CHAPTER IX.D

PROMOTER LEVELS - ACTIVITY AND AGING

OBJECTIVES

The objectives of the present study included four targets that made the experimental work extremely difficult, and this was especially true for a program that was initiated with a team whose members had little or no prior experience in Fischer-Tropsch synthesis research.

The four targets that made for very difficult experimental and/or technical operations were:

1. testing at higher (10-20 wt.%) catalyst slurry loadings that required high gas flows;
2. attaining 90% CO conversion at 3.4 NL/hr-g.Fe and the resulting high gas flow;
3. conducting aging studies for two months using high gas flows and a low alpha catalyst led to the depletion of the solvent more rapidly than it was produced, and;
4. maintaining reasonably stable reactor conditions for two months for the aging studies.

INSTALLATION AND OPERATION OF CSTR REACTORS

During the three years, eight 1-liter continuous stirred tank reactors (CSTR) with the associated gas regulators and sample collection vessels were installed and operated almost continuously. The schematic of the unit is presented in Figure IX.D-1.

The temperatures of the product traps were maintained initially at 200, 60 and 0°C. However, the 200°C hot trap caused products to end up in the 60°C trap that would not elute from the gas chromatograph; thus, the temperature of the hottest trap was maintained subsequently at 160°C. These temperatures, except for the 0°C trap, were not precisely controlled so that the temperature may vary by several degrees during the course of a two month run; likewise, there will be variation of the trap temperatures from reactor to reactor. The carbon number distribution for the traps, based upon ideal solution and vapor approximations, are illustrated in Figure IX.D-2. The collection of liquid/solid samples produce severe demands on the carbon number distribution determinations, especially for low α-catalysts.

CATALYST TESTING CONDITIONS

The test conditions for the experimental program were essentially those reported by Kölbel and Ralek (9.D.1) except that the gas flow rate was to be 3.4NL/hr.g(Fe) instead of the 2.4NL/hr.g(Fe) that was used by Kölbel and Ralek. The operating conditions specified in the contract include the following:

Process conditions

H_2/CO ratio in the feed	0.7
Synthesis temperature	270°C
Pressure, bar	12
Syngas flow rate(Nm^3/hr/gFe)	3.4

Desired activity and selectivity

CO conversion, %	90
CO + H_2 conversion, %	88
Total CO + H_2 used per kg Fe (Nm^3/hr.)	2.6
Hydrocarbons produced per Nm^3 syngas used:	
Total, g.	178
C_{3+}, g	166
STY of C_{3+} in 24 hr (kg/m^3 of reaction chamber)	900

One of the objectives was to determine the preferred pretreatment conditions. The pretreatment utilized initially was one that had been utilized by UOP in their work to qualify a catalyst for Run 1 at LaPorte. This pretreatment involves heating to a prescribed temperature in an inert gas and then switching to a syngas mixture. This "standard syngas" procedure is outlined below.

The catalyst slurry was heated from room temperature to 280°C in an inert gas (helium) flow of 0.6 ft^3/hr and held at this temperature for one hour. The gas was then switched from helium to synthesis gas (H_2/CO = 0.7) and the flow was increased to 2 NL/hr-g(Fe). The stirrer speed was 1100 rpm and the activation was continued for 16 hours. For testing the catalysts prepared by UCI the temperature was decreased from 280 to 265°C during 2-3 hours. The pressure was then increased to 24.7 atm. and the gas flow rate was increased to 2.4 NL/hr-ge(Fe).

At the CAER we have utilized a pretreatment in CO and the "standard" pretreatment is outlined below.

The catalyst slurry was heated at 1.5 to 2.0°C/min. to 270°C in a flow of CO (2.0 NL/hr-g(Fe). The catalyst was held at 270°C in the CO flow for 24 hours. The stirrer speed was 750 rpm. To initiate a synthesis period, the CO flow rate was maintained and a hydrogen flow was initiated to increase the total flow to 3.4 NL/hr-g(Fe).

The standard conditions for chemists have traditionally been 0°C and 1 atm; however, engineers frequently utilize room temperature (25°C) as the normal temperature. Thus, unless noted otherwise, the engineering approach has been utilized in this chapter. In addition, some runs were made before the analytical data were obtained for the iron catalyst; thus the iron content of the added oxide form was assumed to be completely dry. In some cases the added catalyst contained some moisture so that the flow rate would have been higher than reported.

A typical catalyst aging curve is illustrated in Figure IX.D-3. There is typically a period during the initial time on stream where the catalyst exhibits a very rapid decline in conversion during a short time period and this is then followed by a long period of stable activity with very slow decline in activity. Ultimately a time on stream is attained where the catalyst activity will then undergo another period of rapid decline to approach a very low percentage of conversion of the feed. For nearly all of the successful runs during this contract, it was observed that the initial activity of a CO pretreated catalyst increased for a period of 24 to 50 hours following exposure to syngas; thus, it is considered to be very unlikely that there was a rapid initial decline in activity as is illustrated in Figure IX.D-3, at least with CO pretreated catalysts. Insufficient data was collected during this study to define whether this type of catalysts that were prepared exhibited the rapid decline in activity after a long time on stream or whether this type of decline was due to reactor operations. It does appear that an iron catalyst that contains no, or even a very low level of, potassium promoter declines in activity in a linear fashion following a period of stable and high activity. However, this has not been defined for a catalyst that contains about 0.5 wt.% potassium. If the Fischer-Tropsch catalysts that we prepare and test to meet the target CO conversion of 90% were to age as shown in the schematic in Figure IX.D-3, the targeted test conditions would not be very appropriate; however, it appears that testing at 90% conversion is not a problem for the CO pretreated catalysts.

CATALYST LOADING AND REACTOR OPERATION

It could be anticipated that reactor operation would become more demanding as the catalyst loading is increased. The data that were generated in trying to decide whether this is the case are reasonably definitive; however, a rigorous definition of the impact of catalyst loading upon the results of the reactor operation would require a separate and demanding study. The data in Figure IX.D-4 show that CO conversion varied by less than 5% as the catalyst loading in the slurry was varied over the range from 3 to 20 wt.%. The solvent for these runs was varied since the initial goal of the runs was not to test the impact of catalyst loading. The solvent used for catalyst loadings of 3, 5, 10 and 20 wt.% loading was a Ethyl (Ethylflo 164) C_{30} oil. These runs should therefore be directly comparable. The start-up solvent for the 4 wt.% loading was a hydrogenated Fischer Tropsch hard wax; the supplier obtains this wax from Sasol. For the 8 wt.% loading, an Allied-Signal C_{40} polyethylene oil was used. It is not apparent why there should be a gradual decline and recovery of activity as shown in Figure IX.D-4 for catalyst loading and, because of the press of time constraints to proceed to catalyst testing, the study was not pursued to learn whether this slight deviation was reproducible. During the course of the experimental program runs were made with portions of a common batch of catalyst at slurry solids loading of 5, 10 and 20 wt.%; the solvent for each of these loadings was the Ethyl C_{30} oil. The results for these loadings suggest the same conclusion - the conversion is not strongly dependent upon catalyst slurry loading - but do show a wider range for CO conversion (about 10% between the extremes rather than only about 3%) as the slurry loading increases from 5 to 20 wt.% (Figure IX.D-5). As part of the support work conducted at the CAER for the LaPorte Run 2, a common batch of catalyst was tested at 10 and 29 wt.% loading using Ethyl C_{30} oil (Figure IX.D-6) and a vacuum distillation residue of a Allied-Signal polyethylene wax (Figure IX.D-7). The Ethyl C_{30} oil, based on g.c. analysis, has a narrow carbon number distribution as would be expected for an oil that is based on the trimer fraction of 1-decene oligomerization. The Allied-Signal wax showed a wide carbon number distribution that peaked in the C_{40}-C_{50} carbon number range, as reported by UOP and verified in our study. This wax was subjected to a vacuum distillation by increasing the temperature until the onset of thermal cracking made it difficult to maintain a low pressure. The vacuum distillation residue contained very little C_{40-}, and represented approximately the heavier half of the original sample. The data using both solvents indicate that conversion is much lower at the 29% solids loading than it is at 10 wt.% loading. The CO conversion in the C_{30} oil is about 40% at 29 wt.% loading whereas it is 90% at the 10 wt.% loading (9.D.6); for the distilled Allied-Signal wax the 29 wt.% loading leads to a CO conversion of about 55% compared to 90% for the 10 wt.% loading (9.D.7). Furthermore, due to the high gas flow needed to maintain a syngas flow of 2.4NL/hr.-gFe for the 29 wt.% loading, the activity declines more rapidly with time on stream for the higher catalyst loading. This decline is more rapid in the C_{30} oil than in the heavier wax, as would be expected if the loss of conversion is primarily related to loss of solvent. Since the conversion is higher in the heavier distilled Allied-Signal wax residue than it is in the lighter Ethyl C_{30} oil, it appears that mass transfer limitations are not a major factor in determining the CO conversion level.

REACTOR OPERATION - INITIAL PROBLEMS

A number of problems were encountered during the early portion of the contract. The reactors utilized in this study contain a hollow impeller shaft with holes near the top and bottom of the shaft. These holes are intended to cause a down draft of the gas contained in the dead space of the reactor and in this manner effect contact between the liquid and gas phases contained in the reactor. Experiments using water as the liquid phase and nitrogen as the gas phase showed that such mixing did occur. At a stirrer speed of 500 rpm, gas bubbles began to appear at the opening at the bottom of the hollow impeller shaft and disperse into the liquid phase. Pictures indicated that dispersion of the gas bubbles into the liquid phase was about as great at 750 rpm as they were at 1,000 rpm. Likewise, experiments with several catalysts and the light oils that were utilized as start-up solvent indicated that the CO conversion did not increase significantly when the stirring rate was varied between 750 and 1150 rpm; thus, unless specified otherwise the stirring rate was 750 rpm.

During the early runs at the high gas flow rates needed to operate with 20 wt.% slurry, it became apparent that solvent was being lost from the reactor at a faster rate than it was being produced. Thus, the liquid level slowly decreased and in at least one instance the reactor was completely "dry" when the run was terminated. One approach would have been to deliberately run the reactor so that the head was at a much lower temperature than the liquid; in effect we would have reflux in the reactor so that a higher fraction of the lighter liquid would be retained. However, this reflux would have made it difficult to obtain an accurate product selectivity for the runs. Even so, there was some temperature difference between the liquid level and the very top of the reactor, as illustrated in Figure IX.D-8.

In the initial runs, the diameter of the tube connected to the sintered metal filter was small (1/8 inch o.d.). While the filter was immersed in the liquid, the gas would leave as a bubble surrounded by an oil film. This caused the oil to leave the reactor at a rapid rate so that the reactor would be depleted of most of the liquid within one week of operation. This problem was solved, or at least eliminated in most cases, by having the size of the tube of the filter enlarged to 1/4 inch o.d.

In many runs, a foam would develop inside the reactor. In these runs, especially with some of the runs using the catalysts prepared by UCI prior to LaPorte Run 2 and with catalysts prepared at the CAER that contained alumina rather than silica, this foam formation caused the run to be terminated after only one to two weeks on line. In the case of the alumina containing catalyst, it was found that the catalyst produced much more of the alcohols than the silica containing catalyst did. It is assumed that the alcohols that were produced acted as a surface active agent to effect foaming. However, it does not appear that the higher amounts of alcohols were formed with many of the UCI catalysts so that there must be an additional reason for the foam formation in addition to the presence of large amounts of alcohols. The foam would fill the reactor and then exit the reactor through the gas exit line; in addition to the gas/liquid mixture exiting the gas line solid catalyst would be carried over with the foam. Thus, in addition to losing reactor oil, catalyst was lost from the reactor. The stirrer, as provided by PPI, has two blades, one with impellers perpendicular to the shaft and the other with an angle of about 30°; the 30° angle blade was moved up the stirrer shaft to near the top of the reactor. This measure was very effective in decreasing the problems encountered for foam formation and its interference with the operation of the reactor.

The major problem that has been encountered to date, and one that is still not solved nor explained, is the sudden drop in conversion followed in many cases by a recovery of conversion. This is described in a later section.

ATTAINMENT OF TARGETED ACTIVITY AND AGING RATE

The data in Figure IX.D-9 show that both the targeted activity and catalyst aging rate were met or exceeded for a material that contains 3.6 atomic percent Si and 0.71 atomic % K.. Following a 24-hour pretreatment at one atmosphere in synthesis gas ($H_2/CO = 0.7$), the activity increased from 84% CO conversion to about 93% CO conversion after 24 hours of time on stream. Following this maximum CO conversion at 3.4 NL/hr.-g.Fe, the conversion decreased rapidly to the 88% CO level. At the 88% CO conversion level, the aging rate was slow. During a three-month period (2,016 hours) of time on stream, the activity declined from 93 to 83% CO conversion. Thus, during the three-month period, the CO conversion declined at a rate of 0.83%/week; this is lower than the 1.0%/week that was the targeted value. If the initial rapid decline of the CO conversion to the 88% level is ignored, the aging rate for a three month period (200 to 2216 hours) is 0.42%/week.

One of the objectives of the work was to demonstrate a continuous precipitation procedure and that the preferred preparation procedure would lead to catalyst batches with a constant activity. A variety of silicon containing catalysts were prepared during the course of the study and these, when promoted with potassium, led to a catalyst that had an initial activity in 80 to 95% CO conversion at 3.4NL/hr.-gFe (Figure IX.D-10). Again, the conversion is shown for the period of approximately constant activity is shown. The details of the catalyst composition are given in Table

IX.D.1. The data in Figure IX.D-10 show that different preparations of the same, or very similar, catalyst composition leads to materials that have very similar activity

Table IX.D.1

Catalyst Tested that Contain Silica (Pretreatment in CO at 270°C and 175 psig; Synthesis Runs at 270°C, 175 psig and 3.4 nL/hr g(Fe))

Run No. (LGX)	Catalyst Loading (wt.%)	Slurry Oil	Silica, Atomic %	Potassium, Wt.%
035	20	C-30	4.4	0.1
045	20	C-30	4.4	0.5
046[a]	8.0	C-30	4.4	0.5
049[b]	3.0	C-30	4.4	0.5
051[b]	5.0	C-30	4.4	0.5
052[a]	5.0	C-30	4.4	0.5
053	20	C-30	4.4	0.5
088	10	C-30	5.0	0.5
089	10	C-30	5.0	0
092	10	C-30	4.4	0.2
093	10	C-30	4.4	0
095	10	C-30	5.0	1.0
096	10	C-30	5.0	1.5
102	8.0	Pol. wax	4.4	0.5
103	10	Pol. wax	5.0	0.5
112	10	FT wax	4.4	0.5
113	10	FT wax	5.0	2.0
122	4.0	FT wax	4.4	0.5
124	5.0	FT wax	5.0	0
126	10	FT wax	4.4	0.5
128	10	FT wax	4.4	0.5

levels, and it is therefore concluded that the target of providing a preparative procedure that leads to similar activity catalysts from batch to batch has been attained.

Another target of the program was to prepare a 100 pound batch of the preferred catalyst for PETC. Thus, about 160 pounds (approximately 2,000 pounds of slurry) were prepared by a continuous precipitation method at the CAER. This catalyst contained 4.4 atomic% Si and sufficient potassium nitrate was added to the slurry to provide 0.5 wt.% K. The slurry was taken to UCI where it was spray dried and calcined at 350°C. The targeted CO conversion activity (90%) and the aging rate (less than 1% CO conversion/week) were met with this catalyst. As shown in Figure IX.D-9 the material pretreated in synthesis gas ($H_2/CO = 0.7$) at one atmosphere pressure for 24 hours attained a maximum conversion of about 93%. The activity decline was about 0.8% CO conversion/week. Thus, the scale-up of the continuous catalyst precipitation process was scaled to the target of 100 pounds/week and the material that was produced was shown to have a reproducible activity, selectivity and aging rate compared to similar batches prepared on a smaller scale.

The activities of three samples collected at different times or locations during the spray drying are shown in Figure IX.D-11. Shown are data for a sample collected from the cyclone as well as for samples collected in the collection chamber during two periods of operation: the one sample was collected during the early period of spray drying when the flow/temperature conditions resulted in a material that contained significant amounts of moisture (wet chamber) and later when the conditions had been adjusted so that the material that was collected was dry (dry chamber). The activity results in Figure IX.D-11 are for catalysts that were pretreated using the standard CO pretreatment procedure. All three samples provide a similar conversion-time curve for the initial 500 hours on stream, showing reproducibility of the reactor operation. However, the aging characteristics of the cyclone sample appears to be better than for the two chamber samples; it is believed that the drop in activity at later time on stream for the two chamber samples is mostly, if not entirely, due to reactor operation rather than actual differences in the catalyst. A portion of the slurry that was taken to UCI for spray drying was retained at the CAER and the solids collected by filtration followed by drying at 110°C. The CO conversion for the small portion of the catalyst that was dried at the CAER was about 90% and retained most of this activity level during about 2,000 hours of time on stream. The conclusion is that the large scale production of 100 pounds of catalyst produced a material that is the same as had been prepared earlier in smaller batches. This should not be surprising since the same equipment and conditions were utilized for both the small batches and the larger, 100 pound batch; the only difference was that a longer time was required for the continuous precipitation of the material for the 100 pound batch. It is also concluded that a calcination at about 350°C did not materially effect the ultimate CO conversion of the activated catalyst.

Another targeted objective for the work was to determine the optimum level of alkali promoter to produce the maximum activity. This task is complicated because the alkali may impact the ease of pretreatment, the amount and type of carbide phase that is formed, and the rate that the catalyst ages. The data shown in Figure IX.D-12 were obtained during the early portion of the study before the dip tube was installed in each reactor so that the reactant gas would enter at bottom of the slurry; however, subsequent experiments indicate that the general trend of the curve is valid provided it is based upon conversion after a few hundred hours on stream. Thus, with low (4 to 6 atomic %) Si iron catalysts, the optimum potassium level is about 0.5 wt.% (0.71 atomic % relative to Fe) K. However, the time on stream impacts the ultimate shape of the curve and the optimum potassium loading. The data in Figure IX.D-13 show that initially the conversion of the catalyst that does not contain potassium and the one containing 0.2 wt.% potassium have a similar activity up to 50 hours on stream, and very similar activity even after about 120 hours on stream. However, the difference between these two catalysts becomes greater with time on stream since the potassium free catalyst ages at a more rapid rate. In the case of the 0.2 wt.% K catalyst, a portion of the initial activity is regained following the sharp activity drop at about 350 hours on stream. Thus, if we compare catalysts with 0 to 0.5 wt.% potassium after only about 50 hours on stream we would conclude that all of the catalysts had a similar activity (Figures IX.D-13 and IX.D-14); however, if the comparison of activities is after about 300 hours on stream a curve similar to the one shown in Figure IX.D-12 is obtained.

Representative data for longer term testing (1,000 to 2,000 hours) for three catalyst loadings (4, 10 and 20 wt.%) are shown in Figure IX.D-15. The catalysts used in these tests have the same chemical composition. It is noted that the same trend is observed for each catalyst loading: initially there is an increase in activity to attain a CO conversion level that is approximately 90% and then a short period of rapid activity decline that is followed by a period of very slow activity decline. In each of the runs the decline is slight when compared to the more dramatic declines to be described later. For the 10 wt.% loading, the CO conversion declines to a minimum at about 500 hours on stream and then partly recovers the original CO conversion; again, this occurs during many of the runs. As shown later, this rapid activity decline for the low alpha catalysts is at least influenced by reactor operating conditions. In spite of the decline, it is evident that there is little significant difference in the catalyst aging trend, or even the actual magnitude of the trend, for the three catalyst loading levels. Furthermore, once the rapid decline in CO conversion of 10 to 20% has occurred, the catalytic material possesses a stable activity.

The data in Figure IX.D-16 compares the activity trend during long-term testing for a common iron-silica catalyst base which contains additionally 0 or 0.5 wt.% potassium. In the later case the potassium is added by impregnation by adding the required amount of solution containing potassium butoxide to the iron-silica slurry contained in the CSTR. Both catalysts were then activated, using the "standard" CO pretreatment. Again, both catalysts exhibit an induction period in which CO conversion increases to attain in both cases the 90% CO conversion level. In the case of the catalyst that does not contain potassium, the CO conversion begins to gradually decline after about 500 hours on stream and, at first, approximates a linear decline but then appears to begin an asymotocal approach to a low, nearly constant activity. During the linear decline period, the CO conversion decreases at a rate of approximately 0.079%/hr (1.9%/day; 13%/week). The hydrogen conversion declines at a slower rate than the CO conversion during the period of linear decline, and the decrease is approximated linear during the latter 1,000 hours of the run. The decline in hydrogen conversion is approximately 0.041%/hr (0.98%/day; 6.7%/week). Since the catalyst does not contain potassium, the activity for the water-gas-shift (WGS) reaction is low compared to K-containing catalysts. The contribution of WGS to the reaction is more important at high CO conversion levels; thus, the hydrogen conversion is higher during the early portion of the time on stream and therefore declines at a slower rate than would be the case for K-containing catalysts where the hydrogen conversion is lower than that of CO.

CO CONVERSION RELATIVE TO H_2 CONVERSION

The impact of the WGS reaction on the relative conversion levels of CO and H_2 are clearly evident in Figure IX.D-16 for the catalyst that contains 0.5 wt.% K. Initially, at the 90% CO conversion level, the hydrogen conversion is about 78%. This difference has been shown to be due to the dependence of the relative rates of WGS and hydrocarbon synthesis rates on the total CO conversion (Figure IX.D-17). Thus, at high CO conversions, the hydrocarbon production rate is about the same as the WGS reaction; however, at low CO conversion the hydrocarbon synthesis rate is high compared to the WGS reaction. This conclusion is based, however, upon an active catalyst where the two rates are obtained by varying the total flow rates, and not for the case where the catalyst activity is declining. For this reason, the relative rates versus CO conversion shown in Figure IX.D-17 may not be completely applicable to the case shown in Figure IX.D-16. However, the general trend of the relative conversions of CO and H_2 shown in Figure IX.D-16 for the K-containing catalyst is applicable in general.

The conversions of CO and H_2 are shown versus the reciprocal flow rate in Figure IX.D-18 for an unpromoted ultrafine iron catalyst. The "cross-over point," where the CO and H_2 conversions are equal, occurs at a low CO conversion level. As reflected in Figure IX.D-19, the ratio of the CO/H_2 conversion is initially greater than one, becomes equal to one at the cross-over point and then continues to decline to values less than one. The conversion data for a potassium promoted catalyst possessing high catalytic activity (Figure IX.D-20) show a trend that is similar to that of the ultrafine catalyst; however, the cross-over point occurs at a much higher total CO conversion level. The trend in CO and H_2 conversions has been obtained repeatedly for the reaction conditions utilized in this study (270°C, 12.9 atm and $H_2/CO = 0.7$); however, they should not be viewed as a general conclusion that can be extended to all Fischer-Tropsch synthesis conditions.

SAME INDUCTION - DIFFERENT RESULTS

Two catalysts were tested following the same induction (pretreatment) procedure. Furthermore, the two catalysts were prepared to have similar, if not the same, compositions. One of the catalysts was obtained from Ruhrchemie by PETC personnel and provided to us for testing. The other catalyst was prepared by United Catalysts, Inc. (UCI). The activation conditions involved heating to 200°C in an inert gas. The catalyst was then heated to 280°C under synthesis gas ($H_2/CO = 0.7$, 2.0NL/hr-g(Fe); 150 psig) at a rate of 1.5 to 2.0°C/min. and then held at 280°C for 15 hours. Following this activation period, the temperature was decreased to 265°C, the flow of synthesis gas increased to 2.4NL/hr-g(Fe) and the pressure increased to 290 psig. A comparison of the conversion shows that the UCI catalyst had initially an activity that was close to that of the Ruhrchemie catalyst (Figure IX.D-21). However, upon exposure to the synthesis gas the activity of the Ruhrchemie catalyst increased slightly and then began to decline slowly during the more than 700 hours of synthesis. In contrast, the catalyst prepared by UCI showed a precipitous drop in conversion during the first 24 hours of operation, and the activity then continued to gradually decline from about 40 to 20% CO conversion. The UCI catalyst preparation contained a small amount of sulfur. The CO pretreatment of the UCI preparation produced an active catalyst (about 90% CO conversion at a syngas flow rate of 2.4NL/hr.-g(Fe)) so that the sulfur level did not impact the activity during the synthesis. However, the sulfur could have an impact for the syngas pretreatment but this possibility was not fully investigated. The supply of the UCI catalyst preparation was exhausted by the activity tests. A catalyst that had been prepared at the CAER was impregnated with ammonium sulfate to produce the same sulfur level as the UCI catalyst; this modified catalyst had a much lower activity following a CO pretreatment than the unmodified catalyst did. Thus, if sulfur is present in the UCI catalyst, it must be uniformly distributed throughout the solid, and not just present on the surface. These runs were made in support of the LaPorte, TX pilot plant; limited catalyst samples and limited experimental time prevented us from pursuing the study to try to identify the difference(s) between these two samples of very similar chemical compositions that would provide such a wide difference in aging characteristics.

CATALYST ACTIVATION EXTERNAL TO THE REACTOR

One approach to run the LaPorte facility if a suitable wax/catalyst separation is not developed would be to pretreat the catalyst external to the reactor and to replace the reactor catalyst inventory as the slurry is withdrawn. It is realized that this would not be, in general, the approach that would be practiced in a commercial operation. However, this approach would permit reliable productivity and selectivity data to be generated at the pilot plant while an approach for wax/catalyst separation is being developed.

To this end, a catalyst containing 4.4 atomic% Si and 0.71 atomic% K was pretreated in a plug flow reactor with gaseous CO in the absence of liquid hydrocarbon. Following 24 hours of activation, this material was passivated using 1% oxygen in helium flow for three days (passivation for less than three days provided a pyrophoric material when removed from the reactor). The passivated catalyst was then placed in the reactor as would normally be done with a sample that was in the oxide form and subjected to a CO pretreatment for 24 hours. Following pretreatment this catalyst had slightly more than 50% of the activity that the catalyst would have if it was added to the slurry and then pretreated in-situ with CO. Furthermore, the relative CO and H_2 conversion resembles that expected for the catalyst if it had aged to the 50% CO conversion level or if the flow rate had been increased for an active catalyst so that the conversion level was 50% (Figure IX.D-22). Since this catalyst had been passivated and then exposed to air for about a month following CO pretreatment; it would be possible to activate a catalyst in CO at an off-site location and to add additional catalyst at the LaPorte plant site. However, subsequent work showed that it was possible to obtain a more active catalyst if the syngas ($H_2/CO = 0.7$) was used, but at one atm. rather than higher pressure, no additional work was done to define how well the CO pretreated sample could be stored and then reactivated.

SUDDEN CATALYST ACTIVITY LOSS

The CO conversion results for five runs are shown in Figure IX.D-23. These runs were chosen to illustrate the type of sudden activity changes noted during the course of the contract work. Run 51 illustrates a run in which a high conversion was attained and lasted for a period of 200-400 hours (about 200 hours in this instance) and this was followed by a sudden activity decline which then remained at a low level. Run 46 illustrates a run where the initial activity is around the 90% level and then undergoes a decline to attain a lower, but subsequently nearly constant, conversion level. Run 70 illustrates a very rapid decline followed by a reasonably rapid recovery of activity to approach the initial conversion level and then to remain at this high conversion level. Run 71 also shows the rapid decline but a much more gradual recovery of activity than run 70. Run 45 exhibited the initial high conversion at about the 90% level for about 200 hours, then underwent a rapid decline in activity that was followed to a recovery of much of the activity which was then retained for a long period of operation. Attempts to reproduce a run in a reactor equipped to withdraw catalyst samples that could be subjected to characterization have failed to repeat these drops. Furthermore, the time of occurrence of the drop in activity for the same catalyst batch is not reproducible, if in fact it occurs. It appears to us that the drop is most likely due to some reactor operation or condition that is not being controlled in contrast to a sudden change in the composition or activity of the catalyst itself. However, to date we have not been able to identify the factor(s) that is responsible for activity-time curves such as shown in Figure IX.D-23.

Two recent runs provide insight to at least one likely reason for the sudden decline in conversion. Two runs were made with the sample of the 4.4 atomic% Si, 0.5 wt.% K catalyst sample that was collected at the cyclone of the UCI spray drier. These runs were conducted to be identical except for the temperature of the pretreatment.

For run LGX170, 32.2 grams of the catalyst was added to 290 grams of the Ethyl Corporation C_{30} polyalphaolefin oil. After heating to 150°C, a gas flow of 3.4 NL/hr.-g(Fe) was passed through the slurry at one atm absolute and the reactor was heated at 2°C/min to 300°C. After attaining 300°C, the reactor was held at this temperature with the syngas flow for a 24 hour period.

After the pretreatment in syngas for 24 hours, the pressure was increased to 175 psig and the synthesis was initiated. The CSTR was operated so that the gas/liquid stream exited the reactor through a vapor exit line at the top of the reactor; the reactor was also fitted with a tube ending with a metal porous filter (0.5 microns) for withdrawing the reactor wax (rewax). During the first 648 hours of the synthesis, the gas/liquid was withdrawn continuously except for a period when the rewax was withdrawn through the metal porous filter that was immersed in the reactor slurry (1 to 3 hour period). The rewax was withdrawn once each 24 hour period. During the 648 hour period, the CO conversion declined from about 85% to 55% (Figure IX.D-24). During the period between 648 and 792 hours, the rewax was not withdrawn and the CO conversion increased from 55% to 78% CO conversion. The reactor wax (39 grams) was withdrawn at 792 hours on stream. Following the withdrawal of the rewax, the CO conversion quickly declined to 69%. During the period following 816 hours on stream, reactor wax was not withdrawn and the CO conversion was reasonably constant at about 75%.

Another run (LGX171) with another portion of the same batch of the catalyst that was used for run LGX170 was made by heating to 270°C without gas flow (rather than 300°C used for the run described in the paragraph immediately above). After heat-up, the catalyst was pretreated in a syngas flow of 3.4NL/hr.-g(Fe) at one atm. for

24 hours. Because of the lower pretreatment temperature, less of the C_{30} oil should have been carried from the reactor in the gas flow. Following the pretreatment, this portion of the catalyst was utilized for the synthesis under identical reactor conditions. During this run, the reactor operation and the CO conversion were very stable (Figure IX.D-25). Reactor wax was withdrawn daily (except for week-ends) during this operation; normally the amount of reactor wax was less than two grams.Thus, during more than 2500 hours of time on stream (3.7 months) the CO conversion was greater than 80%. However, at about 2800 hours on stream this catalyst showed a rapid decline in activity so that the reactor run was terminated at 3,000 hours on stream. Unfortunately, this reactor was not equipped with a working catalyst withdrawal tube so that samples of the catalyst could not be withdrawn during this period.

Considering the data for syngas conversion that was generated during these two runs, it appears almost certain that at least one reason for the occurrence of a rapid decline in syngas conversion is that the level of the slurry declines to a point where it causes some upset of the reactor operation. A number of reasons could be advanced for the impact of liquid level on the reactor operation (such as catalyst agglomeration, catalyst settling, poorer gas liquid mixing due to larger vortex, etc).

IRON CATALYSTS CONTAINING ALUMINA AS STRUCTURAL PROMOTER

Samples of iron catalysts were precipitated from an iron(III) nitrate solution using ammonium hydroxide and operating a continuous precipitation process. The same preparative procedure was used for these catalysts as for the silica containing iron catalysts except that the required amount of aluminum nitrate was added to the iron nitrate solution instead of adding hydrolyzed silica. Likewise, the same standard

CO pretreatment was used for these samples as was done for the silica containing catalysts.

The data in Figure IX.D-26 are for a material containing 4.4 atomic% Al and variable amounts of potassium promoter. These tests were done with a slurry that contained 10 wt.% solids. While there is some difference among the initial CO conversions, they are slight; however, it does appear that the alkali free sample has a lower conversion that the other two catalysts. However, the stability of activity for the sample that contains 0.5% K is much better than for either the alkali-free sample or the one that contains 2.0% K. The data in Figure IX.D-27, generated using 20 wt.% catalyst slurry, lead to the same conclusion: the initial activity of the four catalysts does not depend upon the alkali loading but the aging rate improves as the alkali loading is increased up to 0.5 wt.%.

An increase of the aluminum content to 6.0 atomic % does not appear to have a significant impact upon the initial activity nor upon the aging rate (Figure IX.D-28). The data in Figure IX.D-28 were obtained both before and after the tube to add the feed gas at the bottom of the slurry had been added; it appears that there may be some effect on the initial conversion but that at longer time on stream the impact of the location of feeding the synthesis gas had little impact on the conversion. However, the total conversion during this period was only about 50%, and the location of feed gas addition appeared to have a larger impact at higher conversion levels, especially with a 20 wt.% catalyst loading.

For a catalyst with an aluminum atomic % of 8.0, it appears that the initial activity does not depend upon the K loading but that the initial activity is slightly lower than for the two catalyst series with the lower atomic % Al (Figure IX.D-29). Again, the catalyst containing 0.5 wt.% K provides the superior aging characteristics.

The data obtained with the aluminum containing catalysts is somewhat surprising. It is generally accepted that the metal oxide structural promoter, and especially alumina, ties up some of the alkali promoter in a salt form. It is therefore expected that as the aluminum loading is increased, the amount of potassium needed to give a similar effect should also increase. However, the catalyst containing 0.5 wt.% K provided the superior aging characteristics for the Al atomic % of 4.4, 6 and 8 percent. Thus, if the aluminum added in this concentration range ties up the alkali, it must be only a small fraction of the added alkali.

ZIRCONIA-IRON CATALYSTS

A catalyst was prepared to contain 4.4 atomic% Zr but the catalyst otherwise was identical to one that contained 4.4 atomic% Si. The Zr containing catalyst with 1.0 wt.% K provided an initial conversion that was as high, if not higher, than the Si containing catalyst (Figure IX.D-30). However, the testing of the Zr containing catalyst was too limited to make a valid comparison at this time.

OXYGENATE FORMATION

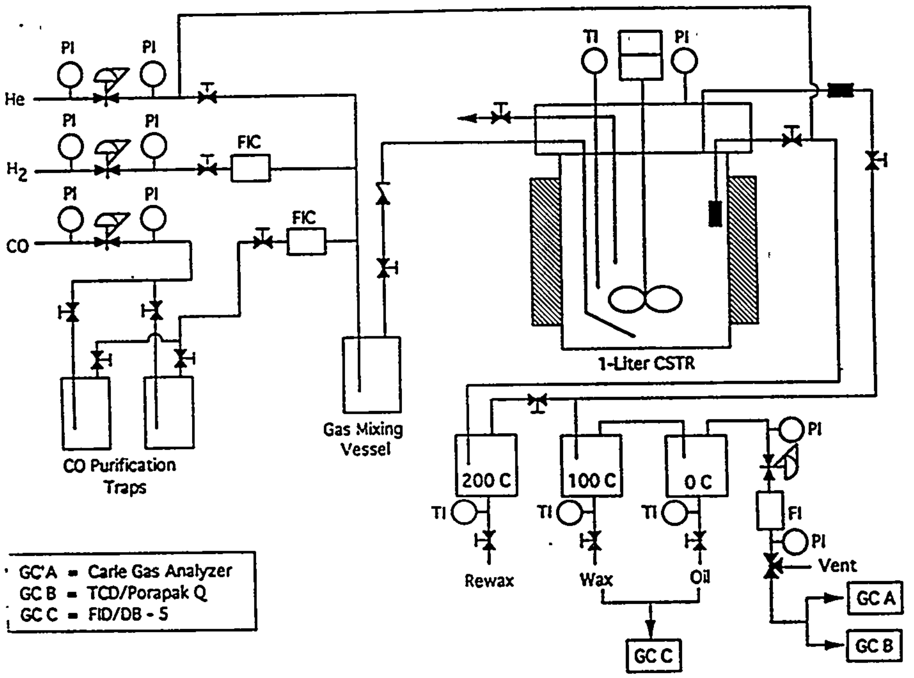
The amount of oxygenates that are produced depend upon both the amount of alkali and the type of metal oxide structural promoter. As the wt.% K is increased in both the Si (Figure IX.D-31) and Al (Figure IX.D-32) containing catalysts, the amount of oxygenates present in the aqueous phase increase. The dominant oxygenates represented in these two figures correspond to alcohols and the ketone or aldehyde that would be formed by their dehydrogenation. Acids were present in both the water and oil fractions but they eluted from the g.c. columns used for the analysis as very broad peaks that could not be quantified. Likewise, the alcohols present in the oil fraction frequently co-eluted with hydrocarbon peaks so that for the present we concentrate only on the oxygenates present in the aqueous phase. However, the concentration of the oxygenates in the aqueous phase should parallel those present in the oil phase.

The amount of oxygenates in the aqueous phase produced by the Si containing catalyst is only about 1% and this increases to about 4% as the potassium content is increased to 0.5 wt.% (Figure IX.D-31). In contrast, the aluminum containing catalyst without potassium produces about 4 wt.% oxygenates and this increases rapidly to about 20 wt.% for the catalyst with 0.5 wt.% potassium (Figure IX.D-32). This difference between the two catalysts is not due to the amount of water produced and collected during the runs with the two catalyst. As shown in Figures IX.D-33 and IX.D-34, for the same feed rate and about the same CO conversion (80-90 %), about the same amount of water is produced. Thus, the aluminum containing catalyst produced much more of the oxygenate products. This is surprising since alumina is a very active alcohol dehydration catalyst, compared to silica. For this reason, it is concluded that both the silicon and aluminum are incorporated in the bulk of the iron catalysts and not as free metal oxides.

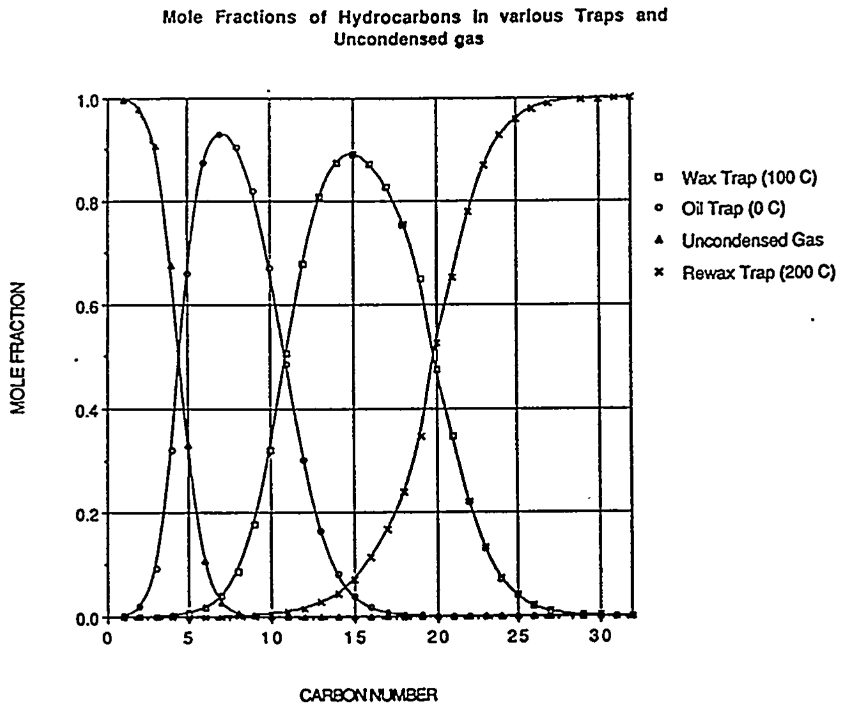
For the more stable activity catalysts (0.5 wt.% K), the oxygenates produced with increasing time on stream remains essentially constant for the silicon containing catalyst (Figure IX.D-35) but increases from about 5 to about 20% during the first 800 hours on stream (Figure IX.D-36). In both cases ethanol is the most abundant oxygenate and this compound comprises about half of the oxygenates present in the aqueous phase.

REFERENCES

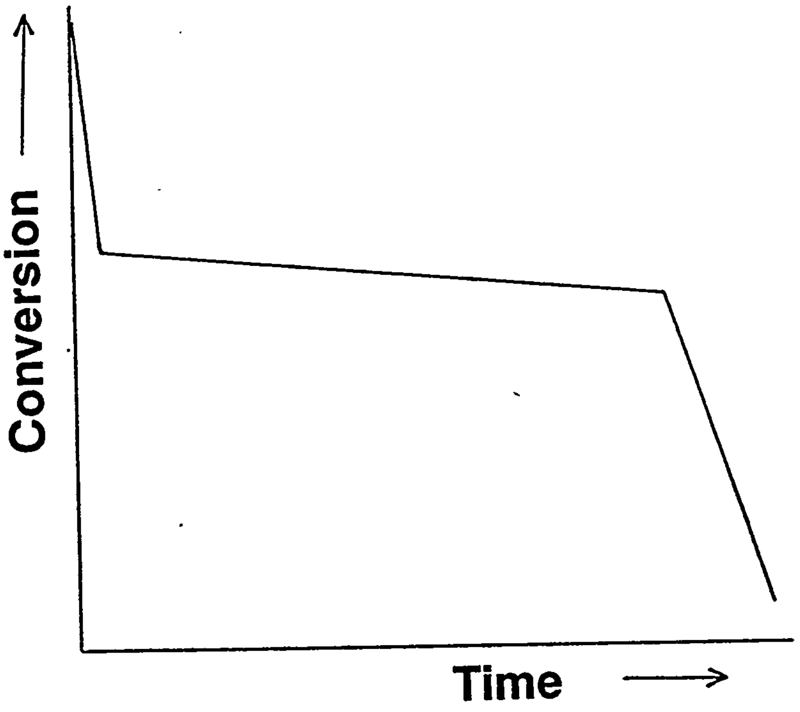
IX.D-1. Kölbel, H. and M. Ralek, 1980. *Catal. Rev.-Sci. Eng.*, **21**, 225.



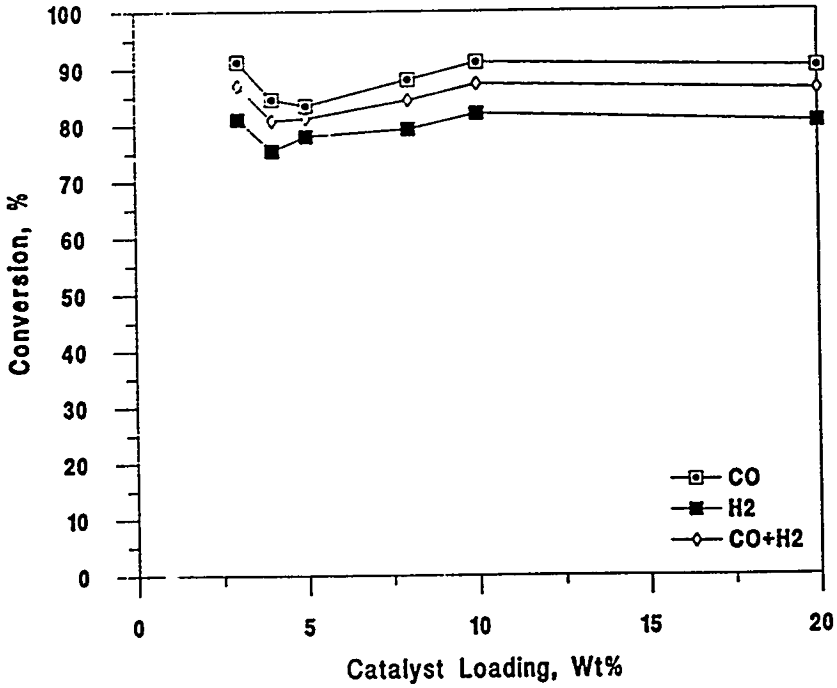
X.D-1. Schematic of the continuous stirred tank reactor (CSTR) system used in this study.



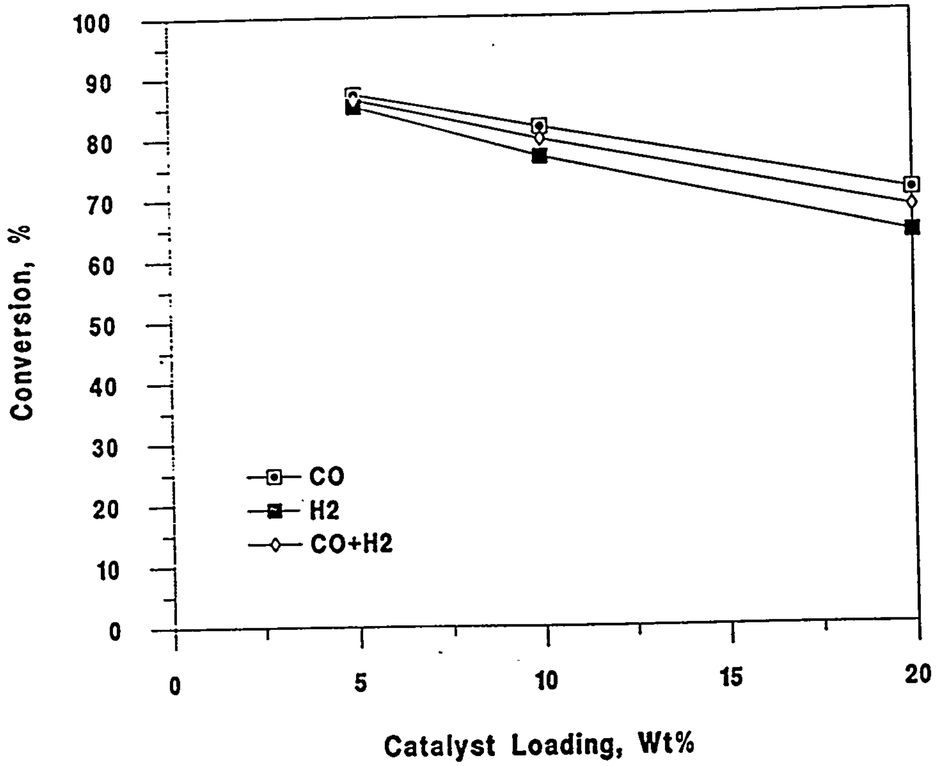
X.D-2. Accumulation, by carbon number, in the traps used in the reactor system employed in these studies.



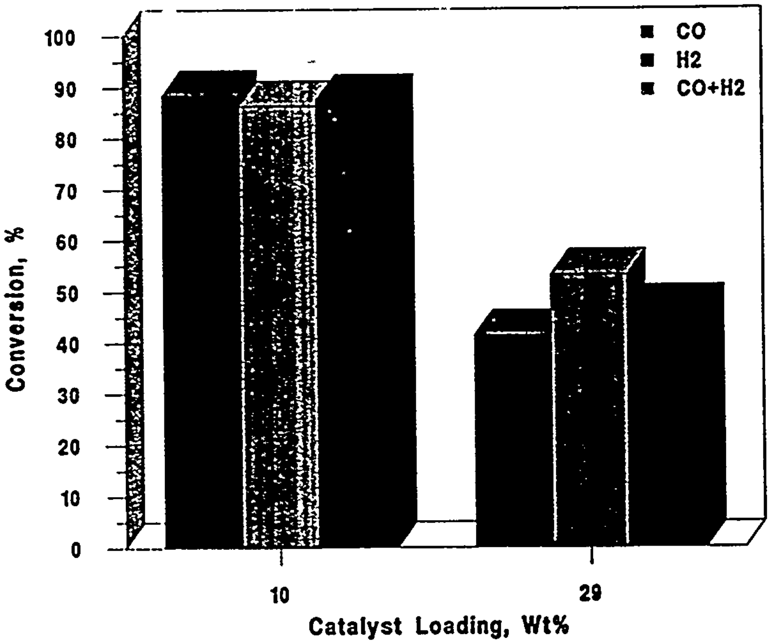
IX.D-3. Schematic of a typical catalyst aging curve.



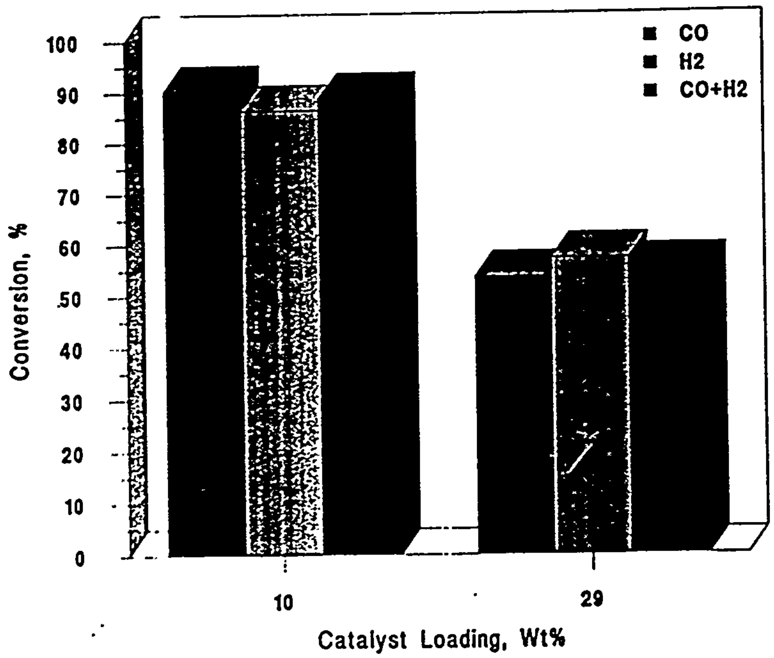
IX.D-4. CO conversion for various loadings of catalyst containing 100Fe/4.4Si/0.71K following pretreatment in CO (run at 270°C, 12.9 atm and $H_2/CO = 0.7$).



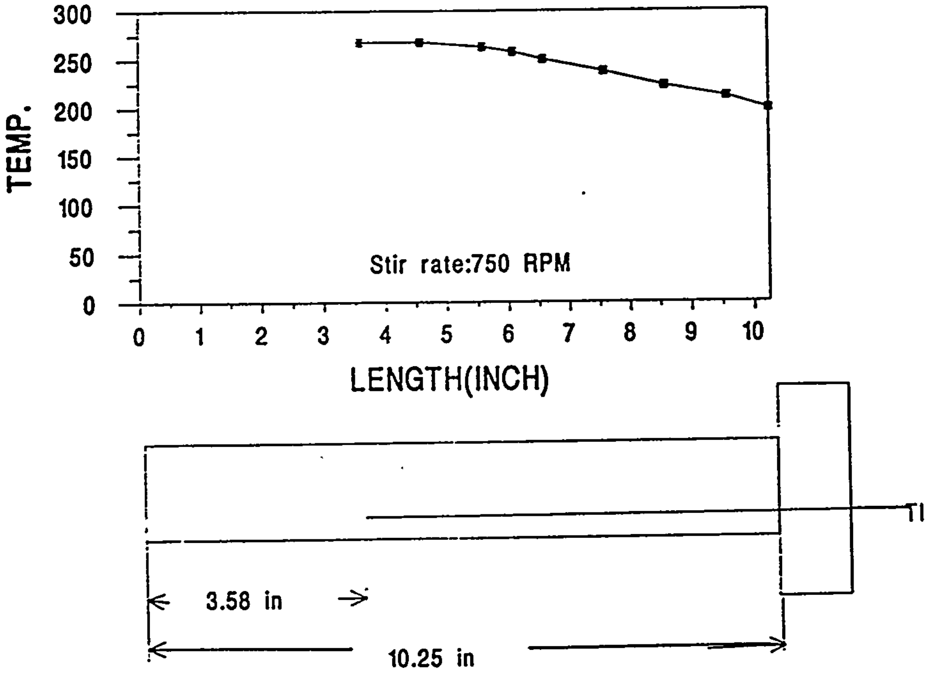
X.D-5. CO conversion for various loadings of catalyst containing 100Fe/5.0Si/0.71K following pretreatment in CO (run at 270°C, 12.9 atm and $H_2/CO = 0.7$).



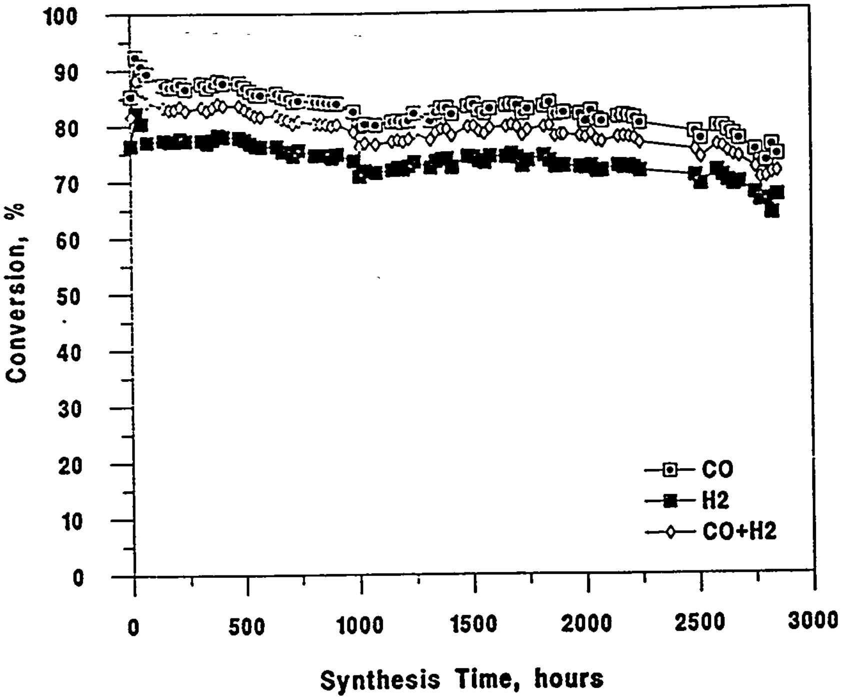
IX.D-6. CO conversion for 10 and 29 wt.% loadings of UCI 1185-149 catalyst following pretreatment in CO using the Ethyl C_{30} oil (run at 270°C, 12.9 atm and $H_2/CO = 0.7$).



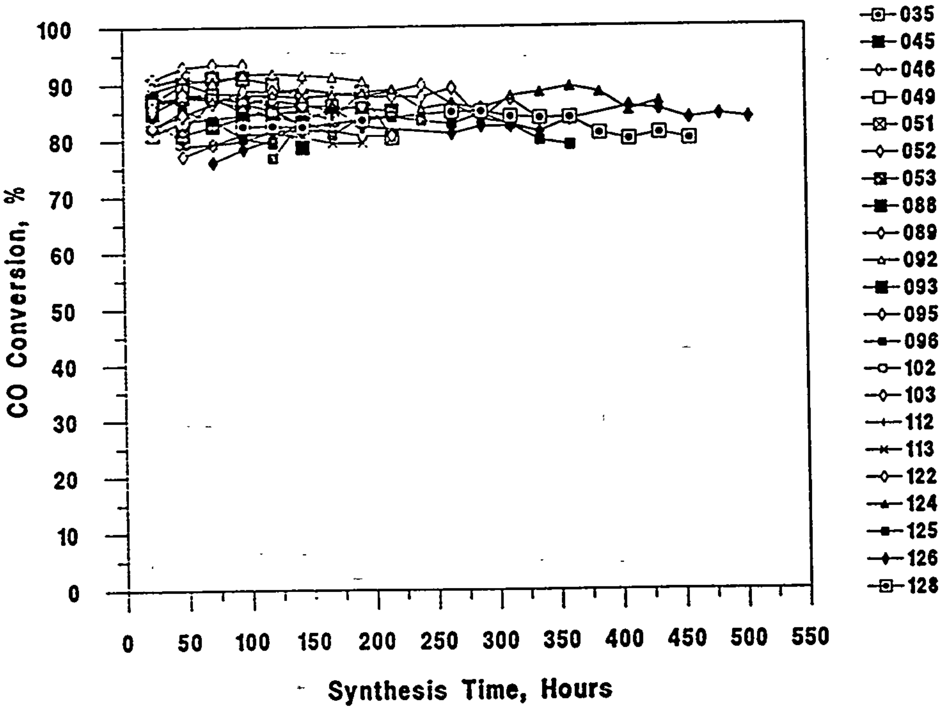
IX.D-7. CO conversion for 10 and 29 wt.% loadings of UCI 1185-149 catalyst following pretreatment in CO using distilled Allied-Signal was (run at 270°C, 12.9 atm and $H_2/CO = 0.7$).



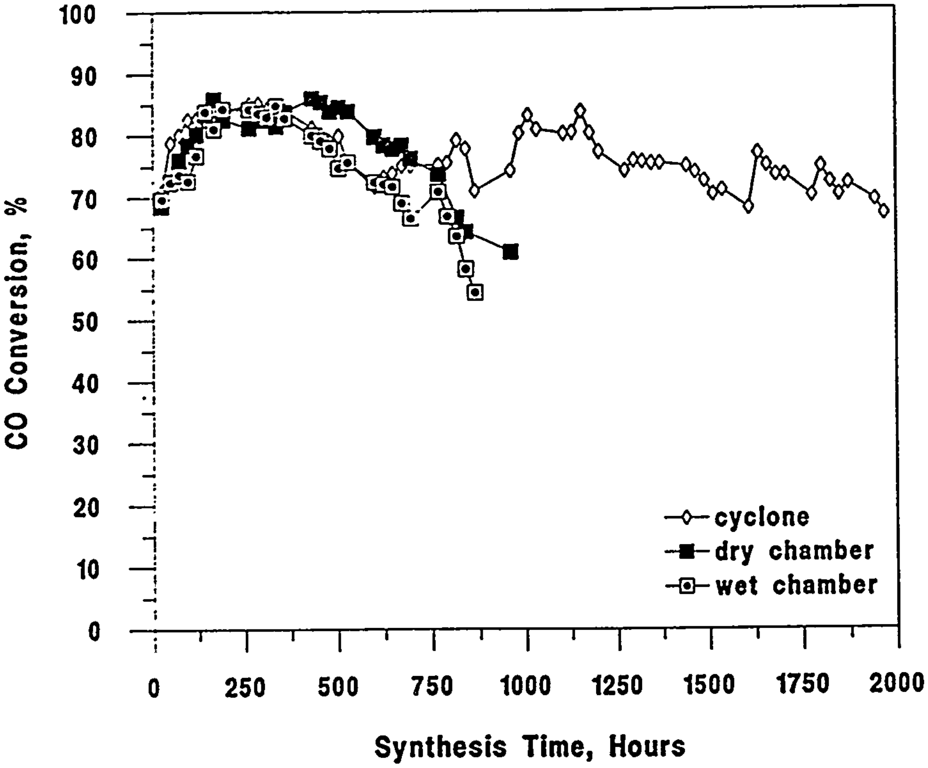
IX.D-8. Schematic of CSTR and the measure temperature profile within the reactor during a run at 270°C.



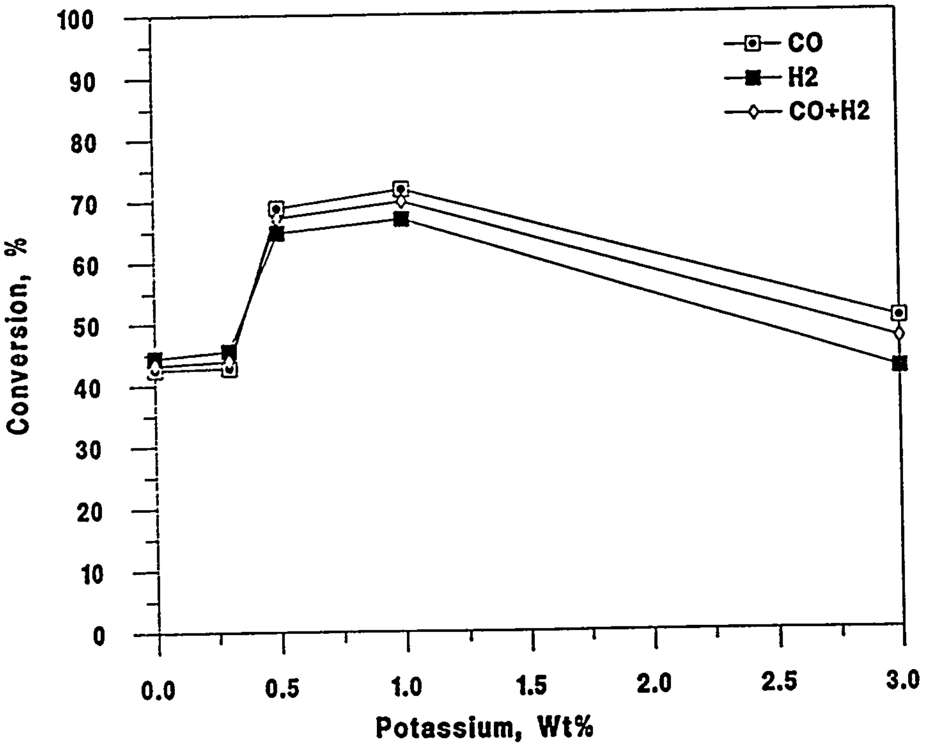
IX.D-9. CO conversion during testing of a catalyst with a composition of 100Fe/3.6Si/0.71K (atomic ratio) following pretreatment in synthesis gas ($H_2/CO = 0.7$) at atmospheric pressure with the synthesis run at 270°C, 12.9 atm and $H_2/CO = 0.7$).



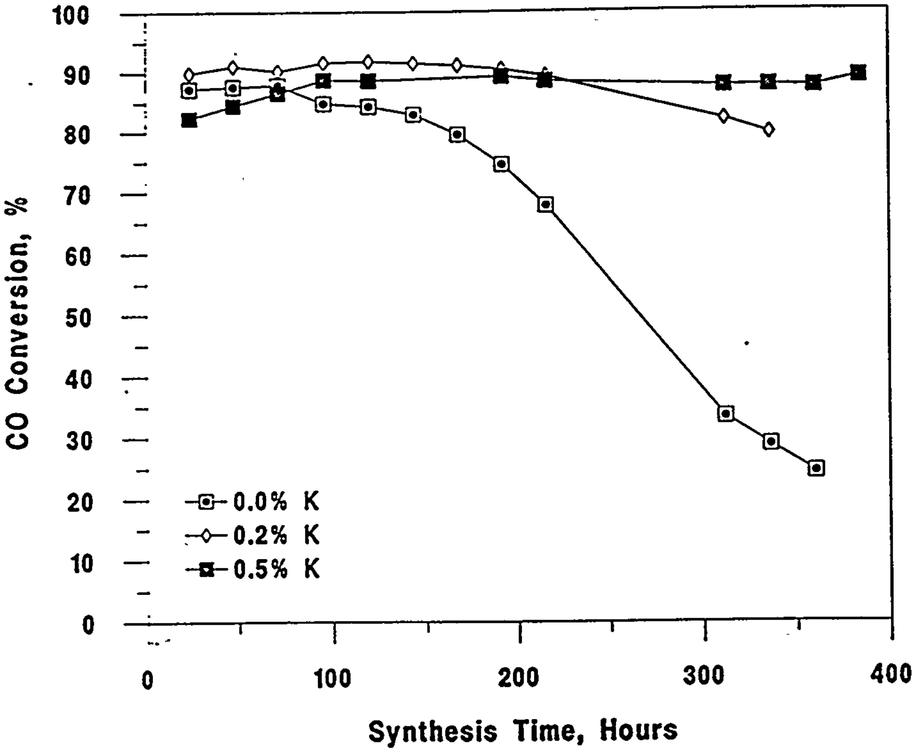
IX.D-10. CO conversion during testing of a variety of silicon containing catalysts following pretreatment in synthesis gas ($H_2/CO = 0.7$) at atmospheric pressure with the synthesis run at 270°C, 12.9 atm and $H_2/CO = 0.7$).



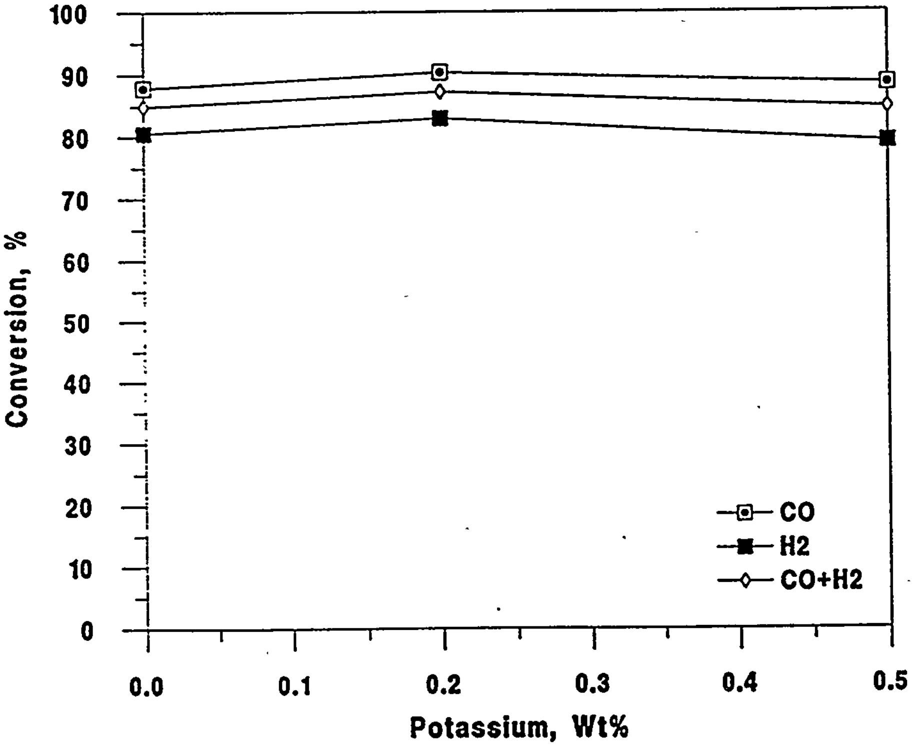
IX.D-11. CO conversion during testing of a three silicon containing catalysts collected at different times or locations in the UCI spray dryer and following pretreatment with CO at the synthesis conditions and with the synthesis run at 270°C, 12.9 atm and $H_2/CO = 0.7$).



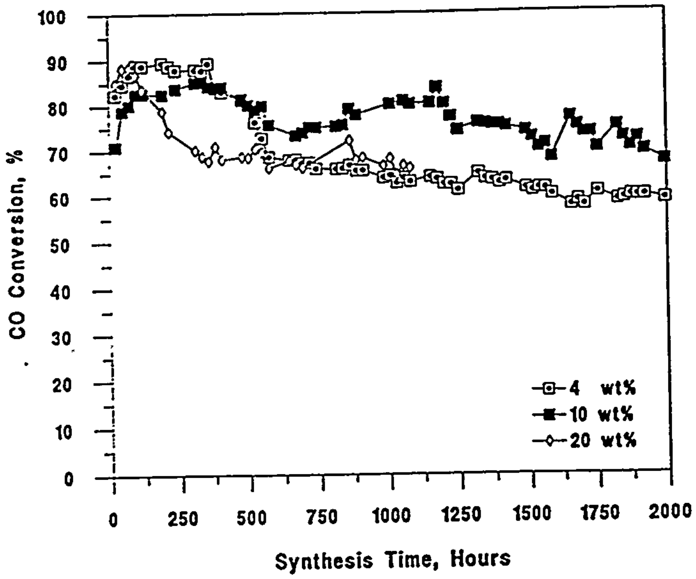
IX.D-12. CO, hydrogen and CO plus hydrogen conversions after more than 100 hours on stream for an iron/4.4 atomic fraction Si catalyst containing various amounts of K promoter (pretreatment with CO at the synthesis conditions and with the synthesis run at 270°, 12.9 atm. and $H_2/CO = 0.7$).



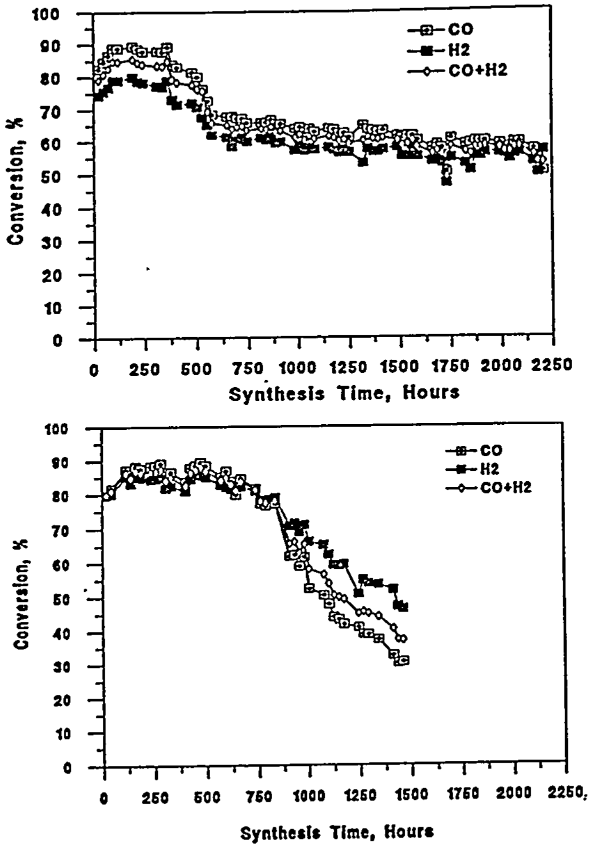
IX.D-13. CO conversion for an iron/4.4 atomic fraction Si catalyst containing 0, 0.2 or 0.5 wt.% K with increasing time on stream (pretreatment with CO at the synthesis conditions and with the synthesis run at 270°, 12.9 atm. and $H_2/CO = 0.7$).



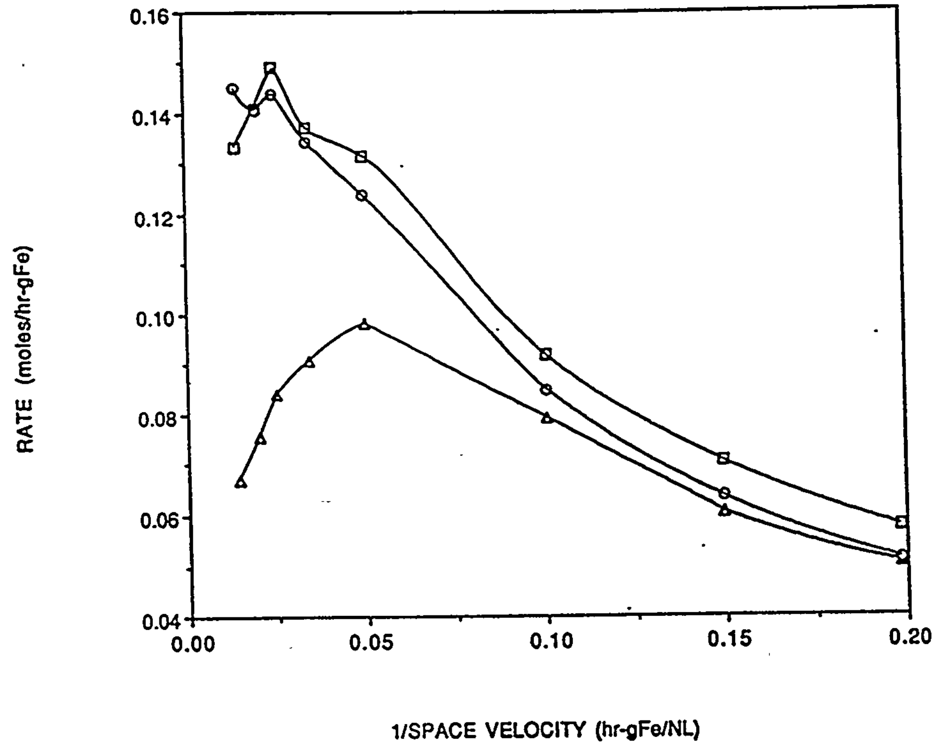
IX.D-14. CO conversion for an iron/4.4 atomic fraction Si catalyst containing 0, 0.2 or 0.5 wt.% K after 48 hours on stream (pretreatment with CO at the synthesis conditions and with the synthesis run at 270°, 12.9 atm. and $H_2/CO = 0.7$).



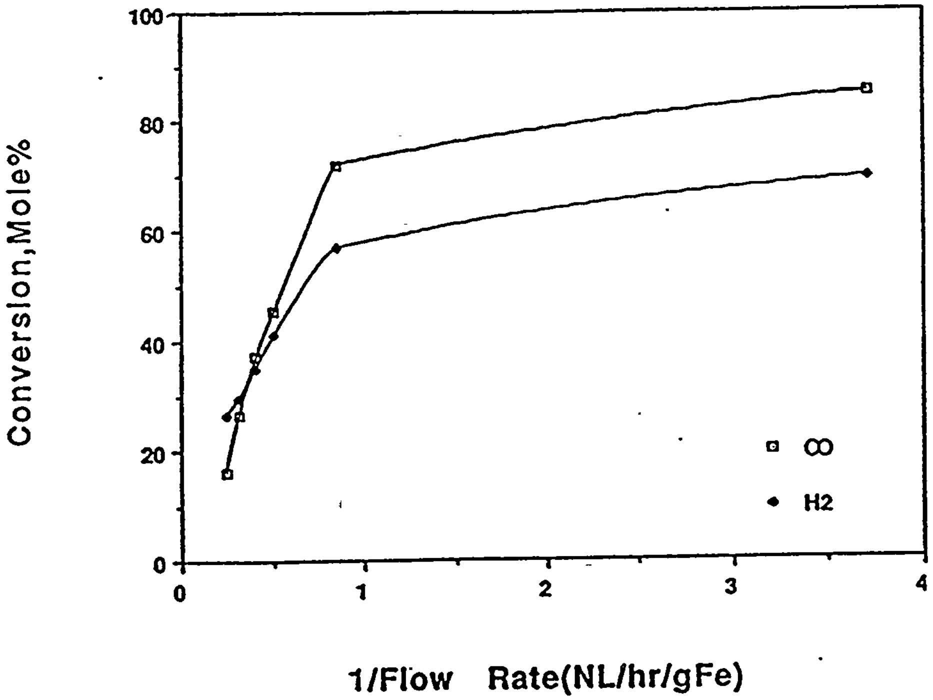
IX.D-15. CO conversion with time on stream for a catalyst (100Fe/4.4Si/0.71K atomic ratio) at 4, 10 and 20 wt.% loading using distilled Allied-Signal wax (pretreatment with CO at the synthesis conditions and with the synthesis run at 270°, 12.9 atm. and $H_2/CO = 0.7$).



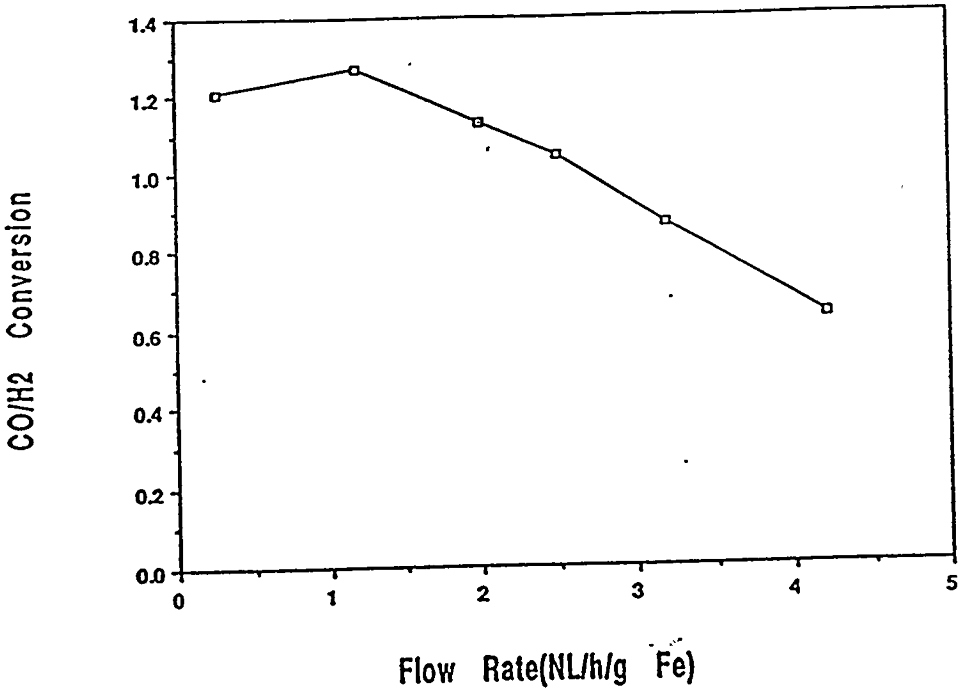
IX.D-16. (top) CO, H_2 and (CO + H_2) conversions with time on stream for a K promoted catalyst (100Fe/4.4Si/0.71K atomic ratio) (pretreatment with CO at the synthesis conditions and with the synthesis run at 270°, 12.9 atm. and $H_2/CO = 0.7$). (bottom) CO, H_2 and (CO + H_2) conversions with time on stream for a catalyst (100Fe/5.0Si atomic ratio) that does not contain potassium promoter (pretreatment with CO at the synthesis conditions and with the synthesis run at 270°, 12.9 atm. and $H_2/CO = 0.7$).



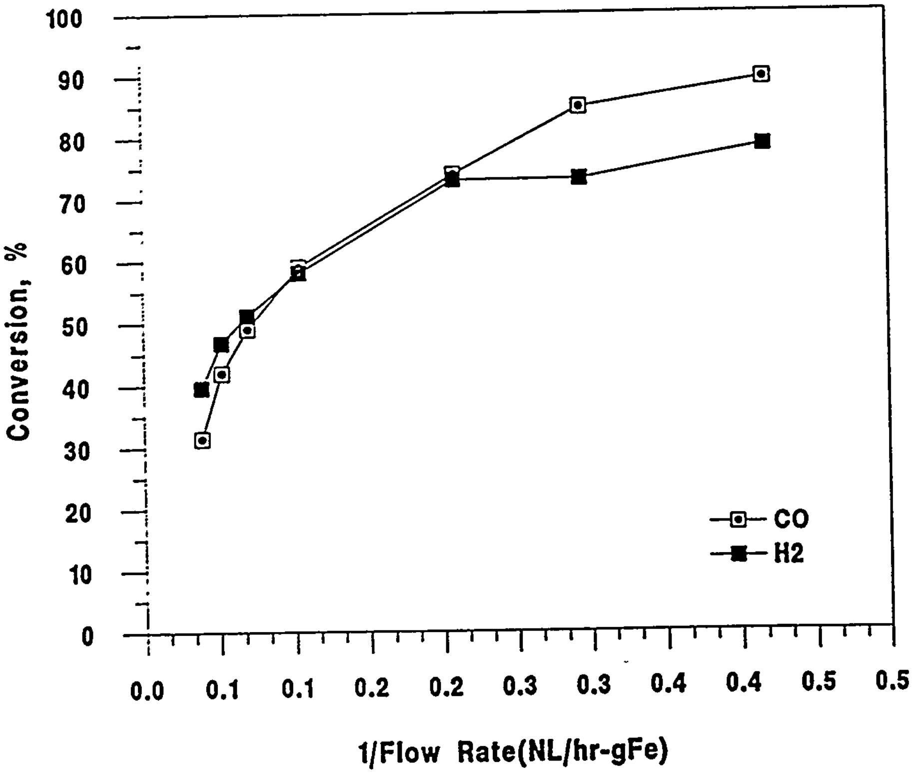
X.D-17. Rates of formation of hydrocarbons by the Fischer-Tropsch Synthesis and CO_2 by the water gas shift reaction during syngas ($H_2/CO = 0.7$) with a promoted iron catalyst (100Fe/4.4Si/0.71K atomic ratio) (pretreatment with CO at the synthesis conditions and with the synthesis run at 270°C, 12.9 atm. and $H_2/CO = 0.7$).



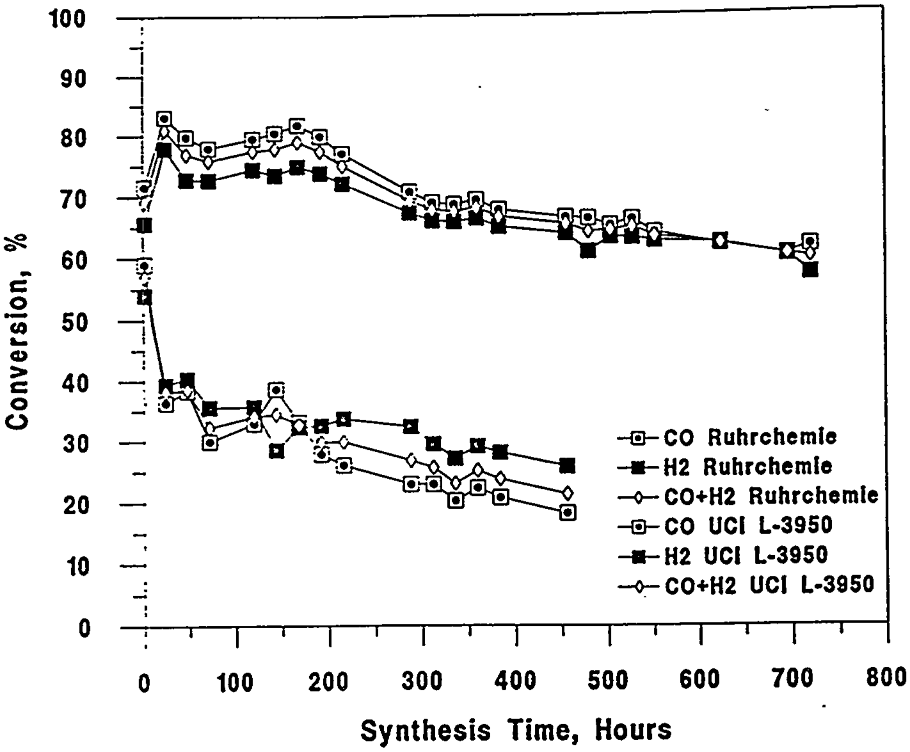
IX.D-18. Conversion of CO and H_2 versus the reciprocal space velocity for an unpromoted ultrafine iron catalyst (slurry, 20 wt.%; temperature, 260°C; total pressure, 8 atm.; $H_2/CO = 1:1$).



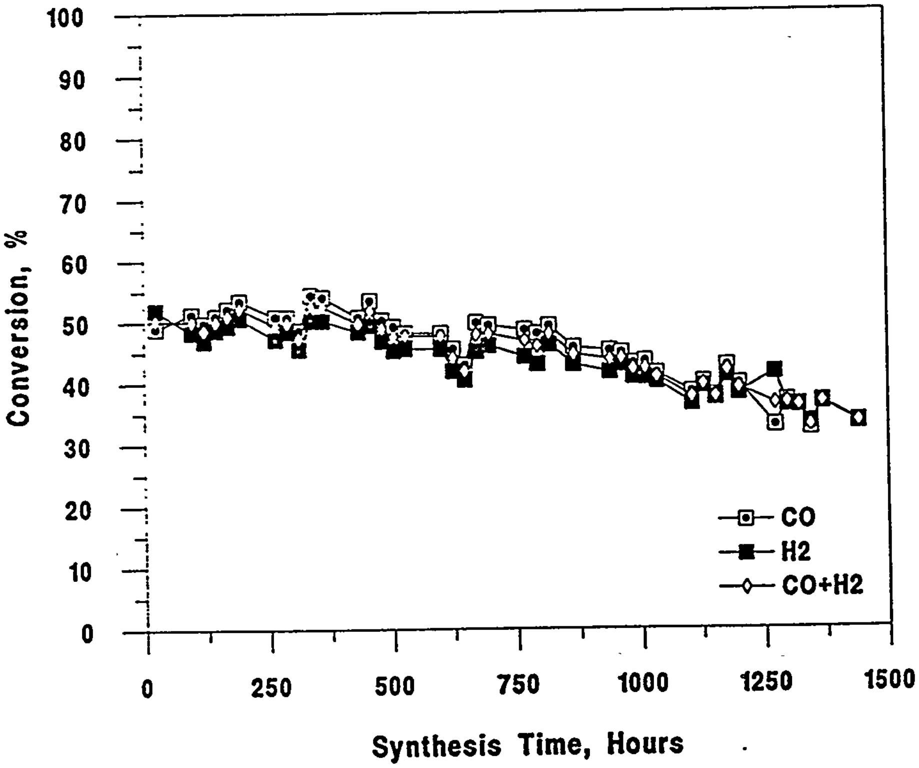
IX.D-19. Variation of the ratio of CO to H_2 conversion versus total flow rate for an umpromoted ultrafine iron catalyst (slurry, 20 wt.%; temperature, 260°C; total pressure, 8 atm.; H_2/CO = 1:1).



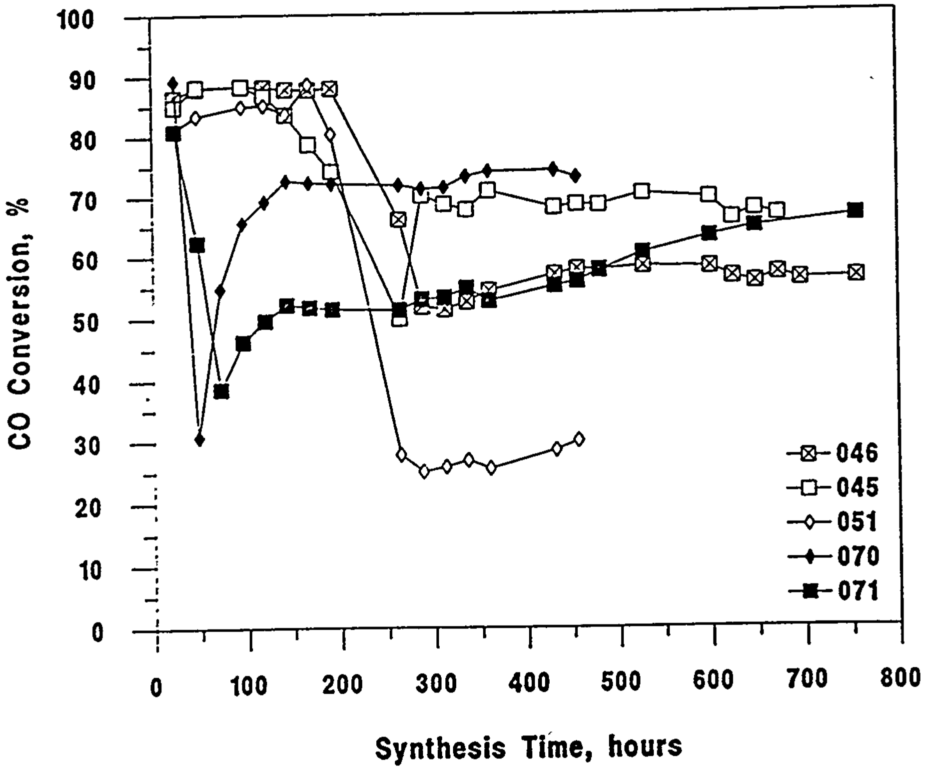
IX.D-20. Conversion of CO and H_2 versus the reciprocal space velocity for a promoted catalyst (100Fe/4.4Si/0.71K atomic ratio) for a catalyst pretreated in CO and the synthesis conducted at 270°C, 8 atm., 3.4NL/hr.-g(Fe) and H_2/CO = 0.7.



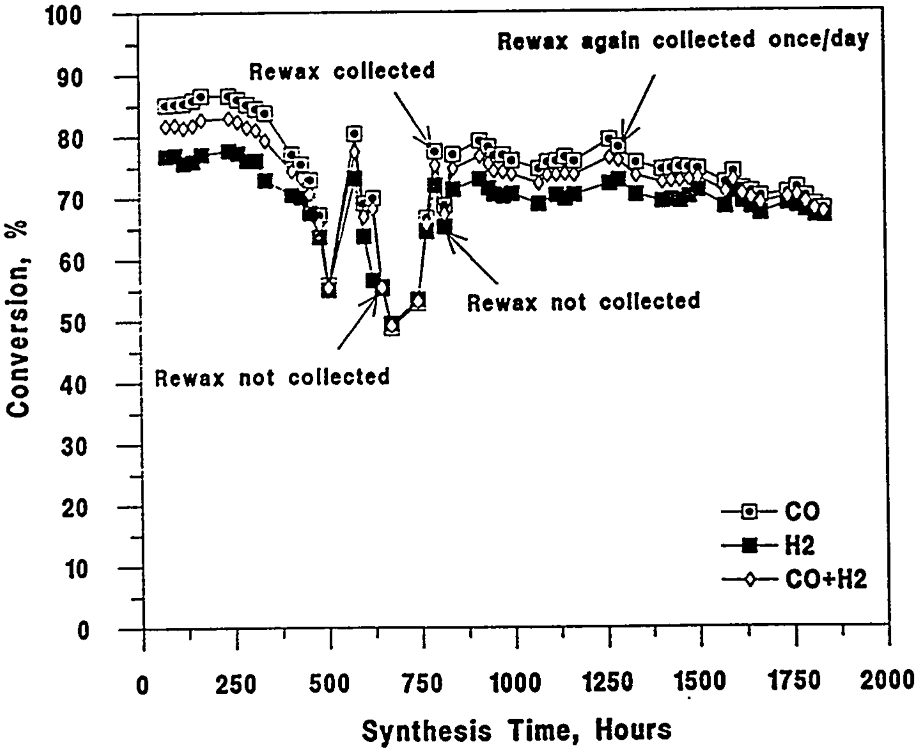
IX.D-21. Comparison of the impact of a syngas pretreatment upon a Ruhrchemie catalyst and catalyst of similar composition prepared by UCI upon the conversion of CO, H_2 and (CO + H_2).



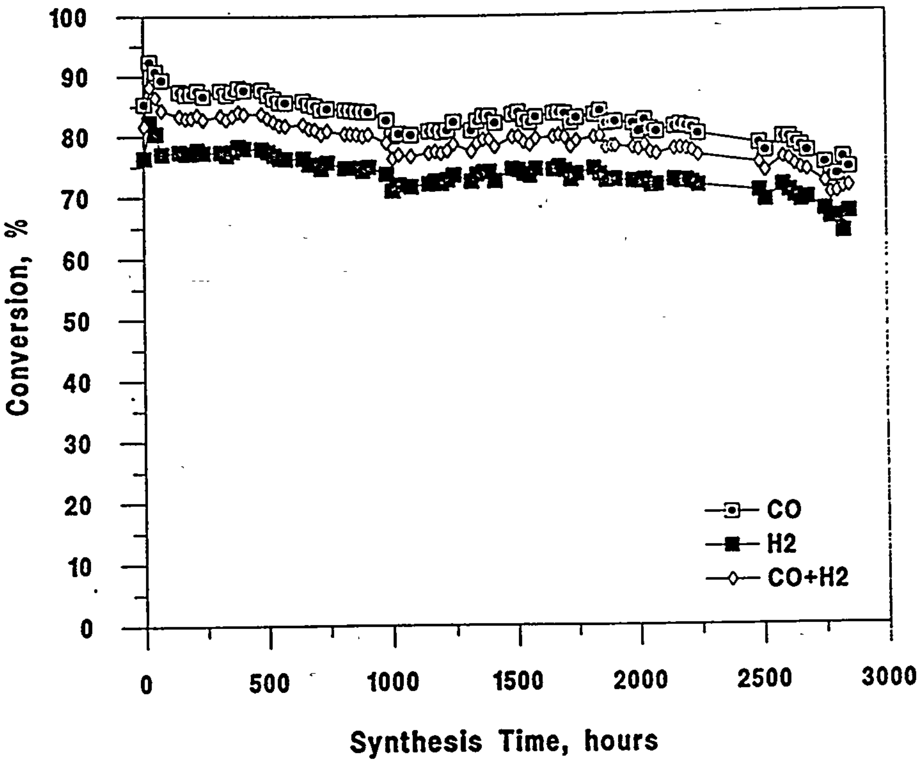
IX.D-22. Conversion data versus time on stream for a promoted catalyst (cyclone sample of a spray dried material with a composition of 100Fe/4.4Si/0.71K) that had been carbided during 24 hours in a gas flow in a plug flow reactor (no solvent present) and then passivated during 3 days in a flow of 1% oxygen in nitrogen. Following passivation, the catalyst was subjected to synthesis at 270°C, 8 atm., 3.4 NL/hr.-g(Fe) and H_2/CO = 0.7 without prior pretreatment.



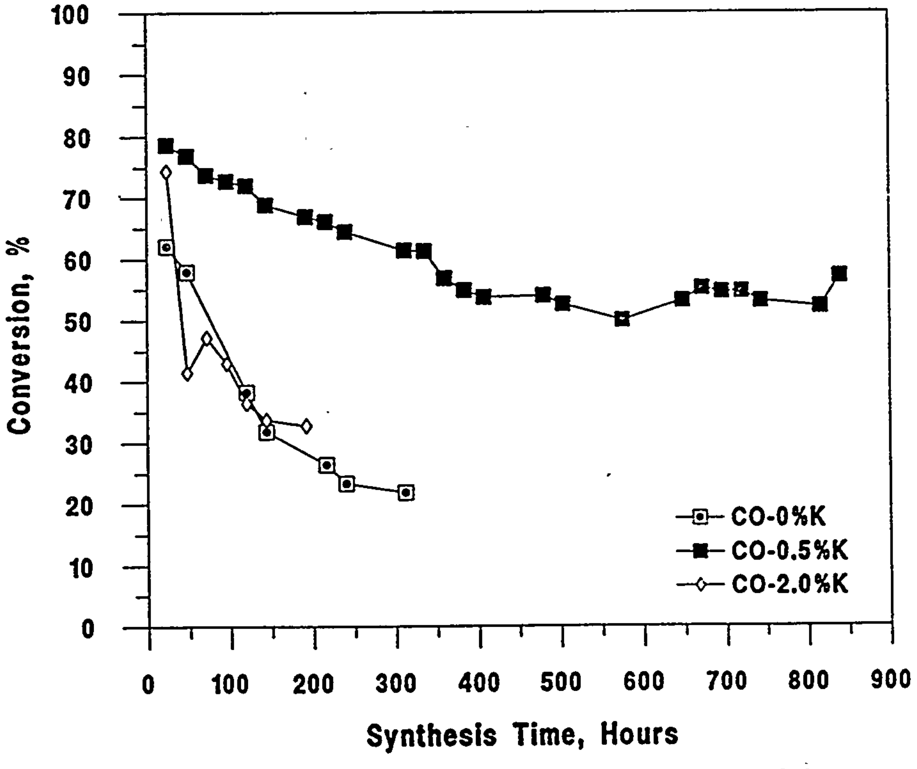
IX.D-23. CO conversion versus time on stream for five runs with a catalyst composition of 100Fe/4.4Si/0.71K that illustrates types of rapid activity loss followed by, in most cases, a partial recovery of conversion.



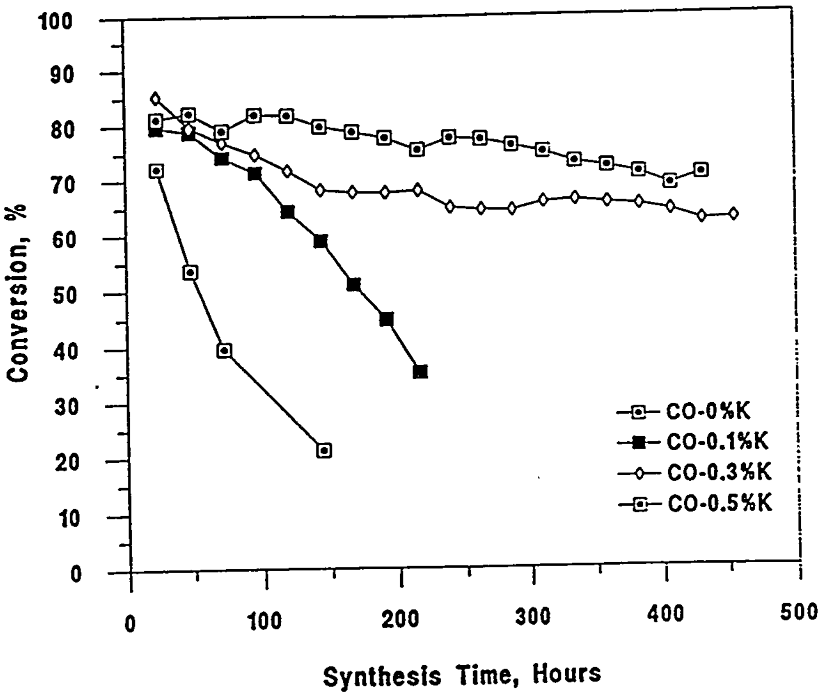
IX.D-24. Conversion of CO, H_2 and ($CO + H_2$) with time on stream for a catalyst (100Fe/4.4Si/0.71K) following pretreatment in syngas at 270°C and 1 atmosphere and synthesis at 270°C, 175 psig, 3.4 NL/hr.-g(Fe), Ethyl C_{30} oil and $H_2/CO = 0.7$. During the activity decline periods, the withdrawal of reactor liquid samples was discontinued, allowing recovery of CO conversion.



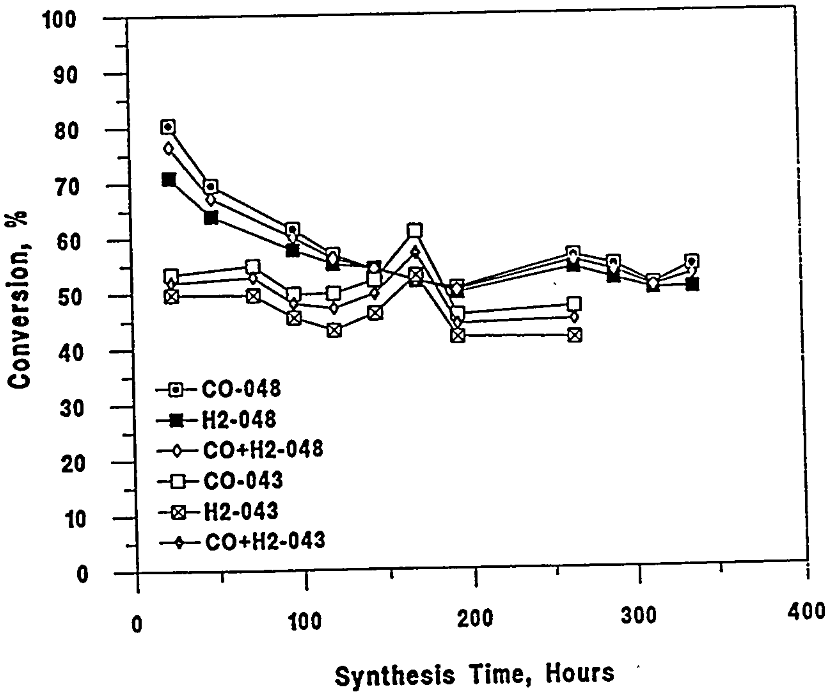
IX.D-25. Conversion of CO, H_2 and (CO + H_2) with time on stream for a catalyst (100Fe/4.4Si/0.71K) following pretreatment in syngas at 270°C and 1 atmosphere and synthesis at 270°C, 175 psig, 3.4 NL/hr.-g(Fe), Ethyl C_{30} oil and H_2/CO = 0.7. Compare to the data in figure (IX.D-24).



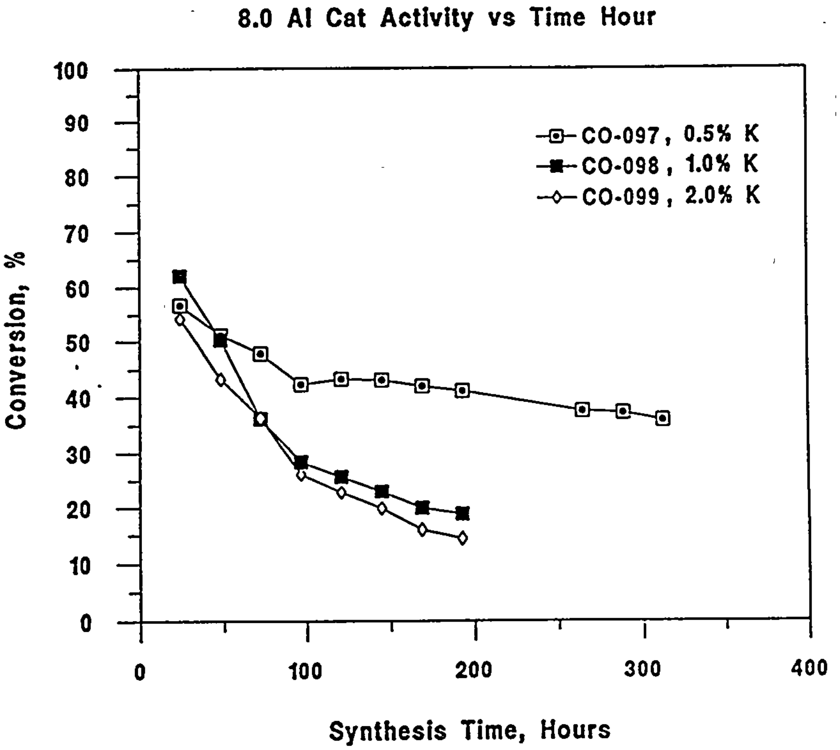
IX.D-26. Conversion of CO with time on stream for an aluminum containing catalyst (100Fe/4.4Al) containing 0, 0.5 or 2.0 wt.% potassium following pretreatment in CO at 270°C and 1 atmosphere and synthesis at 270°C, 175 psig, 3.4 NL/hr.-g(Fe), Ethyl C_{30} oil, 10 wt.% slurry and H_2/CO = 0.7.



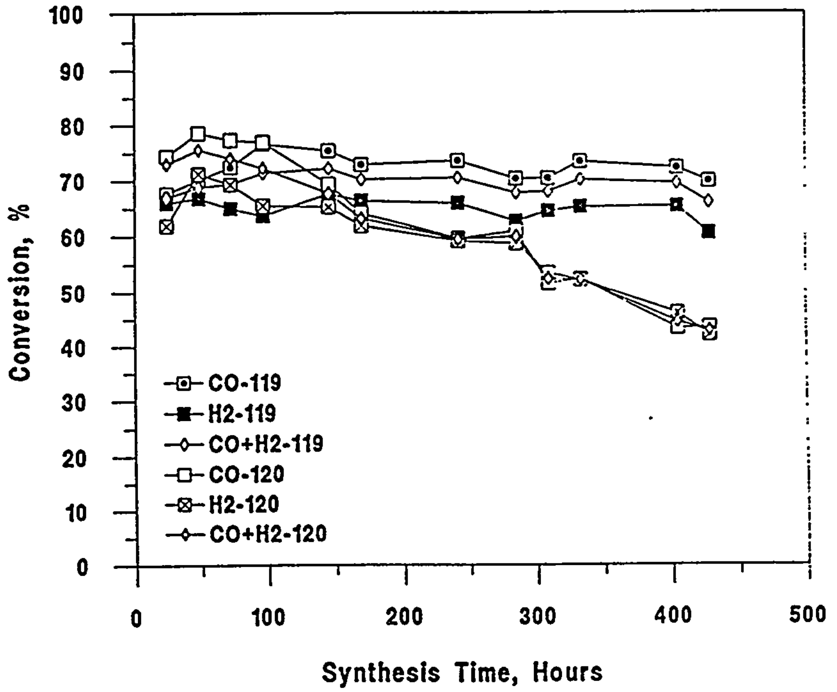
IX.D-27. Conversion of CO with time on stream for an aluminum containing catalyst (100Fe/4.4Al) containing 0, 0.2, 0.3 and 0.5 wt.% potassium following pretreatment in CO at 270°C and 1 atmosphere and synthesis at 270°C, 175 psig, 3.4 NL/hr.-g(Fe), Ethyl C_{30} oil, 20 wt.% slurry and $H_2/CO = 0.7$.



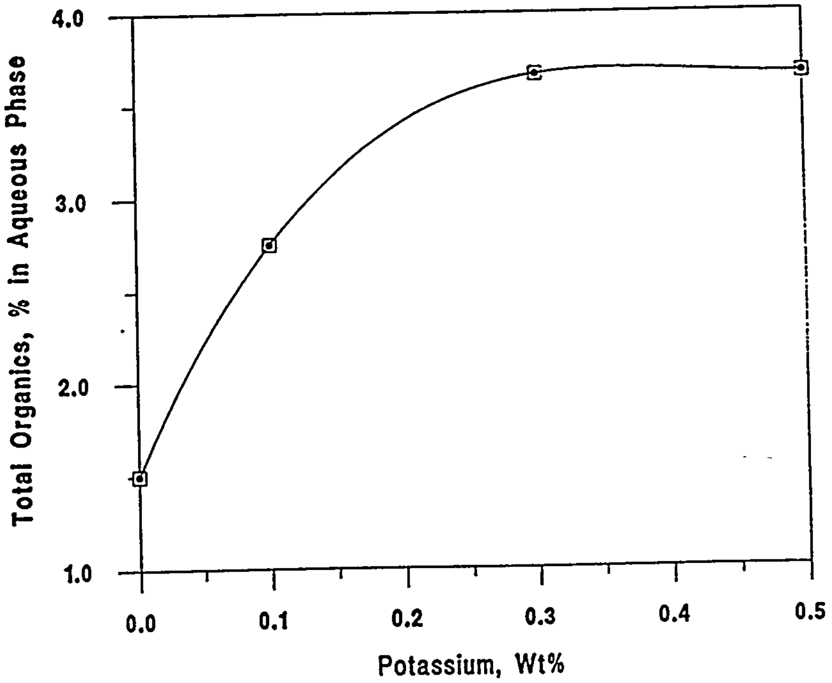
IX.D-28. Conversion of CO, H_2, and (CO + H_2) with time on stream for an aluminum containing catalyst (100Fe/6.0Al/0.71K) following pretreatment in CO at 270°C and 1 atmosphere and synthesis at 270°C, 175 psig, 3.4 NL/hr.-g(Fe), Ethyl C_{30} oil, 20 wt.% slurry and $H_2/CO = 0.7$. Runs were made before and after the gas inlet tube was extended so that the feed gas entered the reactor at the bottom of the slurry.



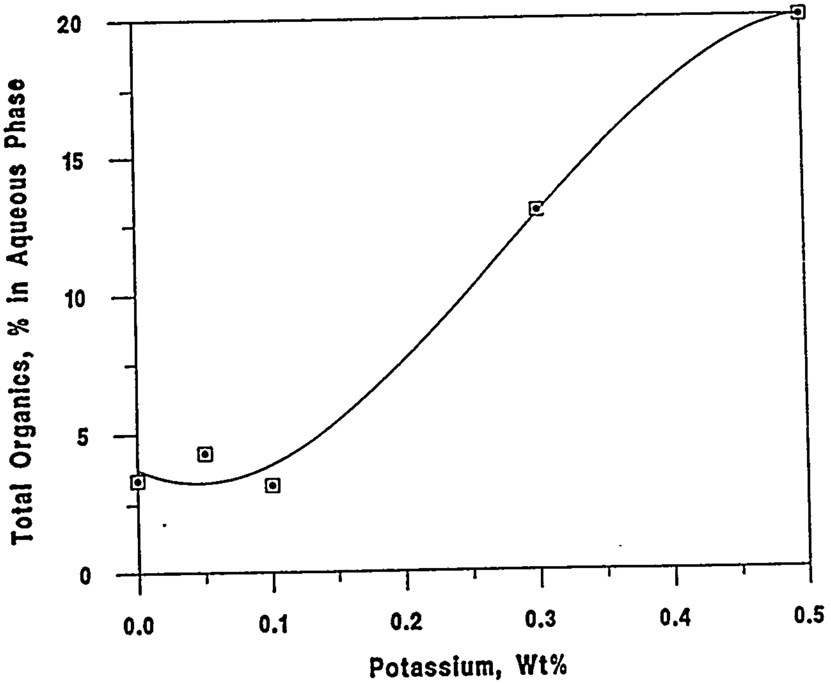
IX.D-29. Conversion of CO with time on stream for an aluminum containing catalyst (100Fe/8.0Al) containing 0.5, 1.0 or 2.0 wt.% potassium following pretreatment in CO at 270°C and synthesis at 270°C, 175 psig, 3.4 NL/hr.-g(Fe), Ethyl C_{30} oil, 20 wt.% slurry and $H_2/CO = 0.7$.



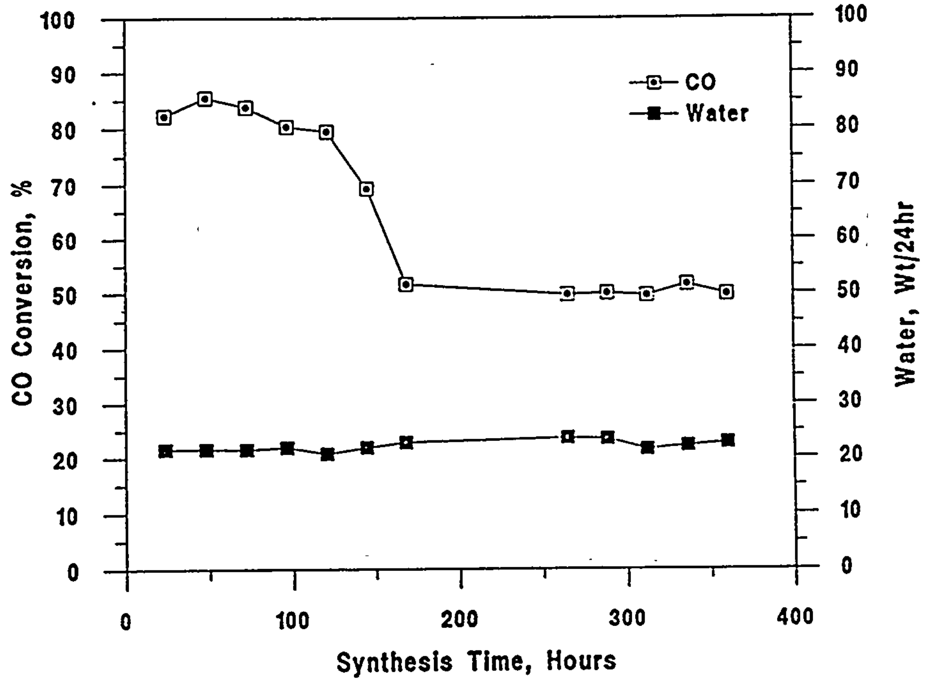
IX.D-30. Conversion of CO, H_2, and (CO + H_2) with time on stream for an aluminum containing catalyst (100Fe/4.4Zr/0.71K) following pretreatment in CO at 270°C and synthesis at 270°C, 175 psig, 3.4 NL/hr.-g(Fe), Ethyl C_{30} oil, 20 wt.% slurry and $H_2/CO = 0.7$.



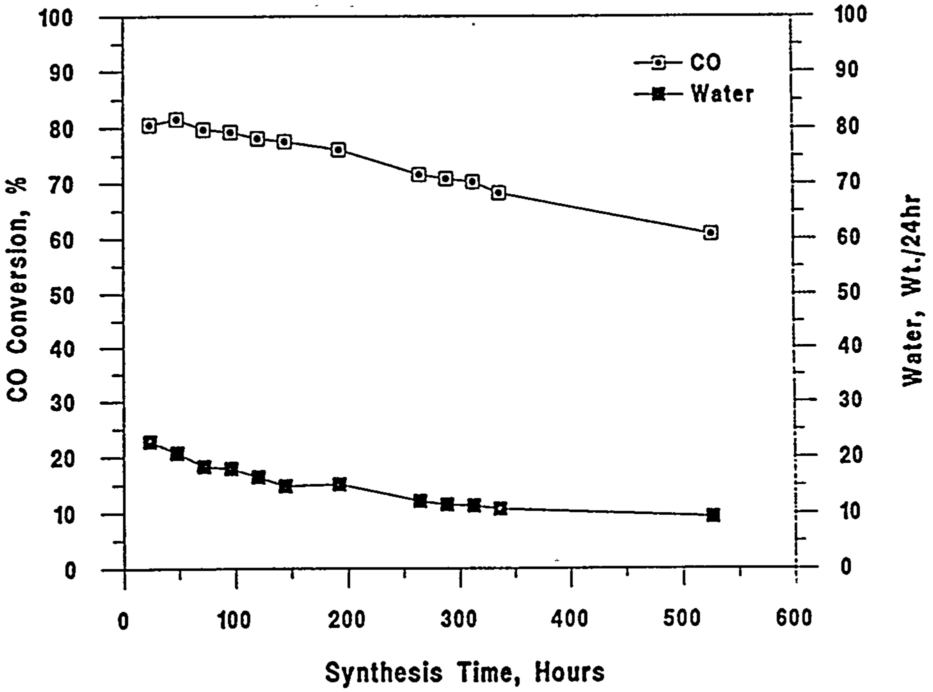
IX.D-31. Total oxygenates in the aqueous phase after more than 100 hours on stream for a catalyst (100Fe/5.0Si) containing varying weight % potassium promoter following pretreatment in CO at 270°C and synthesis at 270°C, 175 psig, 3.4 NL/hr.-g(Fe), Ethyl C_{30} oil, 20 wt.% slurry and $H_2/CO = 0.7$.



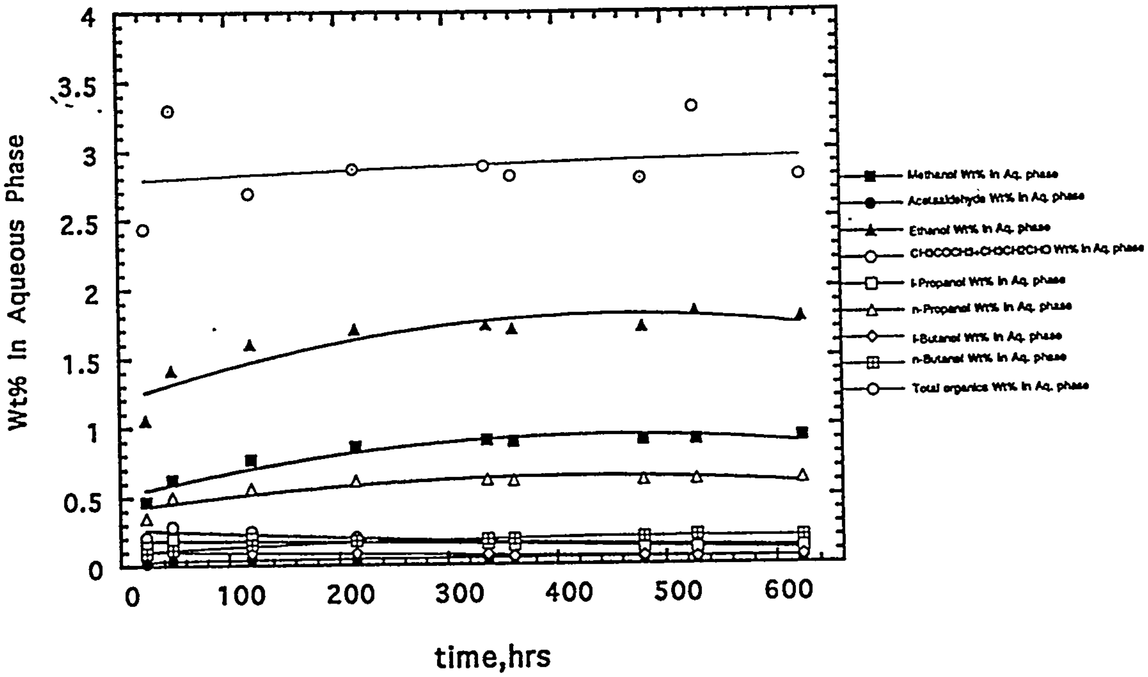
IX.D-32. Total oxygenates in the aqueous phase after more than 100 hours on stream for a catalyst (100Fe/4.4Al) containing varying weight % potassium promoter following pretreatment in CO at 270°C and synthesis at 270°C, 175 psig, 3.4 NL/hr.-g(Fe), Ethyl C_{30} oil, 20 wt.% slurry and $H_2/CO = 0.7$.



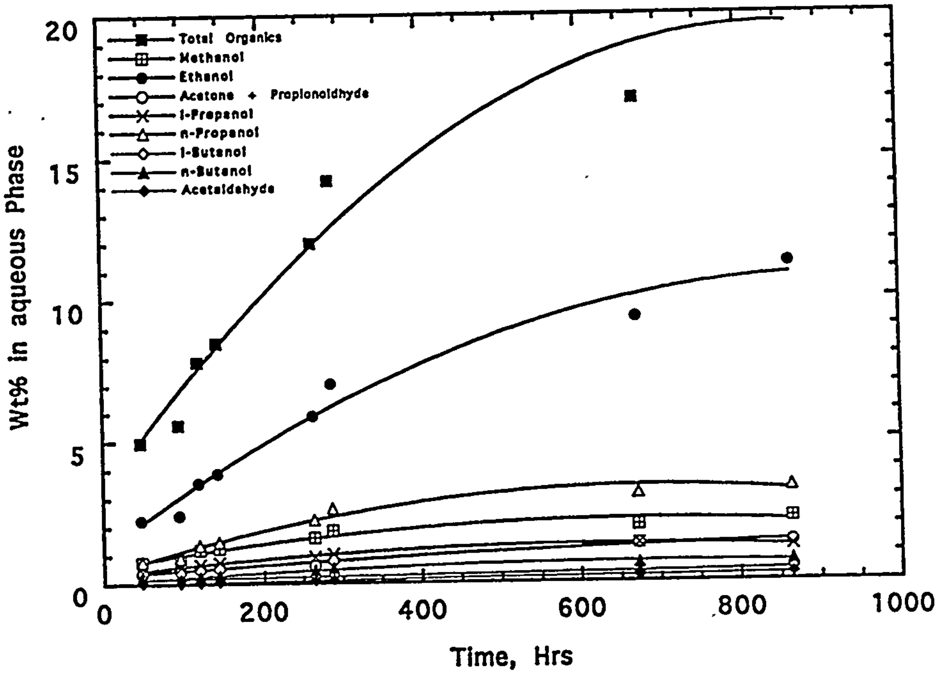
IX.D-33. Variation of the CO conversion and the production of water during synthesis with a promoted catalyst (100Fe/5.0Si/0.71K) using the same conditions as in Figure IX.D-31.



IX.D-34. Variation of the CO conversion and the production of water during synthesis with a promoted catalyst (100Fe/4.4Al/0.71K) using the same conditions as in Figure IX.D-32.



IX.D-35. Formation of total oxygenates and the distribution of oxygenate compounds during synthesis with a catalyst of the composition 100Fe/4.4Si/0.71K (conditions as in Figure legend IX.D-31.



IX.D-36. Formation of total oxygenates and the distribution of oxygenate compounds during synthesis with a catalyst of the composition 100Fe/4.4Al/0.71K (conditions as in Figure legend IX.D-32.