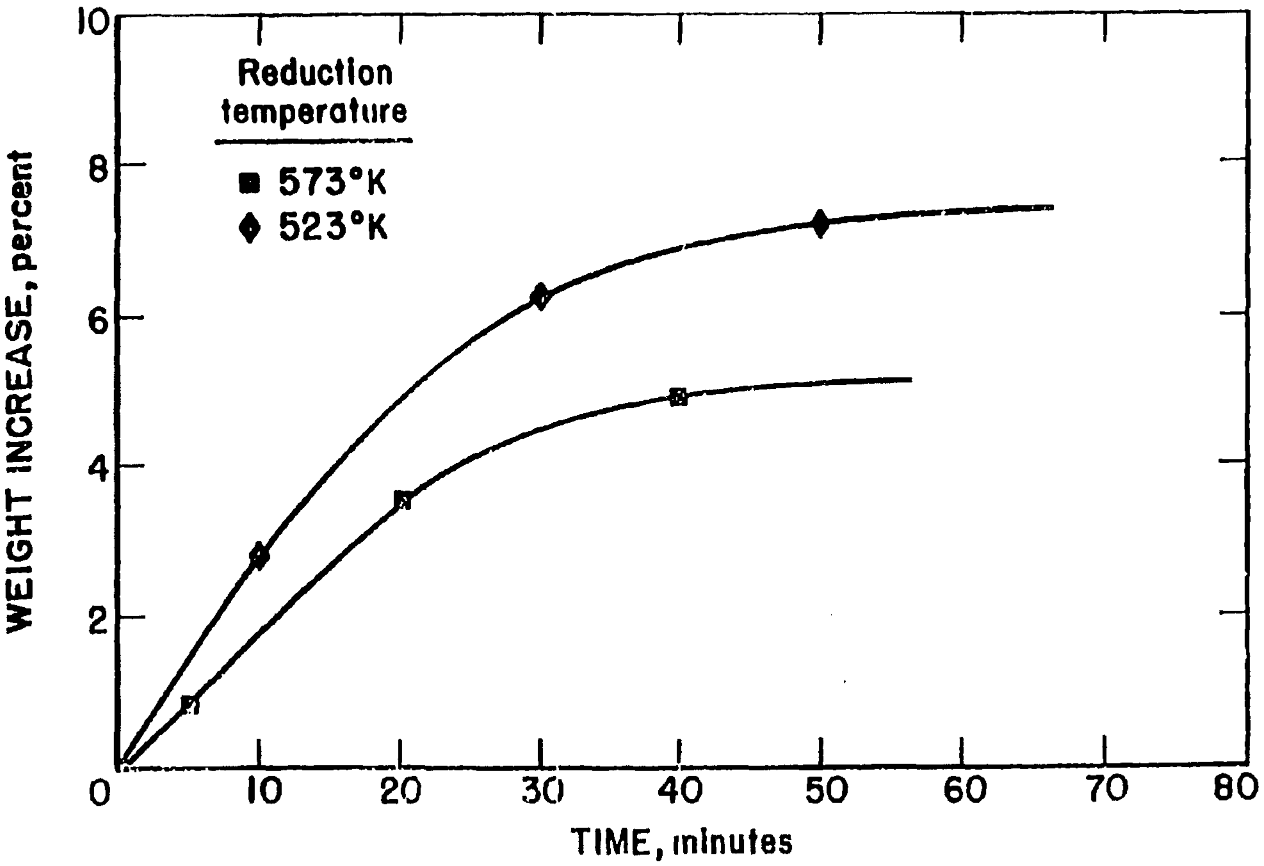

Figure II - Carbiding of Precipitated Iron Catalysts in CO at 493°K.

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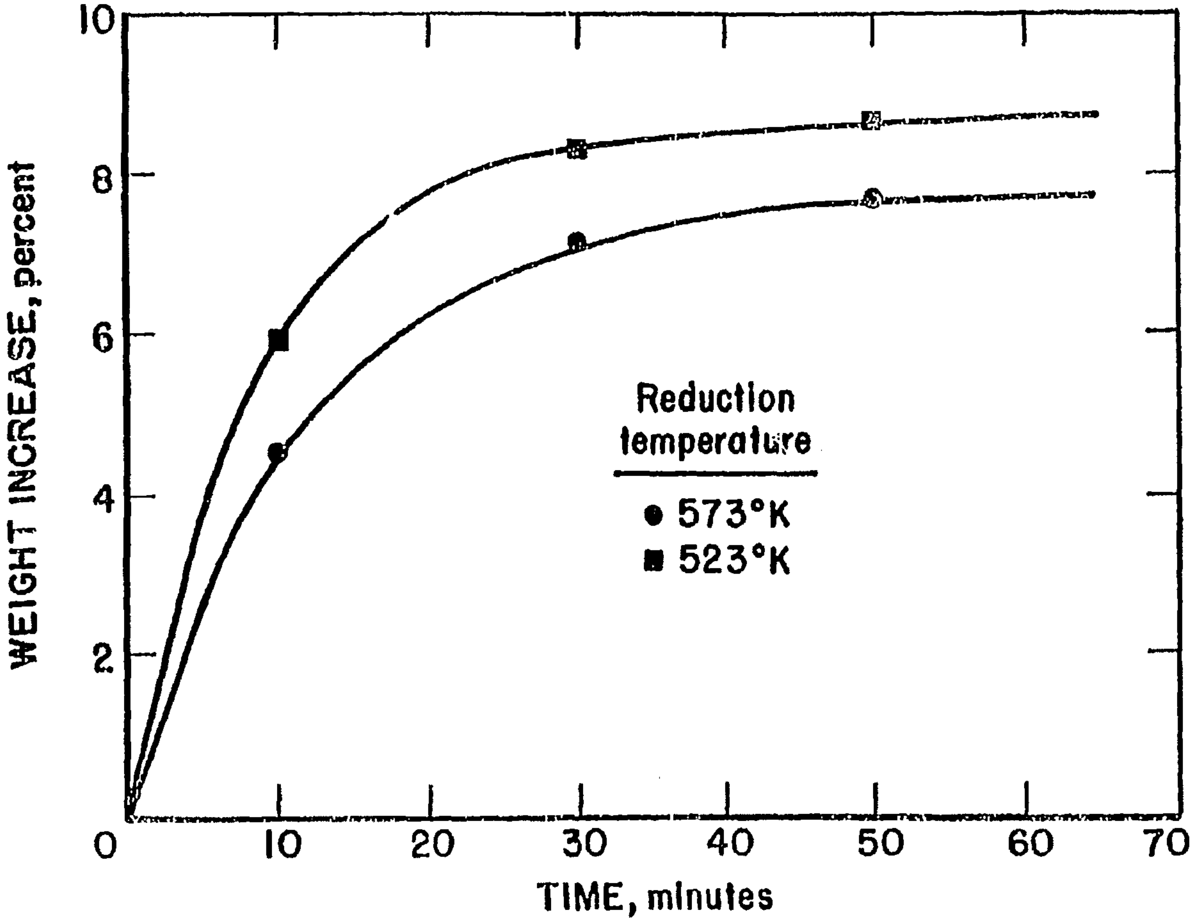

Figure 12 - Carbiding of Precipitated Iron Catalysts in Syn Gas (1/1) at 493°K.

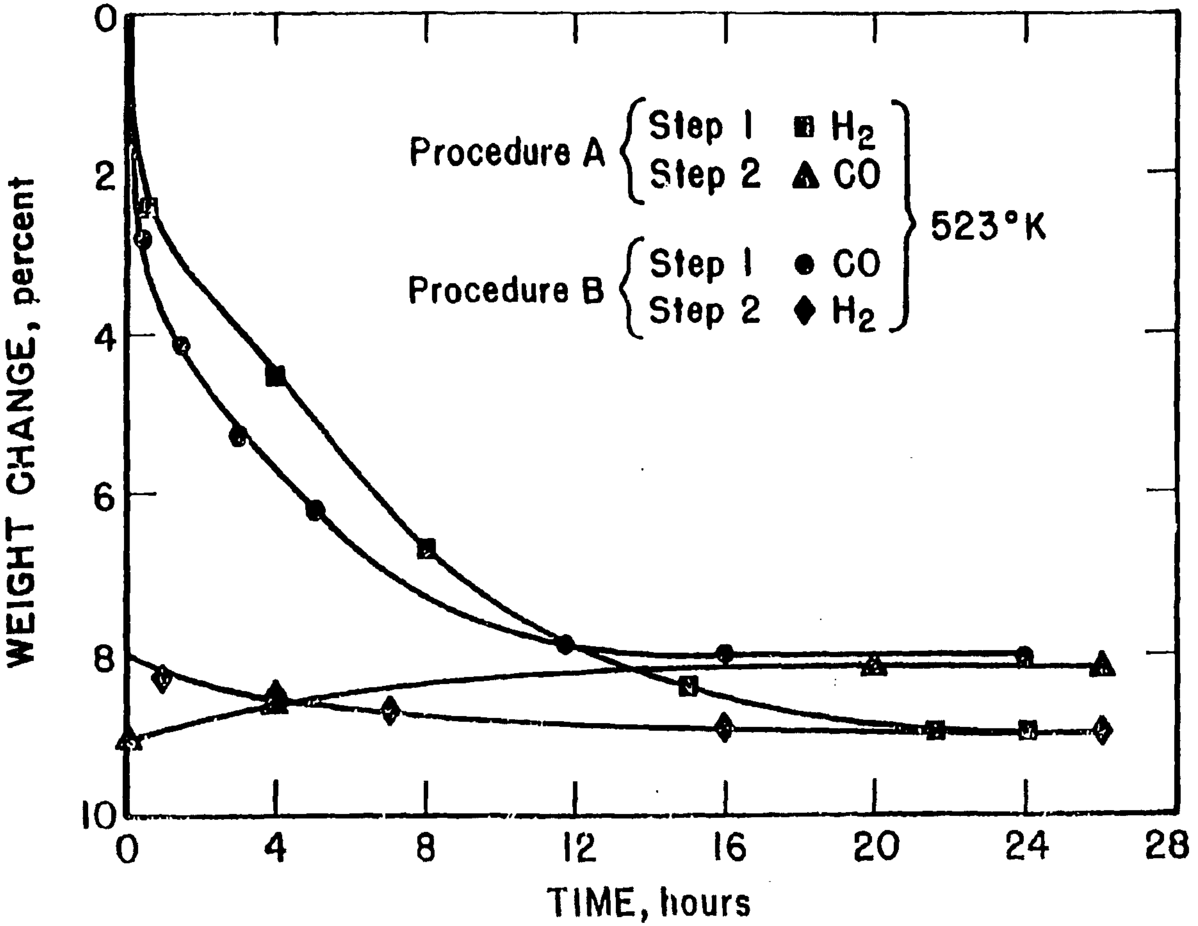

Figure 13 - Activation of Fe-Mn (1/9) Catalyst.

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results in a significant rate decrease. This decrease is consistent with the observation that cobalt forms a carbide less stable than that of iron.

The importance of the gas used for carbiding is shown in Figures 9 and 10. The faster carbiding rate of iron catalysts in syngas, as opposed to carbon monoxide, has been reported previously by Butt(4) and Delgass.(5) The importance of reduction temperature on the rate of carbiding is shown again in Figures 11 and 12. The catalysts used in microreactor studies were reduced at 523°K and carbided with syngas (H_2/CC = 1) at 523°K at 101.3 kPa.

E. Iron-manganese. It is apparent from Figure 13 that the rates of reduction and carbiding are much slower for this catalyst. Using the activation procedure recommended by Kolbel,(7) treatment first with carbon monoxide followed by hydrogen, the data suggest that the catalyst, at least initially, does not contain any bulk carbide. This catalyst during reduction in H_2 underwent a weight loss of about 9 wt.%. If the catalyst before reduction is a mixture of Fe_2O_3 and MnO, and if only Fe_2O_3 is reduced to metallic iron, the weight loss due to reduction alone would be about 2.5%. Thus, it appears that the MnO must undergo some reduction at the same time as the Fe_2O_3. The iron-manganese catalyst used in the microreactor studies was activated by treatment with CO at 523°K for 24 hours followed by H_2 at 523°K for 24 hours at 101.3 kPa.

In order to simulate as closely as possible reaction conditions likely to be used in a slurry phase reactor, the following conditions were used in our microreactor tests:

Temperature 548°K

$H_2/CO = 1$

Pressure 1379 kPa

Space Velocity 1.8-18 (liter hr^{-1} g^{-1})

The microreactor data are shown in Table 4. The hydrocarbon selectivities were calculated using the A-S-F equation.

TOS (time on stream) = total time catalyst was on stream, regardless of reactor conditions.

$$\text{CO conversion} = \frac{\text{grams carbon converted to } CO_2 \text{ and hydrocarbons}}{\text{grams carbon as } CO,\ CO_2, \text{ and hydrocarbons}}$$

The A-S-F plots for catalysts A, B, C, and D were similar to the plot shown in Figure 4. An A-S-F plot for the iron-manganese catalyst is shown in Figure 14. The deviation of the points for C_1 and C_2 from the straight line is potentially quite significant in any effort to develop a catalyst to maximize gasoline selectivity, i.e. minimize C_1-C_2 and maximize C_{3+} yield. The methane selectivity using this catalyst was 50-60% of that that would be calculated using the A-S-F equation, while the C_2 selectivity was 75-80% of the calculated value.

The following conclusions can be reached:

TABLE 4

MICROREACTOR TEST DATA

Catalyst	TOS(hr.)	Space Velocity	% CO Conversion	D	Selectivity (wt.%) $C_1 + C_2$	$C_3 + C_4$	C_5-C_{11}	$\frac{\text{Propylene}}{\text{Propane}}$
Fused Fe	20	1.8	69	3.4	20.8	25.1	44.8	8.6
	26	1.8	67	3.4	20.8	25.1	44.8	9.0
	43	1.8	63	3.4	20.8	25.1	44.8	8.0
Ppt. Fe	48	9	31	3.0	25.9	28.0	40.7	7.4
	67	4.5	52	2.9	26.9	28.4	39.8	7.5
Fe-Co-K	16	18	41	2.4	36.6	31.4	30.4	6.2
	40	18	39	2.6	32.3	30.4	34.5	6.0
	64	18	34	2.6	33.8	30.8	33.1	6.0
Fe-Mn	8	3.6	57	3.0	17.3	31.6	44.8	10
	21	3.6	59	3.3	14.3	26.2	48.5	10
Ppt. Fe(k)	14	18	57	3.3	21.6	25.6	44.3	7.2

Reaction conditions: $H_2/CO = 1$, 548°K, 1379 kPa

Space Velocity - (liter hr^{-1} g^{-1})

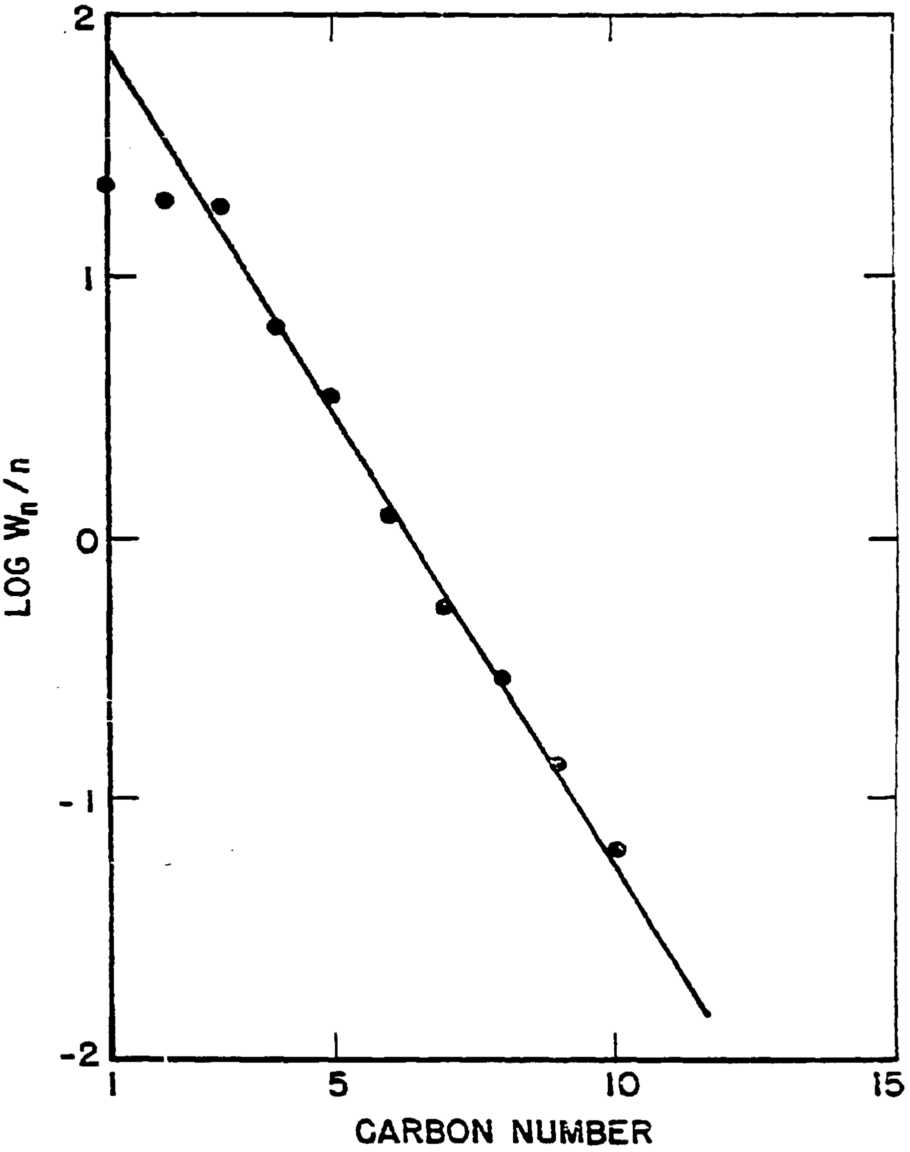

Figure 14 - Anderson - Schulz - Flory Plot for Fe - Mn Catalyst.

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1. Activity. When comparing catalysts on a space-time-yield basis, the potassium-promoted iron-cobalt catalyst and the potassium-promoted iron catalyst are the most active. While the iron-manganese catalyst is quite active on a per gram of iron basis, on a per gram of catalyst basis it is only about 20% as active as the potassium-promoted precipitated iron catalyst. The fused iron catalyst is the least active of any catalyst studied, but this catalyst was reduced at 723°K (vs. 523°K for the precipitated iron catalyst). This catalyst can be reduced at 623°K in about ten hours, and considering the large effect of reduction temperature on carbiding rate as shown in Figure 6, there is reason to believe the lower reduction temperature will result in a more active catalyst.

   While the fused iron, iron-cobalt-potassium, and iron-manganese catalysts showed little change in conversion after being placed on-stream, the precipitated iron catalysts, B and C, declined significantly during the first 12 hours and then stabilized.

2. Selectivity. Olefin selectivity as measured by the propylene/propane ratio decreases with time on-stream, although the degree of polymerization changes little during the first 50 hours. The degree of polymerization decreased in the following order: Fused iron > K-promoted ppt. Fe > ppt. Fe, Fe-Mn > Fe-Co-K

As far as maximizing gasoline yield is concerned, it appears the Fe-Mn catalyst is to be preferred not only because of the high C_5-C_{11} selectivity but also because the olefin content (as measured by the propylene/propane ratio) is the highest of any catalyst in this study. A high olefin yield is desirable because olefins will be more readily upgraded to high octane components in a second stage reactor containing ZSM-5 or some other shape selective zeolite. The low activity of the Fe-Mn catalyst, however, may preclude its use in large-scale industrial reactors.

The present data confirm the results of Kolbel.(7) Kolbel claimed that catalysts containing at least 50% manganese and less than 50% iron, and activated according to the procedure described earlier, resulted in the preferred conversion of syngas to hydrocarbons and oxygenates with a chain length from C_2-C_6. It has been found that the use of manganese oxide as a support leads to a marked decrease in the methane yield not only for iron but ruthenium supported catalysts as well.(8) As shown in Figure 15 (data from ref. 8), the hydrocarbon selectivity for a 1% Ru/MnO catalyst (prepared by impregnation of MnO with an aqueous solution of $RuCl_3$) shows a significant deviation from the A-S-F distribution for methane. One significant difference between the ruthenium and iron-manganese catalysts is that the Exxon patent recommends reduction at temperatures as high as 773°K, whereas reduction of the iron manganese catalyst at temperatures as low as 523°K was sufficient to effect reduced methane yield.

There is no indication in the literature of reduced methane yield for iron and ruthenium catalysts using alumina or silica as the support. There is considerable speculation at the present time that the unusual selectivity of manganese oxide supported catalysts is associated with the variable valency of manganese and the capability of compounds of manganese to be reduced to stable lower oxidation states. These catalyst studies are being pursued with this idea in mind.

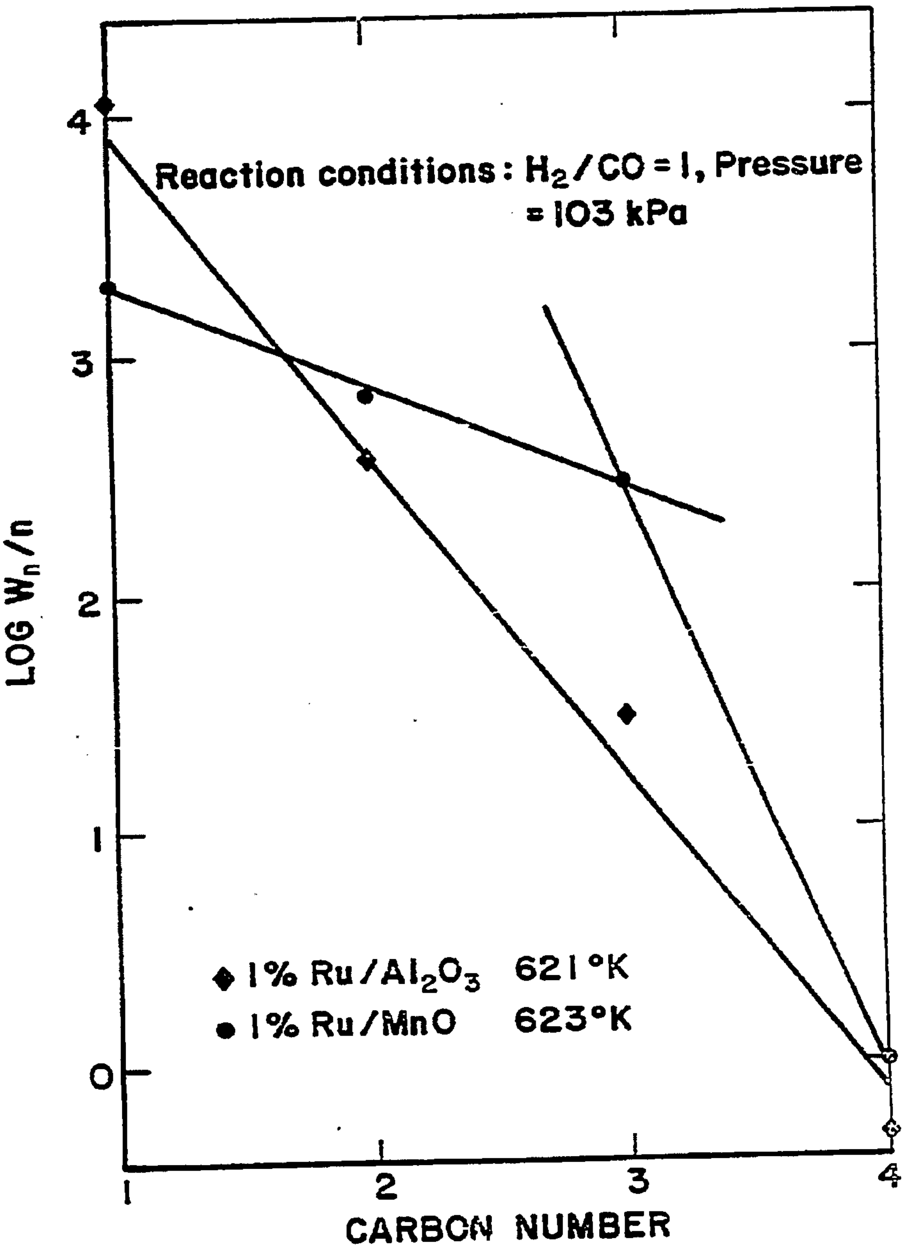

Figure 15 - Anderson - Schulz - Flory Plot for Ru Catalysts.

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