catalyst. Several BET measurements were also made on the 400 series catalysts at various reaction times. The values for the spent/reduced Fe/K-A-402 and -403 were 9.75 and 7.66 m^2/g, respectively. A value of 8.36 was obtained for the fresh/reduced Fe/K-A-404.

4. Activity/Selectivity/Deactivation Measurements

a. GC Response Factors. Calibration of the gas chromatograph flame ionization detector (FID) response factors (RF) resulted in significant changes from previous response factors taken from the literature (1967). Two small cylinders of gases at known concentrations were obtained from Scott Specialty Gases. One cylinder contained paraffins: methane, ethane, propane, n-butane, n-pentane and n-hexane. The other contained olefins: ethylene, propylene, 1-butene, 1-pentene, and 1-hexene. Injections of these gases were made with a 500 μ-liter syringe into the flame ionization detector port. The response factors were determined by dividing the peak area by the amount (wt.) of each component.

Figure 3 shows the plots of several injections. Because the olefin and paraffin average response factors were very close, the same response factor was assigned to the olefins and paraffins for a given carbon number. For carbon numbers greater than 6, a linear extrapolation based on C_5 and C_6 response factors was assumed. Table 2 shows the old and new response factors.

The effect of these new response factors has been to decrease the relative amounts of the heavier hydrocarbons while lighter hydrocarbons increase. The total activity based on CO converted also decreases. Table 3 compares results with the old and new response factors. These calibrations also allow us to positively identify the known gases in the chromatograms based on their retention times.

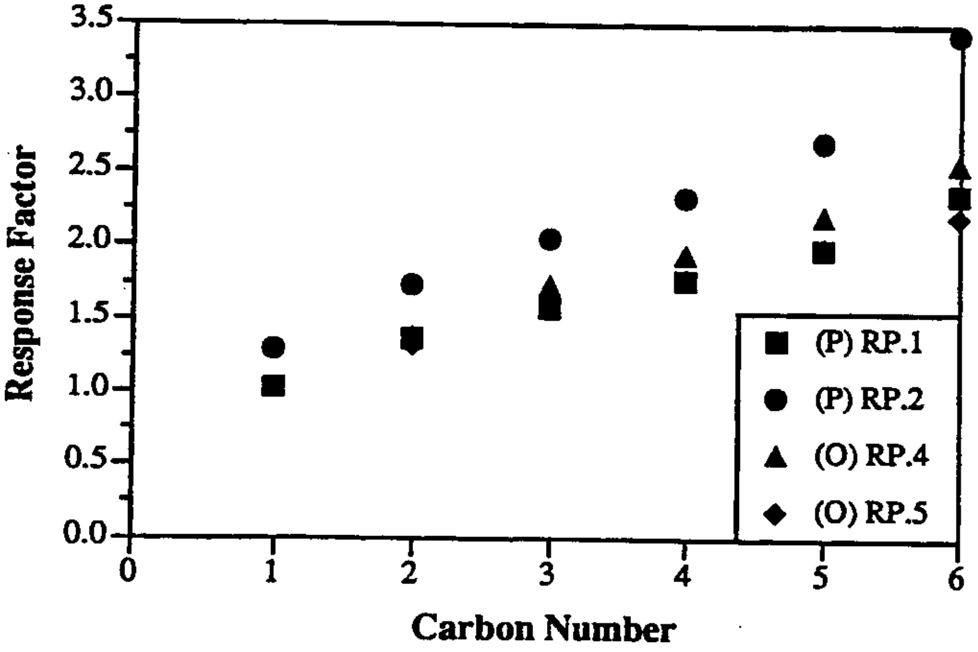

Figure 3. Paraffin and olefin response factors based on calibration gases.

Table 2. Old and new gas chromatograph (FID) response factors for olefins and paraffins.

Carbon #	Old Paraffin RF	Old Olefin RF	New Olefin/Paraffin RF
1	0.97		1.16
2	0.97	1.02	1.50
3	0.98	1.00	1.81
4	1.03	1.00	2.04
5	1.04	1.00	2.32
6	1.03	0.99	2.77
7	1.00	1.00	3.22
8	0.97	1.03	3.67
9	0.98	1.00	4.12
10	1.00	1.00	4.57
11	1.00	1.00	5.02
12	1.00	1.00	5.47
13	1.00	1.00	5.92
14	1.00	1.00	6.37
15	1.00	1.00	6.82

b. Reaction Setup. The reaction was run in a Pyrex reactor cell using about 1 gram of powdered catalyst at a series of temperatures starting at 200° C and was increased in 10° C increments to a final temperature of 230°C. Earliest runs used a reaction gas with a H_2:CO ratio of 2:1. The setup was later modified to allow flows of CO, H_2 and He (from separate tanks) to be controlled independently. A Hewlett-Packard 5890A gas chromatograph equipped with a flame-ionization detector (FID) and a thermal conductivity detector (TCD) was connected in-line downstream of the reactor. A Macintosh computer was used with a program written in this lab to control the chromatograph and take samples automatically at the programmed times. GC samples were taken about every 2 hours (or as desired) at each reaction temperature so that the approach to steady-state could be observed. Samples were run at the initial temperature for 20-24 hours and at succeeding temperatures for about 10 hours each.

c. Fe-100 Series. (Fe-101, Fe-102) Figure 4 shows Arrhenius plots for the first two unsupported catalyst samples. Fe-101 was reduced at 300°C while Fe-102 was reduced at 400°C. Reactions were carried out over these catalysts using a 2/1 mixture of H_2/CO at various temperatures. Hydrogen uptakes of 45 µmoles/g (measured on the spent Fe-102 catalyst) were used for both catalysts. From a previous study done in our laboratory over similarly prepared unsupported iron catalyst at 2/1 H_2/CO and 225°C, a turnover number of 4 x 10^{-3} was calculated [15,49]. This is also plotted in Figure 4. Very good agreement between this data point and the data from this study is evident.

Table 3. Sample selectivity (as weight fraction of hydrocarbons produced) and activity changes as a result of new response factors (catalyst Fe-A-203).

	C1	C2-4	C5-11	Activity (Nco)
Old	0.4053	0.4897	0.1049	2.58E-03
New	0.5269	0.4121	0.0611	2.08E-03

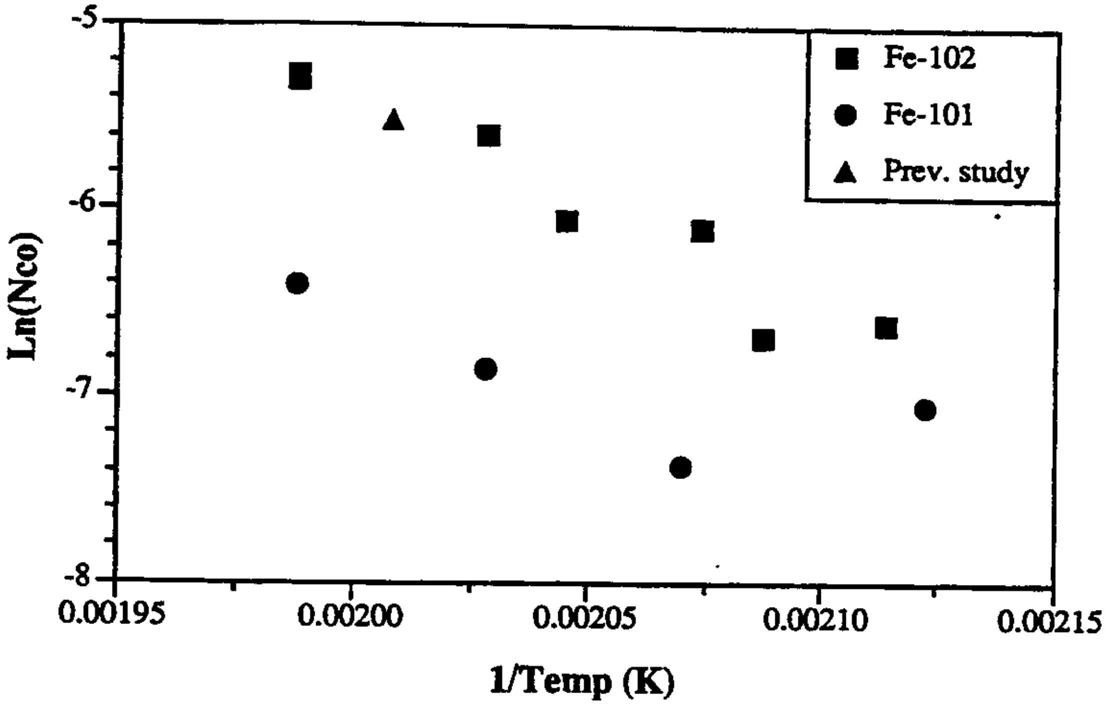

Figure 4. Activities as a function of reciprocal temperature for unsupported catalysts Fe-101 and Fe-102. Data from a previous study were obtained at 498 K, 2/1 H_2/CO.

The temperature sequence of data for Fe-102 was 200, 210, 220 and 230°C followed directly by reaction at 206 and 216°C. It is evident that some deactivation of the catalyst occurred. The turnover numbers at 206 and 216°C are lower than what would be expected for no deactivation. Ideally, they should lie along the line plotted through the other points.

Activation energies for these two catalysts were calculated to be 99 and 88 kJ/mol for Fe-101 and Fe-102, respectively. This compares to the value of 132 kJ/mol obtained in the previous study.

Catalyst selectivity is shown as a function of temperature in Figure 5. As the reaction temperature increases, methane and C_2-C_4 hydrocarbon contents increase slightly while the C_5+ hydrocarbon content decreases. Data from a previous study [15] give lower methane and C_2-C_4 fractions and a higher C_5+ fraction than in this work. The selectivity towards smaller hydrocarbons (namely, methane) with deactivation is seen in Figure 5. At 206°C and 216°C methane appears to be formed at the expense of the higher hydrocarbons (C_5+). The C_2-C_4 fraction is not noticeably affected.

Another result of deactivation can be seen in Figure 6 in which the olefin content of the C_3 to C_7 fraction of the product is plotted as a function of CO conversion. A good fit is obtained when disregarding the data points from the runs following reaction at 230°C. A possible explanation is that at 230°C the surface begins to be covered with more than the steady-state amount of carbon required for reaction. As a result, there are fewer sites for hydrogen to adsorb which increases the degree of unsaturation.

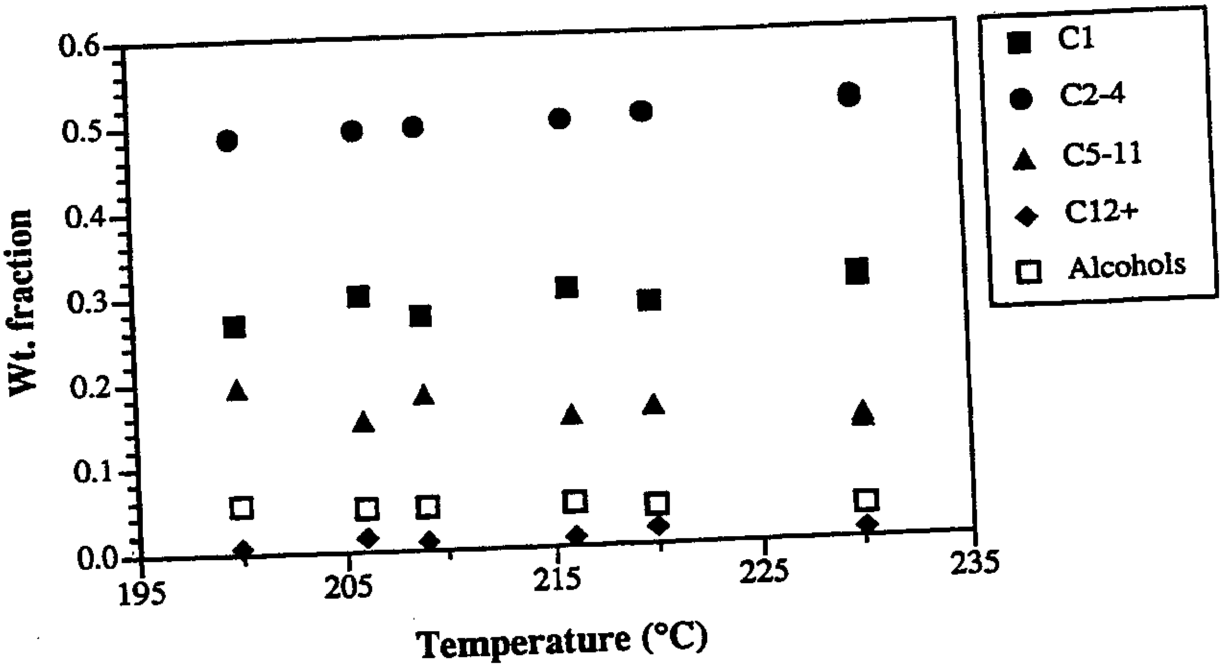

Figure 5. Product selectivity based on hydrocarbons produced (Fe-102).

It should be noted that although the gas chromatograph does not identify hydrocarbons heavier than about C_{15}, heavy waxes were observed at the outlet end of the catalyst sample and along the wall of the sample cell.

After these data were obtained the reaction apparatus was modified to allow separate H_2 and CO

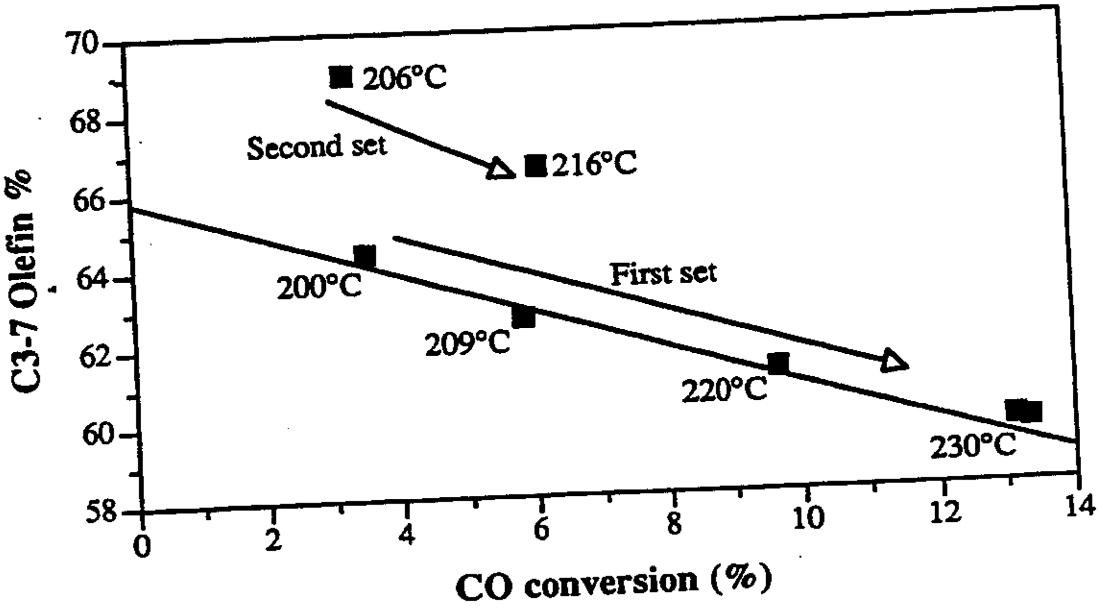

Figure 6. Correlation of conversion with olefin content (Fe-102). Arrows indicate order of runs.

tanks to be used. Originally, a single tank of 2:1 H_2:CO mixture was used and flow control was achieved with a Matheson flow controller. With the new setup, this flow controller controlled the hydrogen flow. Two manually operated, micro-metering valves were used in conjunction with a Matheson flow meter for controlling the CO flow.

(Fe-103) Once this setup was completed, several runs were made to reproduce results obtained previously. A fresh sample (Fe-103) was charged into the sample cell, the sample was reduced in flowing hydrogen at 300°C and two chemisorptions were done. Chemisorption results showed uptakes of 51 and 57 μmoles/g. Hydrogen and carbon monoxide were then reacted over this catalyst at a series of temperatures ranging from 200°C to 230°C. The catalyst was more active than the first sample of unsupported iron reduced at 300°C previously reported for similar conditions (similar flow rates and H_2/CO ratios). For this present case, reaction temperatures above 210°C gave CO conversions greater than 10% and at 230°C the conversion was 18%.

Following this reaction schedule, the catalyst was again reduced in pure hydrogen, only this time at 400°C. The catalyst was then moved from the reaction apparatus so that chemisorption measurements could be made. An uptake of about 35 μmoles/g was measured.

A total flow rate of 30 cc/min (twice the previous rate) was used in the reaction experiments that followed in order to maintain conversion less than 10%. However, the catalyst showed very little activity, producing only C_1-C_3 hydrocarbons. Even when the total flow was reduced, the activity (ie. conversion) did not increase substantially.

(Fe-104) Another fresh sample (Fe-104) was charged into the cell, reduced at 400°C and the hydrogen uptake measured, giving about 20 μmoles/g. After transferring this sample to the reaction setup and running at 190°C, $H_2/CO=2$, and 15 cc (total flow)/min for 7 hours, there was very little conversion of CO to hydrocarbons. Further reaction at 200°C showed similar results.

Several important observations were made following these experiments. The spent catalyst had sintered into large particles, possibly as a result of (1) oxygen reacting with the reduced catalyst or (2) sintering upon decomposition of the iron carbide during rereduction. The oxygen could have come from several sources. After the first sample became inactive, the hydrogen and CO feed lines were checked for leaks and several substantial leaks were found and eliminated. However, the results of the last sample indicated that there was still a problem. Plastic tubing, which had been used for a major portion of the feed lines, is permeable to oxygen. This plastic tubing was changed to stainless steel before further work was done. Another source of oxygen could be in the transfer of the cell from the chemisorption apparatus to the reaction setup. A small, but possibly significant, amount of air is left in the glass connectors connecting the feed line to the sample cell. A change of procedure was instituted to correct this problem. Reduction of the catalyst was thereafter done in-situ during the test setup, immediately followed by reaction experiments. Chemisorption measurements were henceforth conducted on separate samples. In this way, all possibilities of oxygen contacting the active catalyst were eliminated.

It was observed that several chemisorptions did not give reasonable slopes and intercepts. A minor error in the computer analysis program was found but it did not explain the erroneous results. It was later found that the zeroing of the Texas Instruments precision pressure gauge had been done improperly before each chemisorption. Making a crude estimate of the error in the last set of data changed the uptake from 54 to 19 µmoles/g and the slope and intercept took on reasonable values.

(Fe-105) Additional runs were made on a new unsupported Fe catalyst sample (Fe-105). The catalyst was reduced in hydrogen at 400°C after which a 2:1 H_2/CO ratio synthesis gas (15 total cc/min) was reacted over it for about 90 hours at temperatures ranging from 200° to 230°C. The catalyst was then rereduced at 400°C and similar reactions conditions followed. This combination of reduction and reaction was performed a third time. The activity data for these runs are summarized in Figure 7.

The activity of the catalyst (measured by CO conversion) during the first reaction sequence was quite low, ranging from about 0.6% at the lowest temperature to only 2.3% at the highest temperature. An Arrhenius plot gave an activation energy of 86 kJ/mole (see Fig. 7).

After rereduction at 400°C for 16 hours, however, the activity decreased by about a factor of 2 (see Fig. 7). (The total flow had been increased from 15 to 20 cc/min but the H_2/CO ratio was still the same.) Because of the lower activity the maximum reaction temperature was increased to 240°C. Even at this higher temperature the CO conversion was only 1.2%. There was also a significant change in the activation energy to 68 kJ/mole. The third reduction at 400°C was carried out for only 7 hours. Activity

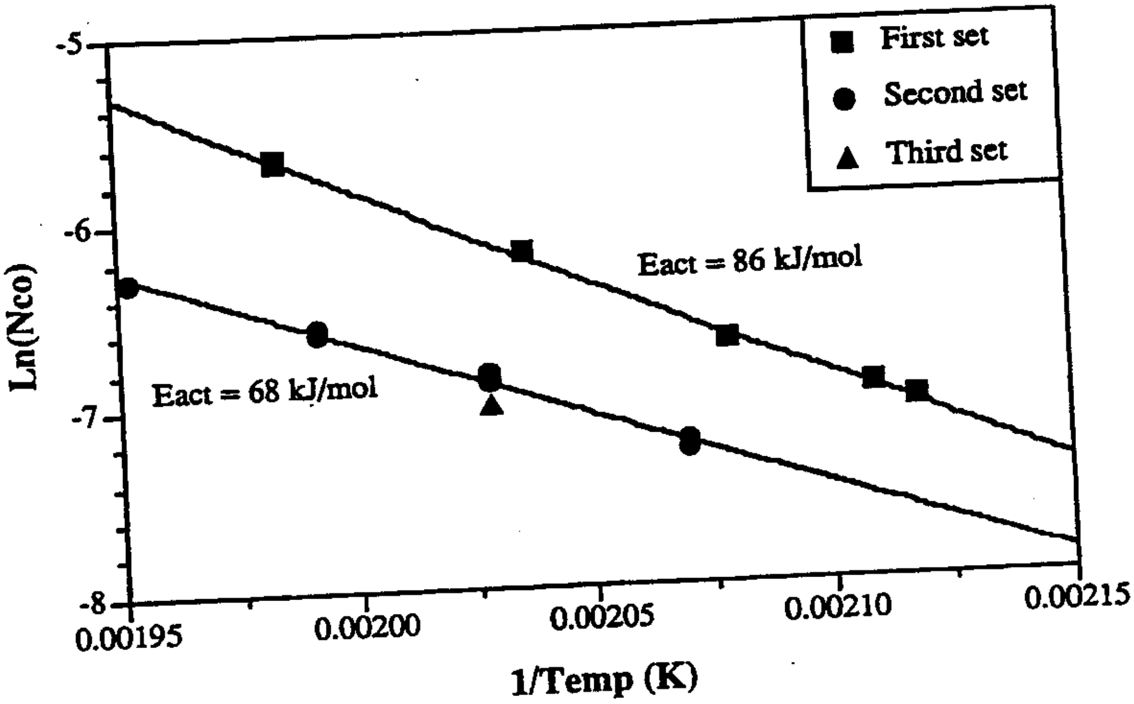

Figure 7. CO hydrogenation activity of unsupported Fe reduced at 400°C; Fe-105, H2/CO = 2, 1 atm.

was only slightly lower than the previous set.

It was obvious from examination of the catalyst that the small iron particles had fused together into much larger ones, probably due to sintering. The decrease in activity at each reaction stage was most likely a result of lower active surface area and not a result of a drop in the specific activity. Reducing the catalyst in hydrogen following reaction may have caused the iron to sinter as the iron carbide decomposed. Hence the most significant decrease in activity occurred between the first and second reaction sequences.

Because of the thermal stability problems with unsupported, unpromoted iron, work thereafter used unsupported iron with 1% alumina as a structural promoter. This catalyst was prepared by calcination (at 200°C) of the mixed iron and aluminum nitrates.

d. Fe-A-200 Series. (Fe-A-201) A new catalyst sample, Fe-A-201, was prepared by decomposing aluminum nitrate with iron nitrate to give a 1% by wt. Al/Fe. This new sample was subjected to the same treatments as the previous catalyst with much improved stability. No significant differences in initial specific activity were observed with the Al-promoted catalyst (Fe-A-201) compared to the unpromoted catalyst. However, the major difference was observed after re-reduction in hydrogen. The Al-promoted catalyst did not sinter and the initial specific activity was restored after re-reduction. This can be seen in the activation energy plot (Figure 8).

Reaction conditions for Fe-A-201 included 3:1 H_2/CO ratio, temperatures ranging from 200-230°C, and reaction times for a given temperature of 12-24 hours. Output data from GC sample #7

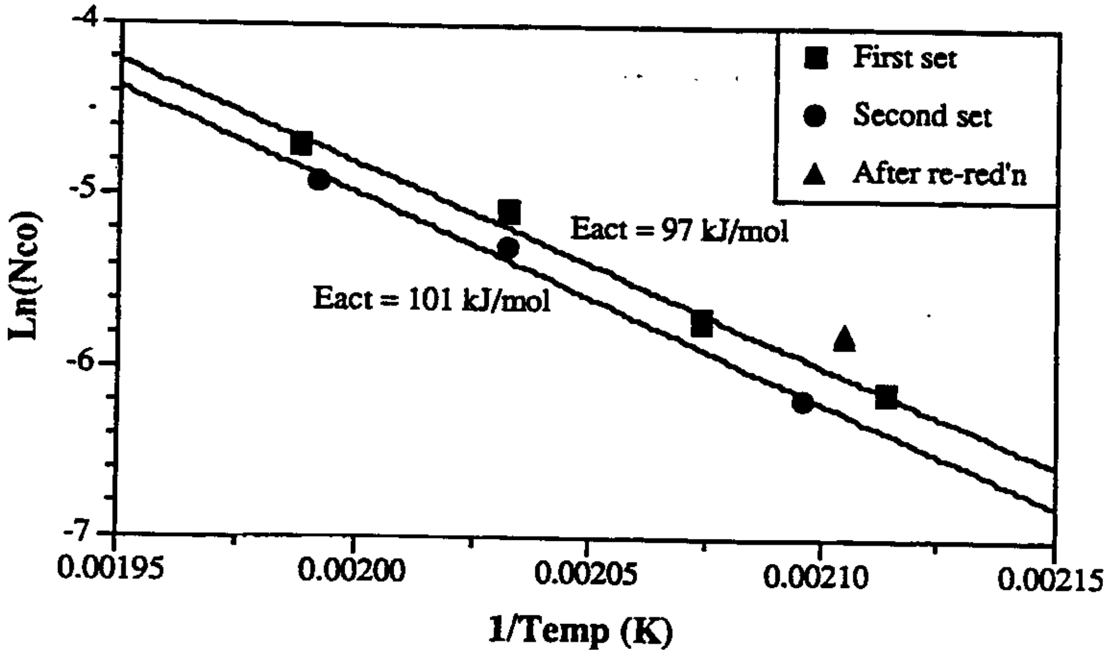

Figure 8. Arrhenius plot for Fe-A-201 (99% Fe, 1% Al) at 3/1 H_2/CO; 200-230°C.

(200°C) are given in Table 4. Figures 9 and 10 show the Anderson-Schulz-Flory (ASF) and product distribution plots that correspond to this sample.

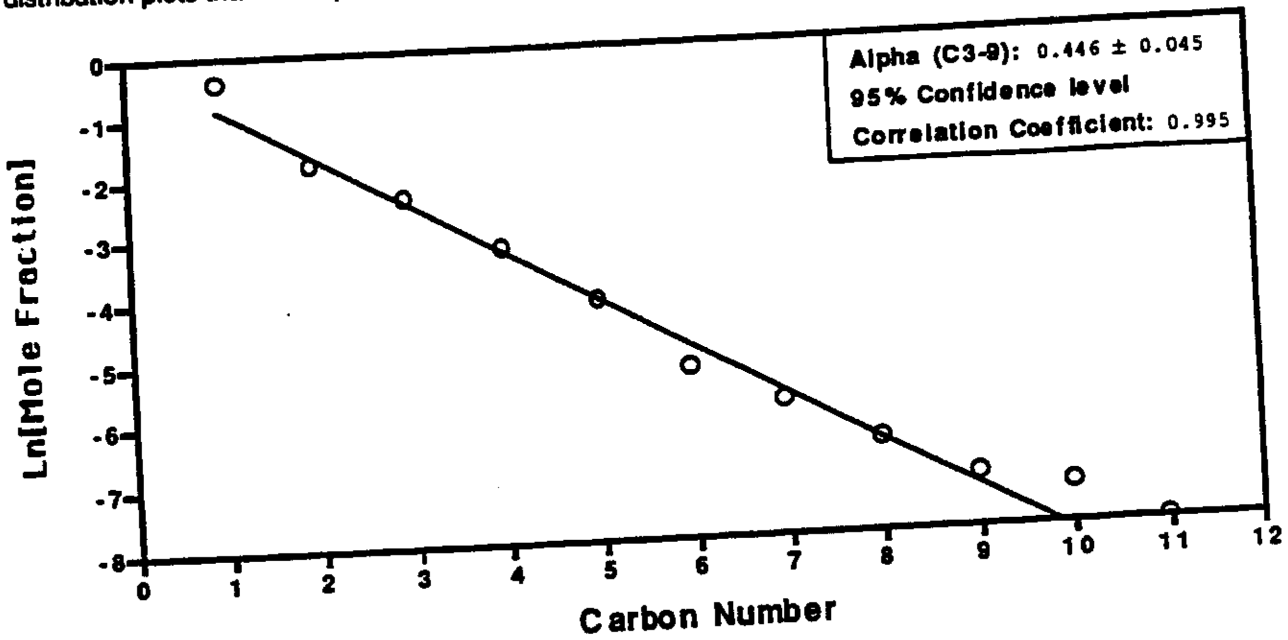

Figure 9. Anderson-Schulz-Flory (ASF) plot for reaction on Fe-A-201 at 200°C.

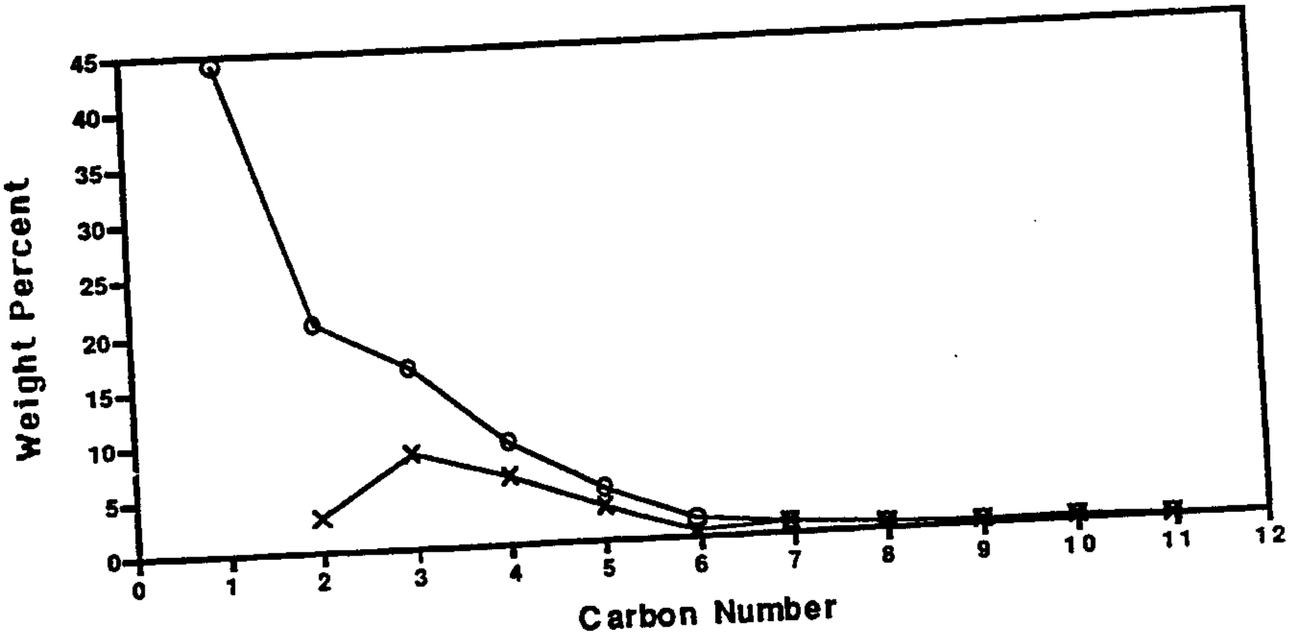

Figure 10. Distribution of total hydrocarbons (upper curve) and olefins (lower curve) on Fe-A-201 at 200°C.

A summary of the data from this catalyst is given in Table 5. Data shown for each GC sample include temperature, hydrogen and carbon monoxide flowrates and conversion, and the CO turnover frequency (Nco). The second page of Table 5 shows the selectivity to hydrocarbons and CO_2 and also the distribution of products based on the total hydrocarbons produced.

Table 4. Reaction parameters and results from GC sample #7 on Fe-A-201 at 200°C.

Run Number 7 **OCT/14/88 11:05:44**

Catalyst: Fe/1% Al

Sample Weight: 1.0281 g **H2 Chemisorption Uptake:** 33.00 μmoles/g

Sample Volume: 1.0000 ml

Reaction Parameters:

Temperature: 473 K **Flows: H2:** 15.00 cc/min

Pressure: 1.00 Atm **CO:** 5.00 cc/min

Reactor Run Time: 1448 Min

H2/CO Ratio: 3.00/1

Space Velocity at 298K and 1 Atm: 1200.0/Hour

Space Velocity at Reactor Conditions: 1904.7/Hour

Reactants Mass Flowrate: 6.965E-03 g/min

Average Molecular Weight of Feed: 8.514 g/gMole

Results:

CO Conversion: 4.2377%

H2 Conversion: 15.7565% **H2/CO Usage Ratio:** 11.155/1

Number of Active Sites: 4.0869E+19

CO Turnover Number: 2.1285E-03 molecules CO/site-sec

Rate Weight Basis: 8.4290E-06 mole CO/g cat-min

Average Molecular Weight of Products: 24.538 g/gMole

TCD to FID Conversion Factor (RK): 1.619

Error in H2 Balance: -12.164%

Product Selectivities:

Selectivity Based on CO Converted (Carbon Atom %)

C1	C2-4	C5-11	C12+	Alcohols	Total HC	CO2
0.2912	0.3218	0.0712	0.0000	0.0110	0.6952	0.3048

Distribution of Total Hydrocarbons (Weight %)

C1	C2-4	C5-11	C12+	Alcohols
0.4407	0.4644	0.0949	0.0000	0.0238

Hydrogen selectivity

Hydrocarbon	H2O
0.4221	0.5779

C3-7 Olefin Content (mole Basis): 0.5884

C3-7 Olefin/Paraffin ratio (mole Basis): 1.4294

	Weight Fractions				Mole Fractions						
C#	**Par**	**Ole**	**Alc**	**Total**	**Par**	**Ole**	**Alc**	**Total**	**OleCont**	**O/P**	**Ln(Tot)**
1	.4407		.0000	.4407	.6741		.0000	.6741			-0.3944
2	.1516	.0312	.0238	.2067	.1238	.0273	.0127	.1638	.1808	0.2207	-1.8094
3	.0780	.0854	.0000	.1635	.0434	.0498	.0000	.0932	.5344	1.1477	-2.3726
4	.0312	.0631	.0000	.0943	.0132	.0276	.0000	.0408	.6768	2.0936	-3.2001
5	.0165	.0318	.0000	.0483	.0056	.0111	.0000	.0168	.6652	1.9867	-4.0893
6	.0112	.0070	.0000	.0182	.0032	.0020	.0000	.0052	.3901	0.6395	-5.2514
7	.0000	.0115	.0000	.0115	.0000	.0029	.0000	.0029	.9900	99.0000	-5.8503
8	.0000	.0068	.0000	.0068	.0000	.0015	.0000	.0015	.9900	99.0000	-6.5069
9	.0000	.0041	.0000	.0041	.0000	.0008	.0000	.0008	.9900	99.0000	-7.1261
10	.0000	.0036	.0000	.0036	.0000	.0006	.0000	.0006	.9900	99.0000	-7.3595
11	.0000	.0022	.0000	.0022	.0000	.0003	.0000	.0003	.9900	99.0000	-7.9601

Table 5. Summary of reaction conditions and results on Fe-A-201.

GC Sample #	Date	Temp (K)	Rxn Runtime (min)	Runtime (hr)	CO conv (%)	H2 conv (%)	Nco (33 µmoles/g)	LN (Nco) (33 µmoles/g	1/T 1/(K)	HC Selectivity
1										
2							First set			
3	10/13/88 13:37:28	473	159	2.65	3.28	22.90	1.647E-03	-6.409	0.00211	0.5327
4	10/13/88 19:18:31	473	157	2.62	2.96	14.25	1.487E-03	-6.511	0.00211	0.6921
5	10/14/88 01:37:58	473	872	14.53	3.93	14.67	1.975E-03	-6.227	0.00211	0.6970
6	10/14/88 10:20:00	473	1402	23.37	4.28	14.60	2.150E-03	-6.142	0.00211	0.6970
7	10/14/88 11:05:44	473	1448	24.13	4.24	15.76	2.129E-03	-6.152	0.00211	0.6952
8	10/14/88 15:25:51	482	182	3.03	6.66	17.76	3.348E-03	-5.699	0.00207	0.6352
9	10/14/88 22:06:21	482	647	10.78	6.56	17.04	3.295E-03	-5.715	0.00207	0.6370
10	10/14/88 22:52:14	482	693	11.55	6.43	17.45	3.230E-03	-5.735	0.00207	0.6530
11	10/15/88 11:54:06	492	742	12.37	11.94	20.12	6.000E-03	-5.116	0.00203	0.5283
12										
13	10/15/88 13:03:49	492	812	13.53	12.20	22.23	6.130E-03	-5.095	0.00203	0.5626
14	10/15/88 13:49:53	492	858	14.30	12.08	22.66	6.069E-03	-5.105	0.00203	0.5489
15	10/16/88 13:50:21	503	1332	22.20	8.97	16.68	9.006E-03	-4.710	0.00199	0.5730
16	10/16/88 14:36:11	503	1378	22.97	8.92	17.65	8.962E-03	-4.715	0.00199	0.5728
							Second set			
17	10/17/88 12:13:23	477	1262	21.03	2.06	8.71	2.071E-03	-6.180	0.00210	0.7510
18	10/17/88 13:15:51	477	1332	22.20	2.02	8.81	2.031E-03	-6.199	0.00210	0.7514
19	10/18/88 00:41:07	492	577	9.62	4.93	11.99	4.956E-03	-5.307	0.00203	0.6539
20	10/18/88 14:11:56	502	742	12.37	7.22	14.18	7.249E-03	-4.927	0.00199	0.5915
21	10/18/88 15:10:06	502	800	13.33	7.29	14.78	7.328E-03	-4.916	0.00199	0.5869
22							After re-red'n			
23	10/19/88 13:22:40	475	917	15.28	3.04	10.79	3.055E-03	-5.791	0.00211	0.7732
24	10/19/88 16:15:06	475	1042	17.37	2.96	9.66	2.975E-03	-5.817	0.00211	0.7772

Table 5 (cont). Summary of reaction conditions and results on Fe-A-201.

GC Sample #	CO2 Selectivity	H2O Selectivity	H2 flow (cc/min)	CO flow (cc/min)	Alpha (α)	± (α)	Carbon # (α)	Distribution of total hydrocarbons (wt fraction)					C3-7 Olefin content
								C1	C2-C4	C5-C11	C12+	Alcohols	
1													
2													
3	0.4673	0.7357	15	5	0.388	0.106	C3-8	0.4687	0.4581	0.0732			0.6102
4	0.3079	0.6323	15	5	0.392	0.058	C3-8	0.4338	0.4868	0.0795		0.0435	0.6387
5	0.3030	0.5806	15	5	0.436	0.500	C3-9	0.4321	0.4687	0.0992	0.0000	0.0195	0.6195
6	0.3030	0.5602	15	5	0.461	0.071	C3-10	0.4351	0.4679	0.0949	0.0021	0.0277	0.5998
7	0.3048	0.5779	15	5	0.446	0.045	C3-9	0.4407	0.4644	0.0949	0.0000	0.0238	0.6062
8	0.3648	0.5121	15	5	0.422	0.019	C3-9	0.4214	0.4746	0.1015	0.0025	0.0357	0.5998
9	0.3630	0.5061	15	5	0.433	0.026	C3-9	0.4227	0.4760	0.0988	0.0025	0.0353	0.5968
10	0.3470	0.5153	15	5	0.439	0.044	C3-9	0.4261	0.4749	0.0976	0.0014	0.0343	0.5937
11	0.4717	0.3856	15	5	0.426	0.032	C3-10	0.4500	0.4642	0.0840	0.0018	0.0261	0.5140
12													
13	0.4374	0.4212	15	5	0.538	0.078	C3-10	0.4111	0.4487	0.1340	0.0062	0.0219	0.5320
14	0.4511	0.4203	15	5	0.430	0.028	C3-10	0.4328	0.4791	0.0863	0.0018	0.0335	0.5456
15	0.4270	0.4135	30	10	0.381	0.041	C3-9	0.5011	0.4446	0.0543	0.0000	0.0173	0.5856
16	0.4272	0.4282	30	10	0.363	0.045	C3-8	0.5066	0.4411	0.0523		0.0085	0.5930
17	0.2490	0.5894	30	10	0.367	0.095	C3-7	0.5204	0.4360	0.0436	0.0000		0.6498
18	0.2486	0.5955	30	10	0.334	0.015	C3-7	0.5215	0.4419	0.0367			0.6521
19	0.3461	0.4805	30	10	0.410	0.077	C3-9	0.5035	0.4430	0.0535	0.0000	0.0200	0.6261
20	0.4085	0.4280	30	10	0.345	0.033	C3-8	0.5106	0.4412	0.0482		0.0213	0.6255
21	0.4131	0.4352	30	10	0.343	0.043	C3-8	0.5201	0.4303	0.0496			0.6224
22													
23	0.2268	0.5576	30	10	0.432	0.045	C3-9	0.4941	0.4253	0.0806			0.6023
24	0.2228	0.5402	30	10	0.403	0.102	C3-8	0.4998	0.4255	0.0746	0.0001		0.6081

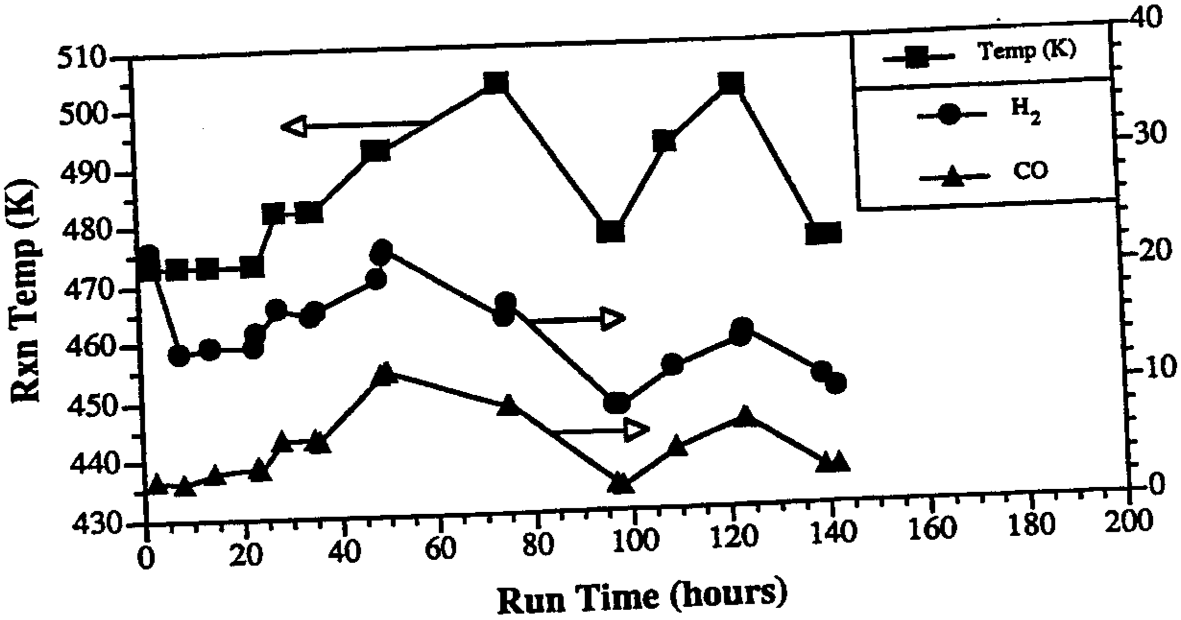

Figure 11. Temperature history and corresponding H_2 and CO conversions (%).

The temperature history is shown along with the conversions of CO and H_2 in Figure 11. The drop in conversions from 50-75 hours is due to a doubling of the space velocity in order to maintain CO conversion less than 10%. (Conversion at 220°C was 12% and doubling the space velocity reduced CO conversion at 230°C to about 9%.)

Figure 12 shows how the specific activity increases with temperature. During the second reaction

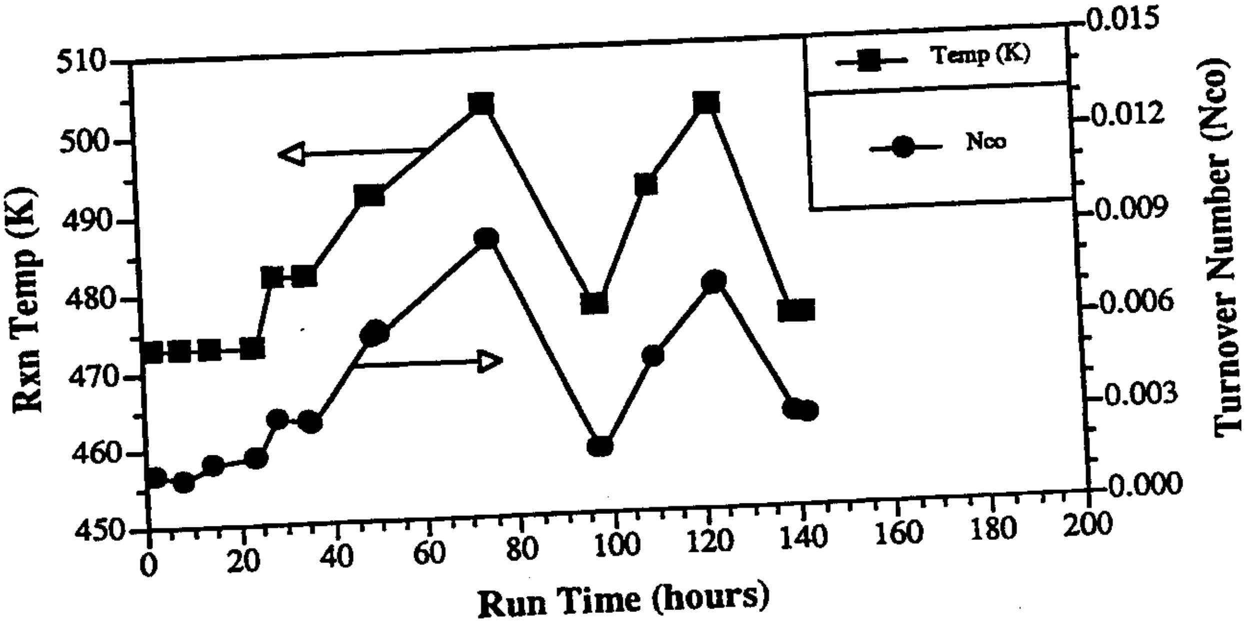

Figure 12. Specific activity (N_{co}) change with temperature.

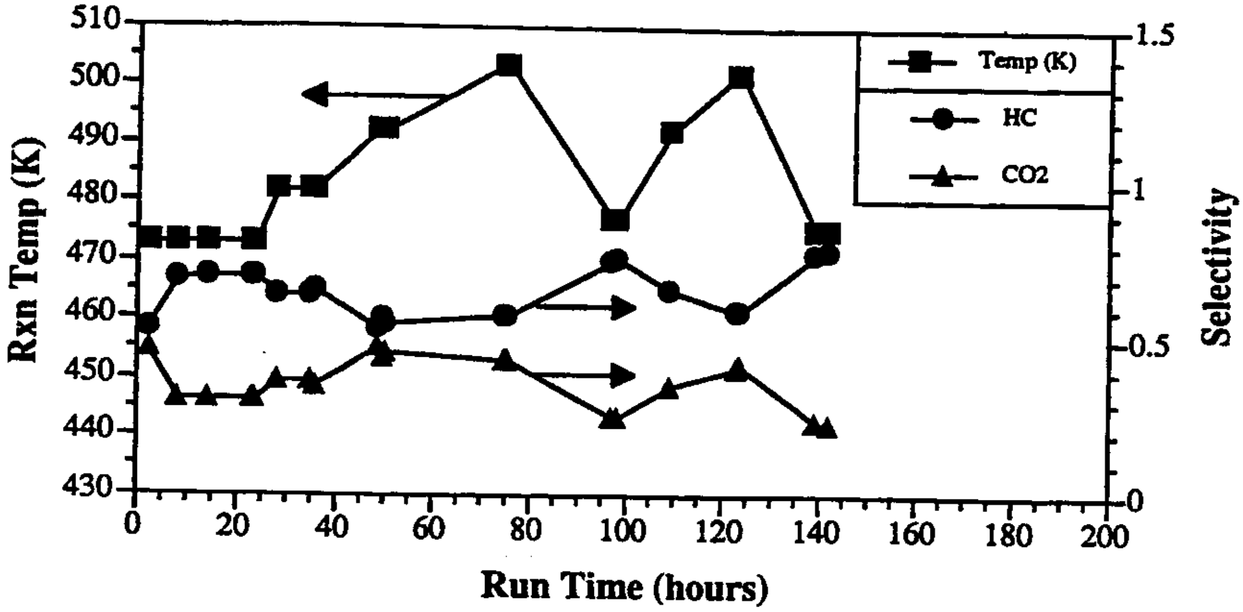

Figure 13. Selectivities to hydrocarbons (HC) and CO_2.

sequence (80-125 hours) the TOF for a given temperature is seen to be less than at the same temperature from the first sequence. This can also be seen in Fig. 8. This decrease in activity is attributed to carbon on the surface.

As the temperature increases, selectivity to hydrocarbon products decreases (Figure 13) while CO_2 selectivity increases. The selectivity to the different hydrocarbon fractions is more complex (Figure 14). The relative amounts of the three fractions shown do not change significantly over the first 50 hours of reaction (200-220°C). However, as the temperature reaches 230°C (503K) fractions of methane and C_2-C_4 hydrocarbons increase and decrease respectively. Over the second reaction sequence very little further change is observed. What is the cause of this behavior? One possibility is an increase in carbon on the surface at 230°C temperature. This carbon coverage may be maximum at this temperature and may correspond to the maximum production of methane. Another possibility is that the effect was caused by the increase in space velocity. Although the partial pressures were unchanged, there may have been some mass transport limitations due to the high conversions (CO:12% and H_2:23%).

(Fe-A-203) Following chemisorption measurements reactions were run on Catalyst Fe-A-203 at temperatures ranging from 200 to 230°C and at H_2/CO ratios from 3/1 to 1/1. The schedule previously set up in which the catalyst was reacted at 200°C for 20-24 hours followed by reactions at successive 10° increments in temperature for 12 hours was not adhered to strictly. This previous schedule was chosen because the catalyst appeared to reach a steady-state condition after about 24 hours on stream. However, because of deactivation at higher temperatures the schedule was changed. Table 5 shows the reaction sequence and conditions for the runs performed on this catalyst. Shown are the intended H_2/CO

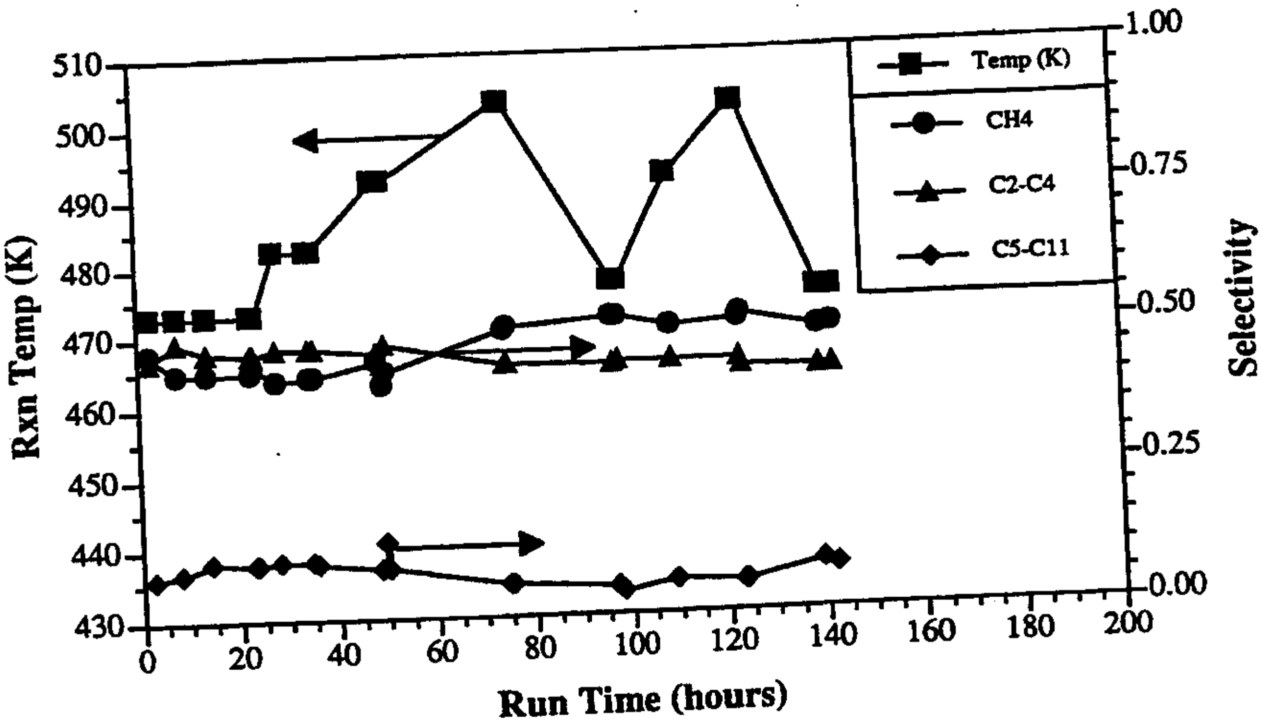

Figure 14. Selectivity to various hydrocarbon fractions.

ratios, the actual flows of H_2, CO and He (in cc/min), time of reaction at the given temperature, and sample times. Helium was used as diluent in some cases so that reaction results could be obtained at constant reactant partial pressures of H_2 or CO while varying the H_2/CO ratio. However, addition of a reactant line for He increased the instability of the reactant flows and thus some of the flow settings are not precisely at the desired conditions. The catalyst was rereduced at about 400°C between each reaction set to minimize deviations due to deactivation. Finally the catalyst was operated at 230°C and H_2/CO = 1.5 for 67 hours to observe effects of deactivation.

The most reliable results are from 3/1(B) and the deactivation run (see Table 5). Figure 15 is an activation energy plot showing the activity (total CO turnover number) on a log scale as a function of the reciprocal temperature. The catalyst activity at the highest temperature (230°C) is lower than expected based on the trend at the lower temperatures. An activation energy of 88.9 kJ/mol was calculated for the lower three temperatures. This compares with 97 kJ/mol for catalyst Fe-A-201 reported previously (also at 3/1 H_2/CO ratio). The fit is very good for these data considering the reversal of the first two temperature runs (207°C and then 200°C instead of 200 followed by 207). The extended time on stream before reacting at 230°C (71 hours compared to 48 preferred under ideal schedule) may have had an impact on the activity at that temperature. Indeed, longer reaction times deactivated the catalyst by allowing refractory carbon deposits to form which are not easily removed with hydrogen, thus lowering the intrinsic activity.

Table 5. Reaction schedule for catalyst Fe-A-203.

Rxn Set	Reaction conditions	H_2/CO/He flow(cc/min)	Sample times
3/1 (A):	**Reduced fresh catalyst at 400°C for 1 hr**		
	H2/CO = 3 at 200 for 16 hrs	(30/10/0)	
	H2/CO = 3 at 212 for 33 hrs	(30/10/0)	Samples taken at 27 and 28 hrs
	H2/CO = 3 at 227 for 22 hrs	(30/10/0)	Samples taken at 20 and 21 hrs
	Re-reduced at 400°C for 2 hrs		
3/1 (B):	H2/CO = 3 at 207 for 38.5 hrs	(30/10/0)	Samples taken at 24 and 25 hrs
	H2/CO = 3 at 200 for 22 hrs	(30/10/0)	Samples taken at 9 and 10 hrs
	H2/CO = 3 at 220 for 11 hrs	(30/10/0)	Samples taken at 9 and 10 hrs
	H2/CO = 3 at 230 for 17 hrs	(30/10/0)	Samples taken at 9 and 10 hrs
	Re-reduced at 400°C for 2 hrs		
2/1:	H2/CO = 2 at 200 for 25 hrs	(23/10/6)	Samples taken at 21 and 22 hrs
	H2/CO = 2 at 209 for 12 hrs	(22/8/13)	Samples taken at 8 and 9 hrs
	H2/CO = 2 at 220 for 12 hrs	(20/10/10)	Samples taken at 8 and 9 hrs
	H2/CO = 2 at 229 for 18 hrs	(20/10/10)	Samples taken at 9 and 10 hrs
	Re-reduced at 388°C for 16 hrs		
1/1:	H2/CO = 1 at 200 for 27 hrs	(10/11/0)	Samples taken at 8 and 9 hrs
	H2/CO = 1 at 210 for 21 hrs	(10/10/0)	Samples taken at 6 and 7 hrs
	H2/CO = 1 at 220 for 22 hrs	(10/10/0)	Samples taken at 6 and 7 hrs
	H2/CO = 1 at 230 for 35 hrs	(10/10/0)	Samples taken at 9 and 10 hrs
	Re-reduced at 404°C for 12 hrs		
1.5/1: (Deactivation)	H2/CO = 1.5 at 230 for 67 hrs	(20/13/0)	Samples taken at 6, 10, 14, 17, 21, 25, 29, 32, 36, 40, 43, 47, 51, 55, 58, 62 hrs

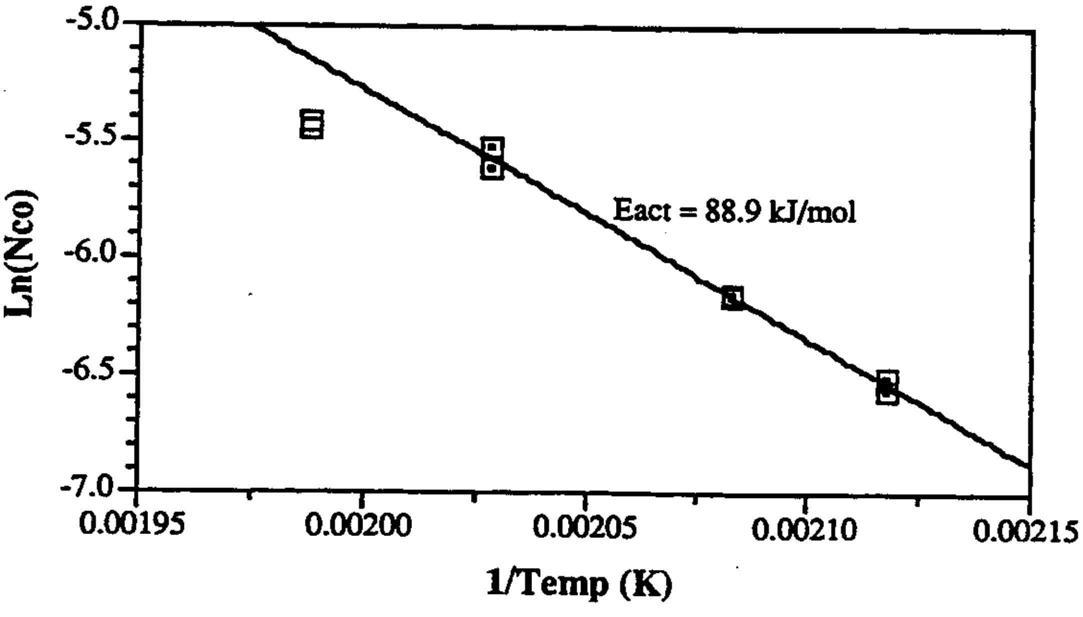

Figure 15. Activation energy plot for catalyst Fe-A-203 at 3/1 H_2/CO ratio.

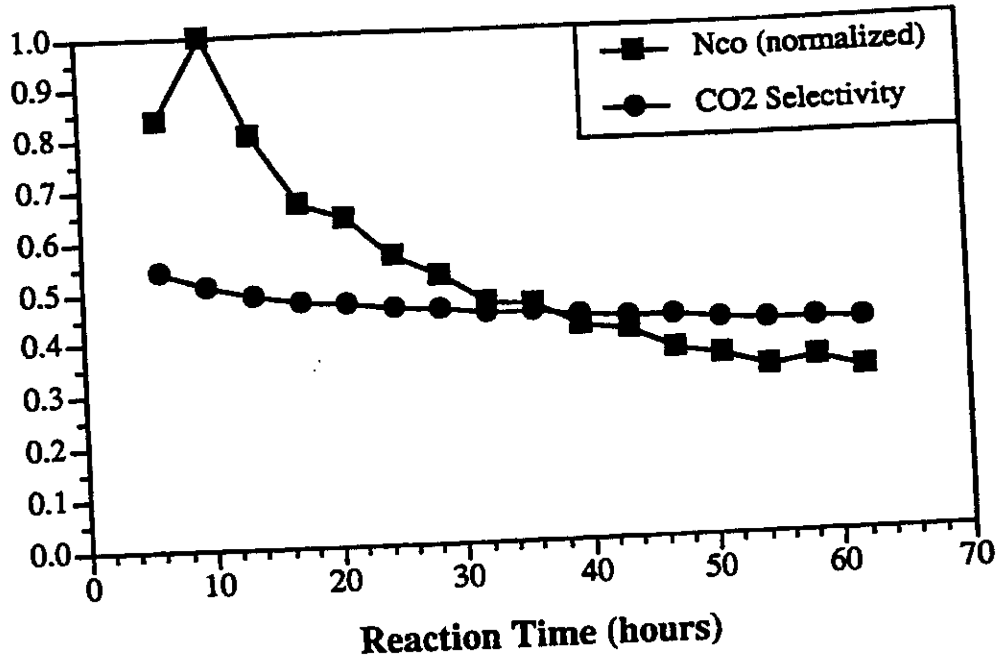

Figure 16. Fe-A-203 deactivation plot.

Figure 16 is a plot of activity (normalized to highest rate) as a function of time. The maximum activity was measured at 10 hours on stream. In the next 40 hours the activity decreased by nearly 70%. Also shown is the CO_2 production (as fraction of CO converted to CO_2). CO_2 production decreases with time from 0.54 at the first measurement to 0.41 at the last. From this plot a deactivation order of 0.9 was obtained [50].

(Fe-A-204.) This catalyst was to be used to supplement Fe-A-203 at H_2/CO ratios of 2/1 and 1/1. However, after reacting at 200-220°C for 48 hours and not being able to obtain steady CO and He flows the reaction runs were cancelled.

(Fe-A-205.) Runs were made for this catalyst sample at $H_2/CO/He$ ratios of 3/1/0, 2/1/1, 1/1/0 and 1/1/2 with the total flow kept constant at 40 cc/min for each. At each set of flows reaction data were obtained at 200, 210, 220 and 230°C. Figure 17 shows the activity data (total CO turnover number) for each set of gas flows and temperatures. The first and third set of data appear to have the expected trend—activity increases with increasing temperature. However, the second set did not exhibit those same characteristics. Activity increased for the lower three temperatures but decreased at the highest temperature (230°C). This drop may be due to deactivation as the samples were taken at 22 and 23 hrs on stream rather than 10-12. The last set (1/1/2) was incomplete due to a crack that developed in the ten-port sampling valve in the gas chromatograph. Because of these inconsistencies the second and fourth sets ($H_2/CO/He$ ratios of 2/1/1 and 1/1/2) were later redone. One of the temperatures at the 1/1/0 ratio was also redone to measure the reproducibility of the data.

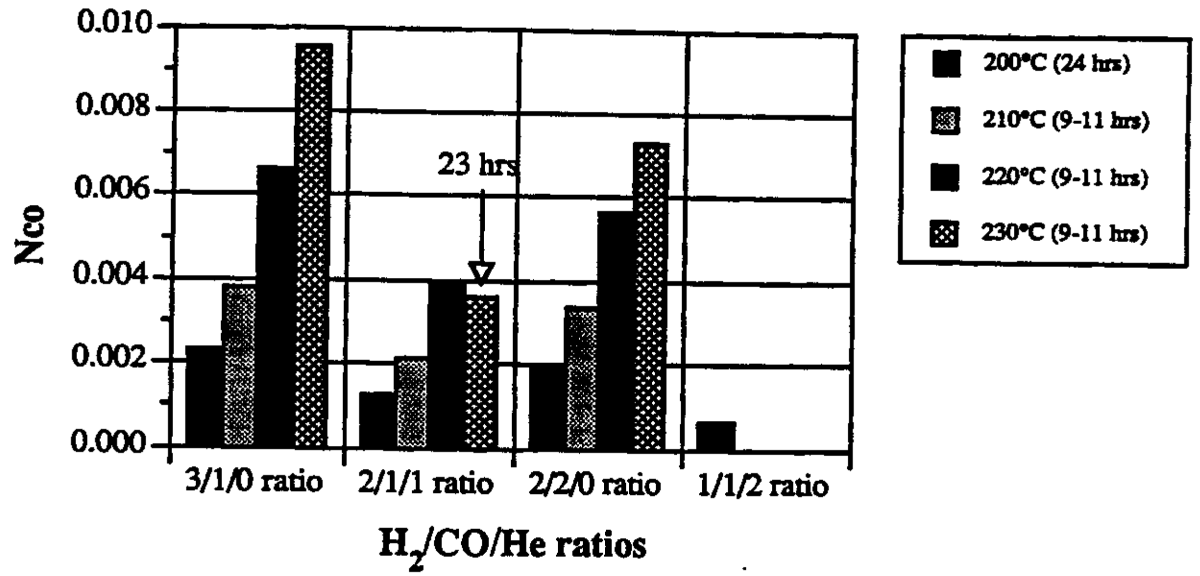

Figure 17. Fe-A-205 catalyst activity (CO TOF).

The activity of the initial fresh catalysts was followed from about 1 to 30 hrs on stream for the 3/1/0 and 2/1/1 ratios at 200°C. Figures 18 and 19 show the catalyst activity in terms of total CO converted and of hydrocarbons (HC) produced. Both figures exhibit similar characteristics but the deactivation effects are more pronounced in the 3/1/0 run, that is, the total CO consumption decreases

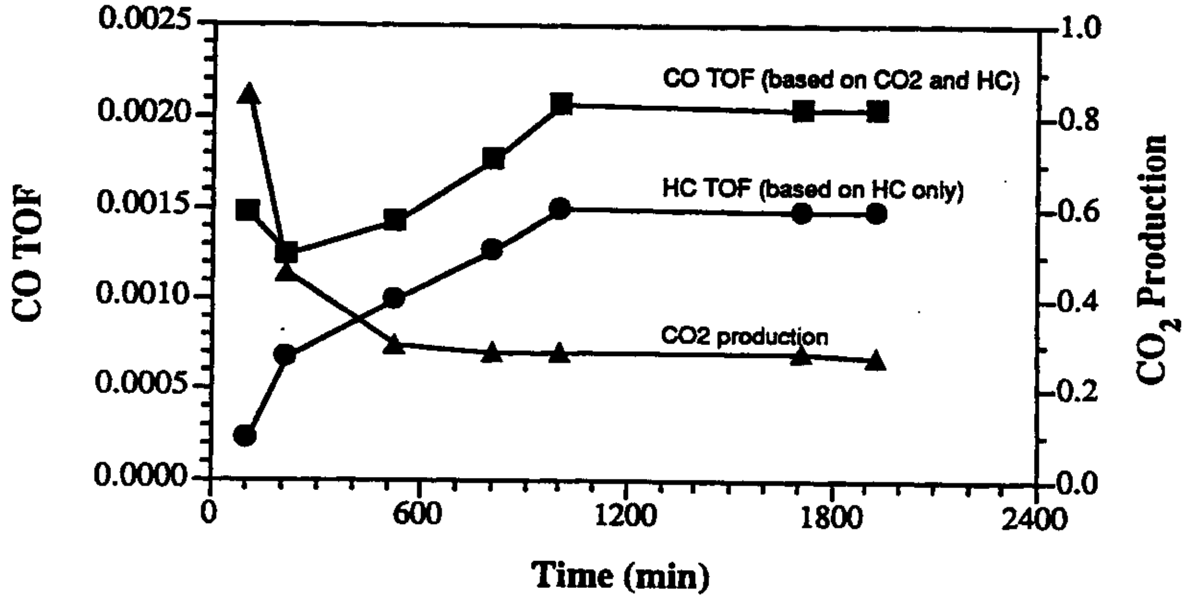

Figure 18. Catalyst activity as a function of total CO consumption and HC production. (Fe-A-205, 200°C, 3/1/0 H_2/CO/He ratio)

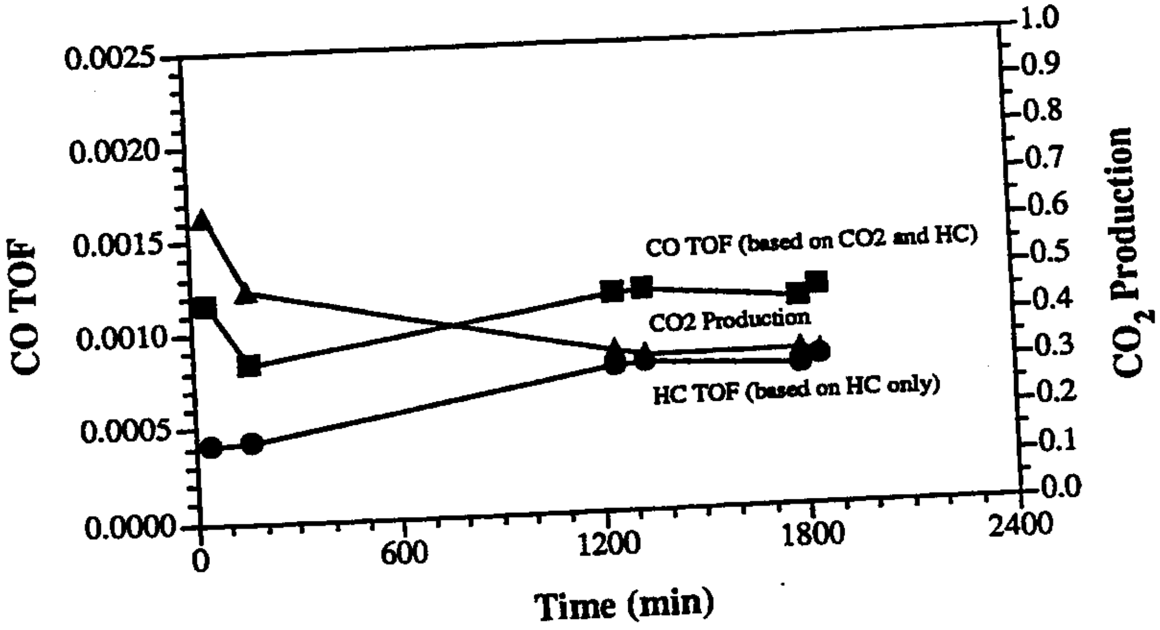

Figure 19. Catalyst activity as a function of total CO consumption and HC production. (Fe-A-205, 200°C, 2/1/1 H_2/CO/He ratio)

initially somewhat and then increases to a constant value after about 20 hours. The reason for this behavior is evident when the total CO consumption is broken down into the CO_2 and HC components. Hydrocarbon production is seen to rise until it reaches a constant value after 20 hours. The drop in total CO consumption then must be due to changes in CO_2 production. Indeed, the CO_2 production (shown as fraction of CO converted to CO_2) decreases from initial values of 85% (3/1/0) and 65% (2/1/1) to about 30% in both cases. Initially, the reaction to produce CO_2 accounts for most of the CO consumed but as the catalyst becomes more covered with carbon the reaction of CO to hydrocarbons becomes the dominating reaction.

Activation energies were calculated from the activity data by plotting the natural logarithm of the CO turnover number against the reciprocal temperature (Arrhenius plot). Figure 20 shows the data and the regression parameters. The lowest three temperatures were used to calculate the activation energies since the effect of deactivation appears to be significant at 230°C as seen by activities that fall below the regression lines. The values of 102 and 107 kJ/mol are consistent with previous values of 97 kJ/mol for Fe-A-201 (at 3/1/0 H_2/CO/He).

From this new set of data it is possible to calculate reaction orders (x and y) in the reaction rate expression $-r_{CO} = k(P_{CO})^x (P_{H_2})^y$. To calculate x, for example, requires that data be obtained at a constant partial pressure of H_2 at two or more pressures of CO. Taking the logarithm of both sides of the rate expression and lumping all constants together gives an expression of the form $C = x \, LN(P_{CO})$ where C is a constant. A plot of C versus $LN(P_{CO})$ yields a regression slope equal to x. Figures 21 and 22

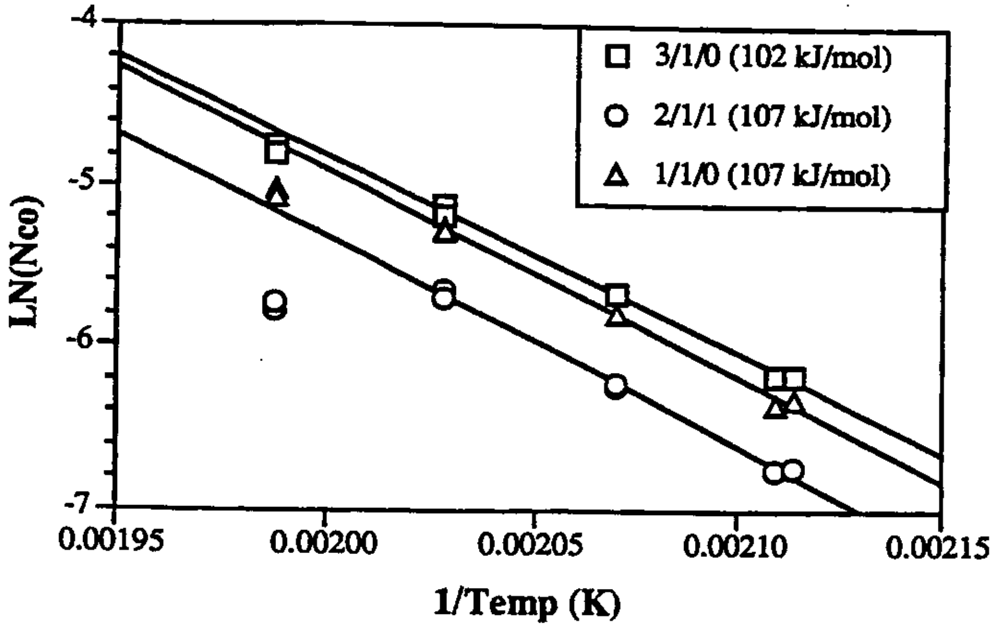

Figure 20. Arrhenius plots for Fe-A-205.

show the plots from which the coefficients were calculated. The rate expression becomes $-r_{CO} = k(P_{CO})^{0.60} (P_{H_2})^{1.36}$ with the values obtained from these plots. For the conditions of these experiments this indicates that the rate is more dependent upon the hydrogen partial pressure than the CO partial pressure but that increases in either one will increase the rate. Extrapolating to conditions outside the bounds of these experiments may result in incorrect conclusions.

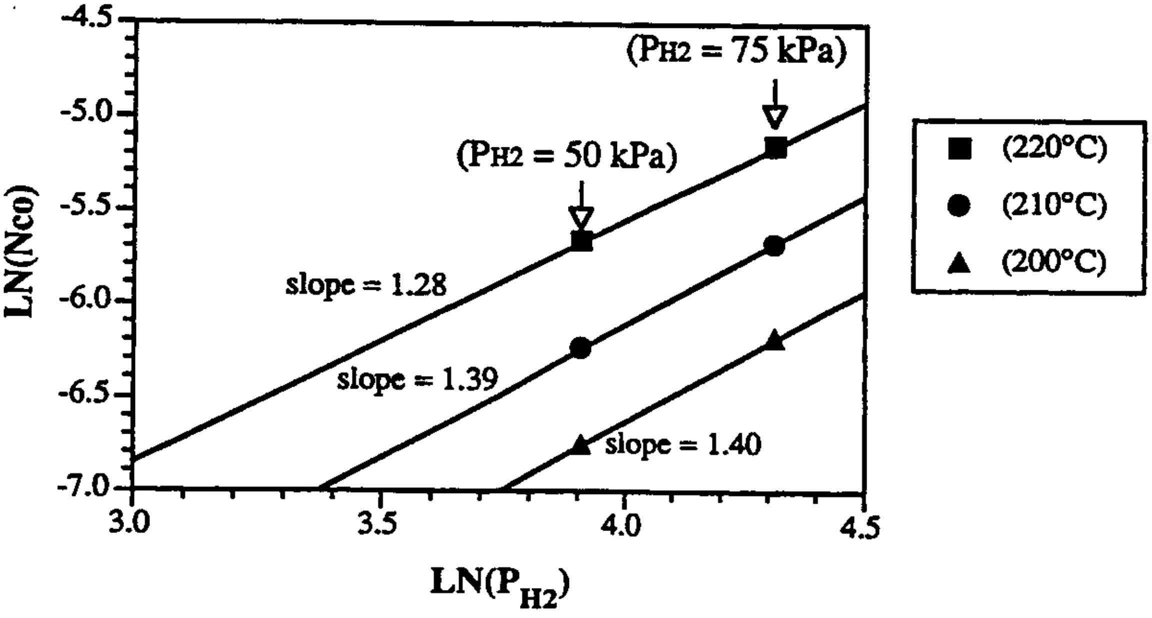

Figure 21. Reaction orders for constant P_{CO} (25 kPa) at 200-220°C.

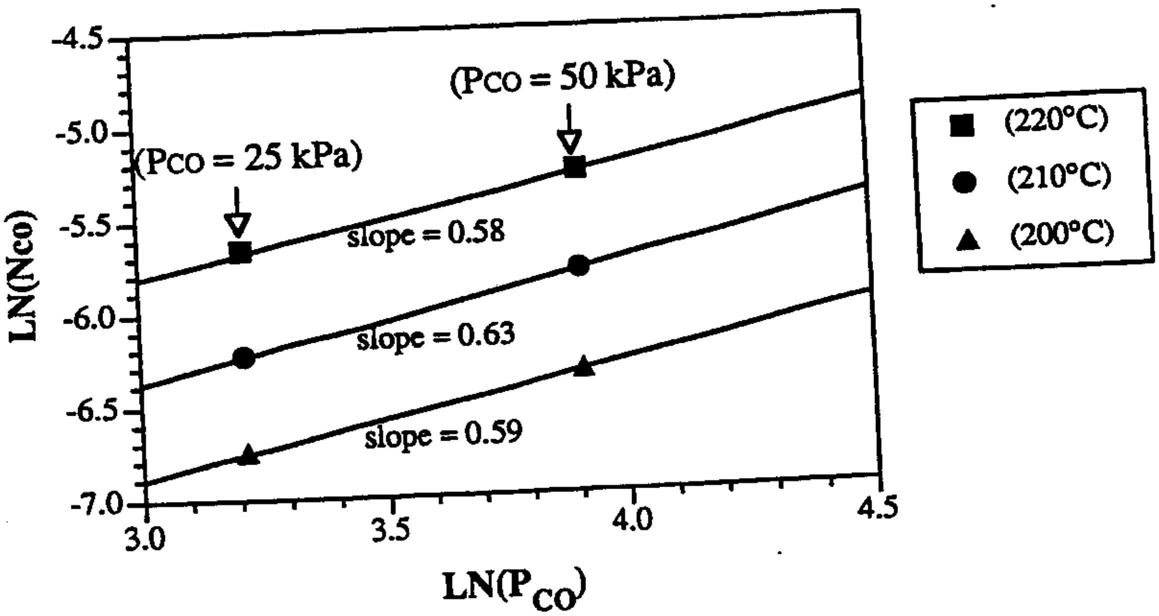

Figure 22. Reaction orders for constant P_{H_2} (50 kPa) at 200-220°C.

e. Fe/K-A-300 Series. (Fe/K-A-301) Reaction conditions were initially 200°C and $H_2/CO = 3$. Temperatures were increased in 10 degree increments after reacting at each temperature for 10 to 24 hours. The catalyst was not active enough for the thermal conductivity detector to register a methane peak until the reaction temperature reached 250°C. The CO conversion did not exceed 3% until a reaction temperature of 350°C. Based on the low activity of the potassium promoted catalyst it is concluded that the potassium content on the surface of the catalyst was significantly higher than the calculated total molar ratio. A rough estimate of the surface ratio based on hydrogen uptakes of the unpromoted and promoted catalysts gives a maximum K/Fe surface ratio of 20, nearly three orders of magnitude greater than the desired amount. When compared to activity data of catalysts with varying potassium contents [48], the activity of Fe/K-A-301 more closely resembles a catalyst having a K/Fe ratio of 0.2 to 0.3. Because of the low activity of Fe/K-A-301 it was decided that the amount of potassium added to make a new K-promoted catalyst would be decreased to one-fifth of the previous amount. No further reactions were performed with this catalyst.

f. Fe/K-A-400 Series. (Fe/K-A-401) From the results for Fe/K-A-301, it is clear that potassium promoted catalysts require higher temperatures to achieve comparable CO conversions to those of the unpromoted catalysts. For this reason, the initial reaction conditions chosen for catalyst Fe/K-A-401 were 230°C at a H_2/CO ratio of 3/1. The activity was a maximum after one hour on stream and decreased by 75% over the next 19 hours.

The purpose of the kinetic study is to obtain kinetic data at conditions where the effect of deactivation is minimal or non-existent. The apparent deactivation at 230°C indicates that lower