VI. TASK 2 STUDIES

Microporous Catalysts With Metal Components
Using CO and H2 Syngas Feed

The objective of Task 2 was to evaluate the most
promising shape selective catalysts (SSC), discovered
during Task 1, as an additive or as a support for Fischer-
Tropsch catalysts for the production of fuel range
hydrocarbons from syngas.

The metal components (MC) were Fe and Co with promoters,
some of which were based upon work reported in the
literature and others which were discovered under this
contract. A listing of all runs, including catalysts and
references to data sources in the Quarterlies, will be
found in Table 30; however, only the more significant run
results will be discussed in this report.

A. Catalyst Preparation

Five methods were tried for preparing metal loaded
molecular sieve catalysts for Task 2 testing: (1) a
physical mixture of the F-T component (MC) with the
molecular sieve (shape selective catalyst, SSC), (2) a
precipitation of the F-T component onto the SSC from
solution, (3) the occlusion of metal carbonyls of the
F-T component into the pores of the SSC followed by
reduction to the metal, (4) pore filling of the metal salt
solution into an SSC extrudate, and (5) intimately mixing
the metal component (MC) and the shape selective component
(SSC). This procedure has not been described in previous

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reports. The procedure involved the dissolution of a metal salt in a solvent (water, acetone, or ethylene glycol) followed by pore filling into the molecular sieve powder. This was followed by drying to remove the solvent. In many cases this yielded a metal component which was largely occluded within the crystallites and not on the external surface. This generally yielded catalysts with lower deactivation rates.

Of these four methods, the intimate mixing proved, ultimately, to be the best. The precipitation methods usually resulted in an inactive catalyst as did the ion exchange route. The occlusion of metal carbonyls also resulted in inferior catalyst activity due to low metal loadings. The details of the preparation for the Task 2 catalysts are given in the following review of the test results. A number of additive promoters were employed in these studies. These were coded during the course of the project. These are:

X1..cationic salts of manganese (in particular, nitrate)

X2..cationic salts of iron

X3..is ruthenium trichloride

X4..molybdenum salts (ammonium heptamolybdate, usually)

X5..is rhodium trichloride

X6..is chloroauric acid

X7..is potassium promoted iron

X8..cationic salts of gold

B. Syngas Series

The product development began with screening runs in the Third Quarter of the contract. A total of 91 runs were made on 78 different catalysts. A reference run was made on a state-of-the-art F-T catalyst. Table 30 presents a list of all of these runs. This discussion will not review every run, but rather cover the evolution of the development effort. Additional runs will be discussed at the end because of the knowledge they bring to the subject of F-T catalysis. In addition, a brief comment will be made on the attempts to develop a water gas shift catalyst that would work in conjunction with the F-T catalysts.

The effort began with iron (Fe) F-T catalysts in conjunction with molecular sieves as the shape selective catalyst (SSC). Additives were used to promote these catalysts as well. Initial efforts were on the Fe based catalysts. This was followed by efforts on cobalt based materials. This review will follow the same pattern.

1. Fe Based Fischer-Tropsch Catalyst Studies

a. Reference Fe Catalysts. Runs 10011-6 and 10011-15

The catalyst used for Run 10011-6 represents a state-of-the-art F-T iron catalyst. It is a potassium promoted iron oxide containing no shape selective components. Its performance will be the standard against which molecular sieve containing catalysts will be compared. Consequently, it will be discussed in detail.

This catalyst was tested extensively with over 450

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hours on stream. The performance of the catalyst was studied under many conditions for two reasons: (1) conditions had to be chosen to maximize the C5+ product and then altered in an attempt to convert the solid condensed product to oil, and (2) to provide a reference material to compare with molecular sieve containing catalysts at a variety of test conditions. The details of the run are tabulated in Tables 8A-8H in the Seventh Quarterly Report. A summary of the conversions and product selectivities is presented in Figure 58 in this report. The boiling point distribution and Schulz-Flory (S-F) carbon distribution are also given in the Seventh Quarterly Report for a range of operating conditions.

Run conditions covered a range of temperatures from 250 to 340 C, pressures from 30 to 100 psig, and hydrogen to carbon monoxide ratios from 1:1 to 2:1.

The addition of potassium to the iron catalyst should be reviewed. The potassium brings a water gas shift (WGS) activity to the catalyst. This allows for the efficient use of low H2 to CO ratio syngas, the kind produced by modern coal gasifiers. With these CO rich compositions, less of the more valuable H2 is lost to by-product water formation. However, more CO is diverted to CO2.

From stoichiometry, the molar ratio of CHx/(H2O+CO2) must be 1.0. This ratio is reported for every sample. In the early stages of the run this ratio was frequently less than 1.0. This was probably caused by further reduction of

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the iron oxide to iron metal producing CO2 and H2O but no hydrocarbons. When the values of the hydrocarbon to water plus carbon dioxide vary during the run, then the results must be considered suspect.

This catalyst showed good water gas shift activity. At 250 C with the 1:1 syngas, half of the CO became CO2 with little water produced. The switch to 2:1 syngas lowered the amount of CO2 produced but kept the water gas shift constant at the same value. With an increase in temperature, the water gas shift increased while the actual percent of CO conversion to CO2 decreased. This was due to the absolute amounts of CO and H2 in the effluent. A drop in pressure increased the amount of CO to CO2 conversion. During this run, the water gas shift activity decreased faster than the F-T synthesis activity.

The addition of potassium to iron F-T catalysts is known to increase the amount of oxygenates in the product, particularly C2+ alcohols. The aqueous samples were analyzed for alcohols. Methanol through butanol were detected, with ethanol being predominant. The amount was relatively small, with less than 1.5 % of the carbon in the hydrocarbon product in the oxygenated form.

The conversion of syngas (the combined CO+H2) showed a significant decline over the first two days (Fig. 58), from an initial 74 % to about 45 %. After this, the conversion remained relatively constant even though the reaction conditions were altered significantly. The

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conversion decreased with the increase in the H2/CO ratio. This was not due to catalyst deactivation, but rather the high H2 concentration was not efficiently used. The H2/CO usage ratio clearly showed this. The 1:1 syngas usage ratio was 0.6. The reaction was using more CO than H2. The introduction of extra hydrogen to such a system would not be expected to be efficient. The usage ratio did increase to about 0.75 for the 2:1 syngas at 250 C. While the combined conversion of CO+H2 decreased with the introduction of the 2:1 syngas, due to the inefficient use of the hydrogen, the percent conversion of the CO actually increased. With lower CO2 production and higher CO conversion, the percent conversion of CO to hydrocarbons was actually 42 % higher at the higher H2:CO ratio feed, even though the combined syngas conversion is lower. As this data indicates, the F-T reaction is very sensitive and the results of a change in test conditions can be very subtle. Looking at syngas conversion only, for example, can imply trends going in the wrong direction. Comparisons of the activities of different catalysts must be made carefully. Finally, the increase in activity with increasing temperature was less than expected, from 41 % at 250 C to only 59 % at 310 C. The small change was probably a sign of deactivation of the catalyst.

The changes in the reaction conditions had a large effect on the hydrocarbon product distribution. The heaviest hydrocarbons were produced at the lowest

temperatures. The methane production was low (4%) with the
1:1 ratio syngas and increased to 7% with the 2:1 syngas.
The methane make stayed below 10 % until the pressure was
reduced to 30 psig at 310 C. Then the methane make jumped
to 27 %. At 340 C, the methane rose again, to 37 %.

The light gases, other than methane, showed much less
change with the various test conditions. The C3's and C4's
did not increase with the drop in pressure or the increase
in temperature to 340 C. The paraffin to olefin ratio of
the C3-C5 product indicated that the whole hydrocarbon
product was probably highly olefinic. The percentage of
paraffins increased with decreased pressure and increased
temperature. The iso/normal ratio of the light paraffins
was low and showed no clear trend with changes in test
conditions. Analysis of the light end products generally
yields little information on the optimal conditions.

At the start, the C5+ yield was 83 % at 250C and
decreased steadily to 33 % at 340 C. The amount of
material that condensed showed an even more dramatic
decrease, going from 68 % of the total hydrocarbons at the
start to only 13 % at the higher temperature. This does
not tell the whole story, however. At 250 C, the
hydrocarbon product was a solid wax. In fact, for all
conditions tested except the final one at 340 C, the
condensed product was a solid. At 250 C with the 1:1
syngas, 23 % of the hydrocarbons were in the gasoline range
(C5+-420 F), 29 % in the diesel range (420-700 F), and 32 %

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of all the hydrocarbons produced boiled above the diesel range. This latter material, wax, may be a good cracking feed, but it has little value in a once through operation without a secondary processing step.

The plots of the simulated distillations of the condensed products were all smooth, showing no high concentration of individual compounds as had previously been seen in the Task 1 tests. These samples had little material boiling below 300 F and many had materials boiling above 1000 F.

This reference catalyst was expected to give a Schulz-Flory (S-F) distribution. The S-F distribution is obtained when the probability of chain growth is independent of carbon number. This distribution gives a straight line when plotted as $Ln(Wn/n)$ vs. n where Wn is the weight fraction of the product with carbon number n. One of the initial product samples had some scatter in the data, but followed the expected straight line S-F distribution. A straight line through the data gave an alpha of 0.83. A later sample, taken at the same reaction conditions, did not yield a straight line product distribution. Up to C20 a straight line was obtained with an alpha of 0.84. At C20 there was a sharp change and the alpha changed to 0.91. This double slope behavior was seen in the rest of the samples from this run.

There are two possible explanations for the double alpha behavior. First, there is the probability that chain

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growth may actually increase with increased molecular weight. The probability of chain termination should increase with the increased ability of the intermediates to desorb from the surface of the catalyst. Because of their low vapor pressure, the heavier hydrocarbons would desorb more slowly from the catalyst. This may lead to a gradual change in the alpha and not a sharp break at C20. A second possibility is that there are two different active sites on the catalyst, each with its own distinct alpha. One site may dominate the production of C20 and lighter materials while the other dominates the production of the heavier materials. If the activities were significantly different, a sharp break would occur at C20.

The double alpha product distribution, when the second is greater than the first, has a greater percentage of wax formation than a single alpha product. The reverse would be desirable, i.e. yielding more fuel range material and less wax. It should be possible to accomplish this with catalysts which exhibit shape selective control.

The catalyst used in Run 10011-15 was a physical mixture of potassium promoted iron and alpha-alumina. The metal component of this catalyst was made by precipitating the Fe from an aqueous solution of the nitrate salt with aqueous ammonia. The Fe2O3-H2O was then impregnated with potassium carbonate. This metal component (MC) was then mixed with one micron particle size alpha alumina powder and pressed into pellets giving an overall catalyst

composition of 50 weight % Fe_2O_3 and 50 weight % Al_2O_3.
This same synthesis procedure has been used successfully in
many physical mixture catalysts with molecular sieves
replacing the alumina. Therefore, this catalyst should be
a good reference for comparison with other physical
mixtures which employ molecular sieves as their shape
selective control component.

The conversion and product distribution are presented
in Figures 59 and 60. The boiling point curves, S-F
distribution curves, and detailed data will be found in the
Second Annual Report (Fig. 27 to 34 and Tables 9A to 9C).

The metal component achieved a high conversion of
syngas at 250 C. The H_2/CO usage ratio of 0.6 indicates
the catalyst could effectively use an even lower H_2/CO
ratio syngas. The usage ratio increased, as expected, when
the feed was switched from the 1:1 to the 2:1 syngas.
These conversion results stem entirely from the metal
component and therefore are fairly consistent among all the
iron physical mixture catalysts.

The methane yield was low, but a little higher than
the F-T reference reported above. The C5+ yield is quite
good, accounting for almost 70 % of the hydrocarbons
produced by weight. The plots of the hydrocarbon
distribution by carbon numbers show adherence to the S-F
distribution. Samples taken later in the run show more
deviation but no distinct break at C20 which was evident
with the reference catalyst.

An interesting phenomenon occurs in the Berty reactor operation upon start-up and following a change in operating conditions. Specifically, the time required to allow the passage of the high boilers from the reactor is appreciable and only after some time do they appear in the effluent. This is very evident in the reference F-T catalyst test where only 1 % of 700+ F product boiled above 700 F in the first samples taken, whereas, this percentage increased to 25 % two days later with no change in operating conditions.

It is important to know the quality of the C5+ gasoline produced by this catalyst in order to determine the impact of a shape selective component on the process. In this case, the distillation curve was smooth, indicating that no single components were present in any significant amount. The Refractive Index and density indicate that the product was olefinic. Few iso-paraffins were present, which was similar to the reference catalyst. The whole product range was high in normal paraffins. This has two major effects. First, the gasoline will have a low octane number, about 55, and too low for fuel without additional processing. Secondly, the diesel fuel will have an unacceptably high pour point. The cetane index would be good, but considerable dewaxing or isomerization would be required before it could be used commercially.

In summary, this catalyst produced hydrocarbon products very similar to the reference catalyst. It has a

somewhat lower alpha, which led to slightly lighter products.

      b. <u>Fe on UCC-101. Runs 10011-7, 10011-8, 10011-11</u>

These three runs represent three variations of preparation of similar catalysts. The first was made by precipitating iron oxide onto UCC-101, a large pore shape selective catalyst. The second was a mixture of potassium promoted iron mixed with UCC-101. The third, had the iron precipitated onto the UCC-101 and was promoted with potassium.

<u>Run 10011-7</u>. This catalyst, prepared by precipitating iron oxide onto the UCC-101, contained about 50 % by weight of iron oxide. A number of preparations of this type had previously failed to provide any useful activity. The results of this test were far superior to its predecessors, but it still was inferior to the catalysts prepared by mixing. Surprisingly, this catalyst had almost no water gas shift activity. A large portion of the CO went into hydrocarbon formation. This was in contrast to the alkali promoted catalysts wherein half of the converted CO went to CO_2. Thus, if the conversion of this catalyst was half that of an alkali promoted catalyst, the rate of production of hydrocarbons from CO would be the same. Since this catalyst lacked water gas shift activity, a 2:1 syngas ratio feed was used. A 1:1 syngas ratio was standard for promoted catalysts.

The conversion and product distribution as a function

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of time are presented in Figures 61 and 62. Detailed run data are given in Tables 9A to 9E and Figures 42 to 51 of the Seventh Quarterly Report, which includes the S-F plots.

The process conditions investigated during this run included temperatures from 250 to 310 C, pressures from 100 to 300 psig, and both 2:1 and 1:1 syngas ratios. The catalyst was much more active than in earlier studies.

The conversion was low at 250 C, averaging 20 %. The $H_2:CO$ usage ratio was 1.85 which indicated that the catalyst was efficiently using the 2:1 syngas since the hydrogen and CO were converted at rates proportional to their concentrations. The usage ratio was high because of the lack of a water gas shift activity. Almost all the CO converted became hydrocarbons and less than 15 % went to CO_2. At 280 C the conversion increased to about 32 % and the H_2/CO usage dropped to 1.6. This was because the water gas shift activity increased relative to the F-T activity. Slightly over 20 % of the CO was converted to CO_2. The hydrocarbons produced were more hydrogen rich.

Switching to 1:1 syngas resulted in lower conversion. The catalyst was not able to use this ratio effectively, because its usage ratio was 1.4 while the feed ratio was 1.0. However, this feed did change the product distribution in the proper manner. The x in CH_x dropped from 2.64 to 2.35 and the catalyst produced heavier hydrocarbons. At 315 C with a 2:1 ratio syngas, the W.G.S. activity increased so much relative to the F-T activity

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that the catalyst could not effectively use the syngas, as can be seen by the 72 % CO conversion and only 47 % H2 conversion.

Besides having poor W.G.S.activity, unpromoted catalysts also have poor product selectivities as well. This catalyst produced 16 % methane and less than 50 % of the product was C5+.

The light hydrocarbons analyzed in the gas phase revealed other aspects of the catalysts performance. This catalyst hydrogenated more effectively than the reference iron catalyst. For example, the C3 and C4 materials were much higher in paraffin content. In addition, the C4-C6 portion was much more isomerized. This was a target of the molecular sieve containing catalyst. The switch from 2:1 to 1:1 syngas ratio yielded a more olefinic product. The methane dropped 45 % after the switch to the 1:1 syngas.

The overall selectivity to C5+ was not outstanding, but this was to be expected for a non-promoted catalyst. Under optimal gasoline production conditions, a catalyst that follows the S-F distribution would produce 51 % in the range of C5 to C12. At 250 C this catalyst produced 43 % in the gasoline range. At 280 C with 1:1 syngas, the catalyst produced up to 50 % in the same range. Thus, the unpromoted catalyst under these conditions had a gasoline selectivity that was close to the theoretical S-F maximum. A large difference occurred in the diesel range. This catalyst produced little diesel range material while the

best gasoline S-F catalysts would produce an additional 15 % of diesel range material.

Analysis of the product distribution yielded only minor deviations from a S-F distribution. Each sample had a single alpha value. Simulated distillation plots showed the expected smooth curves.

This catalyst had a good selectivity to gasoline. Unfortunately, the non-gasoline products were gases instead of heavier liquids. Thus, the selectivity to total motor fuels was poor.

Run 10011-8. This catalyst consisted of a physical mixture of potassium promoted iron and UCC-101. A 50/50 mixture was well mixed and pressed into pellets. The hope was that the deleterious effects of precipitating the iron onto the UCC-101 would be eliminated and that the close contact of the two catalysts would be sufficient to provide for adequate size selective product distribution control.

Plots of conversion and product distribution are presented in Figures 63 and 64. The detailed material balances and related plots will be found in the Seventh Quarterly Report, Tables 10 A to 10 G and Figures 52 to 63.

This run lasted for 17 days. The initial conditions were 250 C with 1:1 syngas feed and 300 psig. At these conditions, an earlier similar catalyst had produced wax. After 100 hours on stream the catalyst had reached a steady state operation, with no wax production. The ratio was adjusted to 2:1 to slow down deactivation while the liquids

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were being analyzed. The next step was to go back to the 1:1 ratio and reduce the temperature to 220 C to increase the diesel fuel yield. However, the conversion suffered so much that the temperature was increased to 230 C. Unfortunately, this did not help and the run was ended.

Generally, the data were satisfactory. Conversion was high at 250 C. The usage ratio of less than 1.0 suggested that the catalyst could efficiently use a lower ratio syngas. The activity was very steady and did not show a large initial drop in activity. The catalyst did not use a 2:1 syngas ratio efficiently. At 220 C the conversion dropped to under 20 %.

The catalyst had high W.G.S.activity. The activity paralleled that of the F-T activity such that the selectivity for CO to either hydrocarbons or CO2 remained constant. The total activity of the catalyst dropped by a factor of 3 during the test.

The extent of chain growth was less than that of the reference catalyst under similar conditions. The methane production was higher. Analysis of other hydrocarbons in the gas phase yielded some additional information. The catalyst had a greater hydrogenation ability than that of the reference and a slightly higher isomerization activity than the reference due to the acidity of the SSC component.

The condensed product was a liquid not a solid. This was not due to the distribution but, because the product was fundamentally different, i.e. it was much more

isomerized. In addition, the boiling range of the products were not as wide as those produced with earlier catalysts. The condensed product had only one S-F alpha. There appeared to be a cut off of products above C22.

The C5+ liquid had other significant aspects. At 250 C the gasoline was obtained in high yield. At 220 C, the selectivity to motor fuels was quite good. A total of 50 % was in the gasoline range and an additional 20 % was in the diesel range. This compares favorably with the 72 % theoretical yield of motor fuel range material predicted for a strict S-F catalyst optimized for maximum C5-C22 product.

This catalyst, while not considered the ultimate of this type, was very encouraging for a first attempt at a physically mixed catalyst. Many goals were met. The mixture gave an isomerized product, a sure indication that the molecular sieve was functioning. No wax formation was observed and excellent selectivity was observed at 220 C although the conversion was poor at this temperature.

Run 10011-11. This catalyst employed a precipitated iron oxide loading onto UCC-101 followed by impregnation with potassium carbonate solution. The powder was dried, pressed into pellets and calcined at 250 C. The effect of promotion can be determined by comparison with 10011-7 and the effect of precipitation vs. mixing can be determined by comparison with 10011-8, both reviewed previously in this section.

The conversion and product distribution during the course of the run are presented in Figures 65 and 66. The run details are presented in the Second Annual Report, Figures 67 to 75 and Tables 11A and 11B.

The conversion provided by this catalyst is much lower than that provided by the physical mixture. Part of this is due to the reduced iron content present in this catalyst, about 25 % less than for the physically mixed catalyst. Another possibility is a low iron surface area in the reduced catalyst. A third possibility is a metal support effect with the molecular sieve. However, although the activity was quite low, the catalyst exhibited no deactivation.

The H2/CO usage ratio was much higher than with the physically mixed catalyst. Much of the oxygen from the CO went into water production instead of CO2, indicating a lower W.G.S. activity. This was true in spite of a higher level of potassium in this formulation. It is likely that the potassium was being tied up by the molecular sieve and it was unable to promote the iron effectively. This was also expected to affect the ability of the molecular sieve to isomerize the F-T products, as well.

The methane yield was high. The product distribution did not show a change during the course of the run, undoubtedly due to the stability of this catalyst. The carbon number plots show a deviation from S-F behavior. This was not a double alpha phenomenon, but rather, a cut off above C25 caused by the UCC-101.

Up to 55 % of the hydrocarbons produced boiled in the gasoline or diesel range. The quality of this product was an important aspect of this catalyst's chemistry. The C4's were olefinic as was the liquid product. The condensed product was liquid at room temperature. The product was more isomerized than that of the reference catalyst. However, the product was not as isomerized as the unpromoted catalyst product from 10011-7. Addition of the potassium to both the iron and the molecular sieve would explain both the low W.G.S. activity and the decreased isomerization activity.

The potassium did have some effect on the performance of the catalyst. Without the promotion, the catalyst did not produce any diesel fuel range product. With this catalyst, over 12 % of the hydrocarbon product boiled in the diesel range. It is apparent from the W.G.S activity, the product isomerization, and the chain growth probability, that the potassium promoter was added to both the MC and the SSC, and it effected both of these components.

c. Fe on UCC 104 and modified UCC-104 (UCC-108).
Runs 10011-10 and 10011-16

These two runs demonstrate the performance of UCC-104, a proprietary molecular sieve with a 6 A pore size. The first catalyst was a physical mixture, while the second catalyst had its iron precipitated onto the UCC-104. In both cases, the catalysts were promoted with potassium.

Run 10011-10. UCC-104 was one of the best catalysts discovered during Task 1 for the oligomerization of propylene. This catalyst was prepared as a physical mixture by the same methods described previously. The conversion and product selectivity are presented in Figures 67 and 68. The run details are found in the Second Annual Report, Tables 10A through 10E and Figures 41 to 61.

The metal component again demonstrated high syngas conversion with characteristics similar to those seen with the physical mixture with alpha alumina. This catalyst did not show an initial deactivation. The temperature increase from 250 C to 280 C did not alter the conversion or the H2/CO usage ratio.

The product distribution was very different from that produced in Run 10011-15 (Reference catalyst with promoted iron on alumina). This catalyst produced more gaseous hydrocarbons than other catalysts. The methane yield was initially over 10 % and increased steadily during the run. The C5+ decreased steadily and accounted for only 50 % of the total hydrocarbons produced initially. This dropped to 35 % by the end of the run at 280 C. The carbon number product distributions deviate from a linear distribution. There appears to be a double alpha behavior with excess products in the C20+ range. This could be due to the moderate pore size of the molecular sieve. One of the functions of the SSC was to intercept growth intermediates, which, in turn affected the probability of chain growth,

alpha. If the molecular sieve could not intercept the larger molecules, possibly for diffusion reasons, the alpha of the heavier hydrocarbons would be greater than those of the lighter hydrocarbons.

Almost all of the C5+ product boiled in the gasoline range with some diesel oil but little heavies. The liquid product was highly isomerized during the run and the gasoline produced should have a good octane number.

The yield of gasoline and diesel fuel on this catalyst was not high but it was not unacceptable. It compared well with other iron based catalysts. The remarkable aspect of this material was the indication of the superior quality of the gasoline.

Run 10011-16. UCC-108 was clearly the outstanding catalyst discovered during Task 1 studies. The physical mixture of promoted iron and UCC-104 (a less active modification of UCC-108) produced an excellent gasoline product in a previous run. For these reasons, a precipitation catalyst was prepared from UCC-108, using the same procedure as described previously for the UCC-101 preparation, including promotion with potassium.

The catalyst was completely inactive for F-T synthesis. There may have been something in the SSC which poisoned the metal component. Nevertheless, the continued inferior performance of the catalysts prepared by precipitation led to the eventual abandonment of this route. The details are in the Second Annual Report, Tables

13A-13B and Fig. 80-81.

d. Fe on UCC-111 (AlPO-11). Run 10225-3

The UCC-111 catalyst showed no oligomerization activity in Task 1 testing (see Run 9972-21 in the propylene section). The catalyst for this test was prepared by physically mixing the components. The iron was promoted with potassium.

The conversion and product distribution were similar to that of the reference catalysts. The catalyst was rather active which led to low H2/CO usage ratios. Conversion was quite constant. The catalyst also yielded a stable product distribution over the course of the test. Details of the run are found in Tables 2A-2C and Figures 23-41 in the Ninth Quarterly Report.

The reason for discussing this catalyst test is the nature of the hydrocarbon product. Although the yield, boiling point distribution, and hydrocarbon type were very similar to the reference catalyst, one major difference was noted. The reference catalyst product was solid whereas the product from this catalyst was liquid. This was discovered to be due to the ability of this catalyst to isomerize the double bonds away from the alpha position. This resulted in a lower melting point and a significantly higher octane number in the gasoline range material.

Since this material was so poor in Task 1 tests, its efficacy in Task 2 when mixed with an active metal component was remarkable. A minimal effect on the

chemistry of the product was anticipated from its low
activity. The outstanding performance of this SSC is
ascribed to its outstanding characteristics as a support
for metal catalysts.

2. Co Based Fischer-Tropsch Catalyst Studies

Cobalt catalysts present difficult problems in terms
of product quality but their high selectivity for gasoline
and diesel oil made them prime candidates for further
study. Cobalt catalysts were usually promoted with
thorium. Cobalt catalysts were known to function
differently than iron in two ways. First, they were much
more active than iron at the same conditions. The catalyst
used in run 10112-04 contained about 20 % cobalt
precipitated on UCC-101, and at 250 C, 300 psig, and 1:1
H2:CO ratio syngas yielded a conversion of 52 %. The
catalyst used in run 10011-11, containing about 50 % iron
precipitated in UCC-101, had a conversion of only 27 %
under the same process conditions. Secondly, they produced
a much more paraffinic hydrocarbon. This latter fact
presented the molecular sieve component with a much more
difficult isomerization task. Accordingly, whereas the iron
formulations were typically equal weight mixtures of MC and
SSC, the cobalt mixtures contained as little as 20 % MC and
still had significant F-T activity. This allowed for a
higher proportion of the SSC in the catalyst which is
desirable in order to achieve higher isomerization
activity. This was the direction taken on subsequent Co

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catalysts after a few runs to establish the proper MC/SSC ratio. Strength considerations required that a small amount of silica binder be used in the formulation.

Oxygenates were not a problem with either the iron or the cobalt catalysts which contained SSC. Potassium promoted iron catalysts are known to produce significant amounts of oxygenates, specifically alcohols and acids. The potassium promoted iron catalyst containing SSC produced less than 1 % oxygenates, which was predominantly ethanol and found in the aqueous phase. The oxygenate production from the cobalt/SSC catalyst was less than that of the iron/SSC catalyst.

iron/SSC catalyst.

a. Reference Cobalt Catalyst. Run 11677-7

This catalyst was prepared to serve as a reference for catalysts containing molecular sieves. This catalyst was prepared by precipitating cobalt oxide with sodium carbonate from an aqueous solution of cobalt nitrate. After washing and drying, the oxide was impregnated with thorium nitrate solution to give 15 weight % thorium on the metal component. The metal component and the alpha alumina were physically mixed in a 3:14 weight ratio, bonded with 15 % silica, formed as 1/8" extrudates, and calcined in air at 250 C.

The conversion and product distribution behavior are presented in Figures 69 and 70. The rest of the detailed data can be found in the Eleventh Quarterly Report, Tables 22-25 and Figures 169 to 198.

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At 270 C the conversion was extremely high (93 %) and the deactivation very small; the W.G.S activity was also high, with more than 80 % of the oxygen rejected as CO2; and the H2/CO usage ratio was less than 1:1. Upon lowering the temperature to 250 C the conversion dropped to about 65 %. The W.G.S. activity followed with 68 % of the oxygen rejected as CO2, which was still much higher than the initial values of Fe catalysts at higher temperatures. The hydrocarbon products were poorer in hydrogen at 250 C than at 270 C, so that the H2:CO usage ratio was lower as well (0.83:1, down from 0.90:1 at 270 C). At 260 C the conversion rose again to 85 % and the W.G.S. activity rose to the same level as at 270 C.

At 270 C the selectivity of this catalyst was poor. The product was extremely hydrogen rich and predominantly lights (more than 45 % methane, 20 % C2-C4, less than 30 % gasoline, 4 % diesel oil, and 0.5 heavies) all of which were almost completely saturated.

When the temperature was dropped to 250 C, the methane production dropped to <15 %. The C2-C4 dropped to 15 %. The lights were more olefinic and the selectivity to gasoline and diesel fuel improved. The liquid product was waxy, which was expected due to the lack of acidity of the alumina. The motor fuel yield was between 68 and 71 %, which is near the 72 % maximum predicted for a S-F distribution.

At 260 C the methane production was high at 32 %, the

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C2 to C4 was up to 21 %, the lights were highly paraffinic, and the production of total motor fuels was low. The S-F plots were straight lines except for excess methane. The liquid products at all three temperatures were mostly n-paraffins.

The most significant finding of this test was the sensitivity to temperature. Since the selectivity varied much more widely with temperature than the conversion, lowering the temperature substantially improved the yield of useful products.

At 250 C vs. 260 and 270 C, the yield was both the highest in desirable fractions and lowest in undesirable by-products.

b. Run 10225-8. Catalyst Co/Th/X4/UCC-101

This catalyst represented the next major advancement in catalyst development. The use of additive X4 greatly improved the stability of this catalyst. The deactivation rate of this catalyst was one-fourth of that of its additive free counterpart. Furthermore, the quality of the product was improved in that it contained a high, stable yield of olefins and was free of suspended wax.

Figures 71 and 72 present the conversion and product distribution vs. time on stream. The detailed data is presented in the Tenth Quarterly Report in Figures 146 to 180 and Tables 21 to 28.

As mentioned, the most notable feature of this catalyst was the stability demonstrated. The initial

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conversion was 75 % which is equivalent to the non-additive counterpart. But, the activity was as high after 480 hours as the counterpart was at 128 hours. The water gas shift activity was low, 37 % initially and fading to 22 % for most of the run (compared with the non-additive version which ran from 37 % to 20 % during the run).

The selectivity was also far more stable. Initially the selectivity to methane was the same as the non-additive counterpart. However, the increase in methane occurred much more slowly. On the other hand, the additive containing catalyst produced more C2-C4 material as the run progressed than did the non-additive material. These two trends offset each other so that the C5+ yields were about equal.

One clue to some of this catalysts behavior lies in the olefin content of the C4's. Instead of falling off, as usually happened, the olefin level held nearly constant throughout the run. Initial production of total motor fuels was 67 % which dropped to 52 % by 480 hours. Finally, the liquid product contained no wax, the first time this was observed with a Co + UCC-101 catalyst. This was probably due to the higher olefin content of the product.

c. Run 10225-16. Catalyst Co/Th/UCC-103

A significant step forward was made with the preparation of this catalyst. The catalyst was prepared by promoting cobalt oxide with thorium while in contact with UCC-103 powder (UCC-103 is a modification of UCC-101).

This was the intimate mixing technique described previously. The mixture was bonded with 20 % silica.

The improvement was in the stability of the formulation. Compared with a reference catalyst (10112-15) this material was both more active and stable. The initial conversion was 80 % which dropped off to only 72 % after 188 hours on stream. The corresponding values for the reference catalyst were 76 % and 52 %. The water gas shift activity was similar in behavior. In addition, the selectivity remained quite stable.

It is believed that the intimate mixing of the components during the preparation of the catalyst was responsible for the resulting behavior. Detailed data are in Figures 99 to 125 and Tables 13 to 16 in the Eleventh Quarterly Report.

d. Run 11677-11. Catalysts Co/Th/X4/UCC-103/UCC-101

Following up on the discovery of the impact of the intimate mixing technique upon stability, a series of catalysts were prepared employing this technique. In addition to the use of the new technique, the incorporation of additives, which had previously shown benefits, were included. In general, the adoption of these techniques results in an enhanced stability of all the catalysts. The catalysts prepared by this technique also had other properties in common. The hydrocarbon products usually had less olefins and were less waxy. (The olefin content could be increased with an appropriate additive.) In addition,

these catalysts exhibited lower water gas shift activity.

Run 11677-11 provided the best results of any tests conducted during this program. This catalyst employed the X4 additive which proved so successful in stabilizing the catalyst reported on in Run 10225-8. The catalyst was prepared by promoting the cobalt with the thoria while in intimate contact with the UCC-103, and then further promoting with X4. The mixture was bonded with 15 % by weight silica and formed as an extrudate. The catalyst contained 4.5 % cobalt and 0.9 % of the X4 additive.

The conversion, product distribution, isomerization of the pentane fraction, and olefin content of the C4 fraction are presented in Figures 73 to 76. Complete data are found in the Third Annual Report, Figures 138 to 141 and 150 to 164. Detailed material balances are in Tables 28-32 of the Third Annual Report.

Some early run irregularities make it impossible to determine if this catalyst suffered some early deactivation. However, after 100 hours, the catalyst exhibited extraordinary stability. The first test of the X4 additive (Run 10225-8, reviewed above), after an initial deactivation, showed a loss of one % of activity every 35 hours during the last 15 days on stream. This was one fourth of that of the reference catalyst and quite remarkable. During the 12 day test of the present catalyst, the deactivation was immeasurably low, possibly as little as 1 % per 1100 hours.

In addition, the product yield and composition was extremely stable as well. Methane production remained constant at 13 percent. This compared very favorably with the one percent increase per 55 hours observed during Run 10225-8, also a very stable catalyst (reviewed above).

As in Run 10225-8, the X4 additive seemed to increase the selectivity to C2-C4 hydrocarbons; this is one of the few cobalt catalysts to produce more C2-C4's than methane.

The C5+ hydrocarbons also remained extremely stable. The initial yield was 69.7 % and a one percent drop was observed over the entire course of the test. The heavies remained constant at a small but steady 2.7 % of the total hydrocarbons. Motor fuels, initially 67 percent dropped about one percentage point during the run.

This product yielded very little iso-pentane, but this is typical of the the behavior of the intimately mixed MC and the chosen SSC materials. On the other hand, usually the intimately mixed catalysts produced a low olefin content in the C4 fraction. In this case, butenes accounted for 66 % of the C4's, and this was constant for the run.

Apart from the usual excess of methane, the Schulz-Flory plot showed a straight line distribution.

This was an important catalyst due to its unsurpassed stability and its good selectivity to liquid products.

It is instructive to compare the outstanding performance of this catalyst with that tested in Run

11885-6. This catalyst was identical to the one used in Run 11677-11 with the exception that the Th promoter was omitted. This catalyst had lower activity and what has now come to be regarded as poor stability. Results are presented in the Fifteenth Quarterly Report.

These findings point to an interrelationship between the Co, Th, and X4 for activity and product distribution as well as stability. As a final note, the effect of employing an extrusion aid during the forming of the catalyst, was tested on this catalyst. No difference in performance was observed between the catalysts formed with or without the extrusion aid.

3. Other Cobalt Based Catalysts Providing Insight

a. Comparison of Cobalt Based Catalysts with UCC-101 or UCC-103 with Catalysts Containing UCC-108

The comparison is based upon the catalyst prepared for Run 11677-10 (a thorium promoted cobalt catalyst prepared in the intimate presence of UCC-101) and the catalyst prepared for Run 11723-3 (the same catalyst preparation with the addition of UCC-108). The key fact learned from the comparison of these runs is that the addition of a second shape selective catalyst (SSC) to a catalyst prepared by the intimate mixing of the MC and a SSC during promotion results in a gross reduction in the impact of the second SSC on the performance of the catalyst.

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b. Performance of X6 as an Additive

The additive X6 was added to a conventionally formed Co/Th/UCC-101 (as tested in Run 10112-15) and tested in Run 11677-3. The results were encouraging. The stability was greatly improved and the product distribution was superior when the additive was present, specifically lower methane production and a higher yield of olefins.

The discovery of the importance of the intimate mixing techniques upon stability required the determination of whether or not the additives which improved stability on the original catalyst formulations would enhance the intimately mixed formations. To this end, the comparison can be made between Run 10225-16 (intimately mixed Co/Th/UCC-103) and Run 11723-4 (intimately mixed Co/Th/X6/ UCC-103. In contrast to the comparison made above, where the X6 additive so dramatically enhanced the performance of the catalyst, in this case, the contribution of the additive was negligible.

However, in a subsequent run (11885-8), the additive improved the efficiency of cobalt use by the catalyst. The preparation employed a different source material for the X6 and incorporated it into the formulation in a different manner. This points to the importance of the techniques used to incorporate additives into these formulations.

c. Tests to Evaluate Coke Inhibitor Additives

In Run 10225-02, the Co/Th/UCC-107 catalyst was found to have excellent activity but it coked rapidly and lost

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activity. It was known that Zn on molecular sieves can inhibit coking in hydrocracking catalyst applications. Thus, the catalyst in question was prepared with the addition of Zn to the molecular sieve portion of the catalyst. The initial activity was high. The behavior followed an interesting trend, presumably because of the hydrogenation activity of the Zn. Early in the run the saturates predominated due to the hydrogenation activity of the Zn and later the olefins increased and surpassed the paraffins as the catalyst coked and the hydrogenation activity was lost. The loss in the isomerization of the pentane followed a similar pattern. The attempt to reduce the coking in this manner was unsuccessful.

4. Water Gas Shift (WSG) Catalyst Studies

Tracking the catalysts for water gas shift (WGS) activity became routine early into these studies. The benefits are obvious. Specifically, the use of the less valuable CO to reduce water to extra hydrogen, the more valuable component of the syngas, was economically a plus. Most of the cobalt catalysts exhibited a little WGS activity and the opportunity to generate more was attractive. To this end, after the major discoveries which realized the successful accomplishment of the Task 1 and Task 2 objectives, a modest effort was initiated to try to improve the WGS activity of the outstanding F-T catalysts that had been developed during the program.

Thirteen runs were devoted to this search. Four were

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devoted to single WGS catalysts with the intent to physically mix them with the F-T catalysts. Nine were combinations of known efficient F-T catalysts developed in this study and WGS catalysts of various compositions. Table 31 is a list of the catalysts and references, the run numbers, the catalyst composition, and the reference to the detailed data in the quarterly reports.

It should be noted that the temperatures required for effective WGS and F-T catalysis are not always thermodynamically compatible. Specifically, at temperatures that favor high WGS activity, the F-T catalysts produce undesirable product distributions. However, the economic benefits are such that an effort was warranted.

A brief review is in order. In the case of the pure WGS catalysts, the first tested (11677-12), Cu and Zn loaded on alumina and tested at F-T conditions, exhibited some initial activity, but this was followed by rapid deactivation (1%/2.4 hours). The catalyst, loaded on UCC-101, tested in Run 11677-13 exhibited a 0.6 % / hour deactivation rate. However, the WGS activity was good and testing with a F-T catalyst was warranted. When loaded on LZ-105-6, a WGS catalyst exhibited no WGS activity. An alternative to this material was to ion exchange the Zn onto the LZ-105-6 and then load the Cu. This was done for Run 11677-20 and no WGS activity was observed.

The combinations of successful F-T catalysts and the

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WGS catalysts were evaluated next. In runs 11723-05, 11723 -07, and 11723-08, the F-T activity was reduced and the WGS activity was negligible. In addition, the stability of the F-T component was reduced. In Run 11723-12, the F-T and WGS components were in separate pellets to clarify the effect of pore size and acidity. This catalyst was ineffective. In Run 11677-20, Cu and Zn loaded on a molecular sieve of moderate acidity, the catalyst was not active. The ion exchange of the Zn onto this same support before loading the Cu also resulted in a catalyst that was not active. An attempt to mix the two catalysts as separate pellets, rather than expose them to each other during the formulation, (11677-18), also failed to achieve the desired WGS goal. Surprisingly, some improvement with time on stream was observed with this catalyst that was never clearly understood. The concept of putting the WGS component onto a small pore zeolite, to protect these sites from deactivation by large F-T molecules, was tested. These catalysts exhibited no WGS activity. In fact, a catalyst which contained a very fine F-T catalyst and the WGS components loaded onto a 4A type zeolite, to insure that F-T products could not poison the WGS components, was totally inactive! The mixture of an active F-T catalyst with separate pellets of a known active WGS catalyst proved to be totally inactive for the WGS and F-T reaction. In this case, the WGS catalyst was a copper exchanged type 13X zeolite, wherein the sodium cations present in the zeolite

had been ion exchanged with copper in solution.

In summary, the attempt to combine WGS activity with F-T activity in the same reactor bed has led, to date, to inferior performance with both the F-T catalyst and the WGS catalyst!

VII. Process Simulation Studies of UCC
Fischer-Tropsch Catalysts in an ARGE-Type
Fixed Bed, Tubular Reactor System

Introduction

It has been shown that, during the latter part of this contract, Union Carbide developed several cobalt based catalysts which demonstrated high C5+ yields and good catalyst stability. In order to evaluate these catalysts, the Department of Energy requested Union Carbide to provide adequate process design data so that a private contactor could perform a techno-economic evaluation of the Union Carbide catalysts.

Methodology Used to Obtain Process Design Data

Towards this end, Union Carbide correlated the test data already available on these catalysts to obtain expressions for (1) the syngas conversion rate, (2) the methane make, as weight percent of total hydrocarbon produced, and (3) the C2+ hydrocarbon distribution. This work has been reported in detail in the Fifteenth Quarterly Report.

Figure 77 shows how these three expressions were then used in a computer program which simulated an ARGE-type tubular reactor system operating at 270 C and 300 psig, at an overall 85 percent syngas conversion, and with a 2.3:1 recycle ratio for the non-condensed <C5 gases in the process configuration presented in Figure 78.

The output from this program was presented in

the form of a series of graphs, each depicting the space velocities and the H2:CO feed ratios required to obtain a fixed methane yield with Union Carbide catalysts having varying specific activities (their syngas consumption rate relative to the Co/UCC-101 catalyst measured during Run No. 10011-14 and reported in the Second Annual Report) and H2/CO usage ratios.

Design Curves for Private Contractor

Figures 79 and 80 are the two primary design curves generated for the Private Contractor. They show the feed H2:CO ratio/the catalyst specific activity/the usage ratio/and the feed space velocity relationships for an ARGE type reactor operating at 270 C and 300 psig, using a 2.3:1 recycle ratio, and having a packed catalyst density of 0.6 gm./cc to obtain an overall 85 % syngas conversion while producing hydrocarbon product containing either 12.3 weight percent methane (Figure 79) or 7.8 weight percent methane (Figure 80).

The use of these two figures is straight-forward. A single point is located for a catalyst having a definite specific activity and a definite usage ratio by using the right hand usage ordinate with the specific activity curves. The feed space velocity and the feed H2:CO ratio corresponding to that point (i.e., corresponding to that catalyst) are then read from the bottom ordinate and the left hand ordinate, respectively.

Comparison of the two figures shows that for a given catalyst (having a defined specific activity and usage

ratio) both the H2:CO feed ratio and the feed space velocity will be higher for the 12.3 weight % methane case than for the 7.8 % case. This is because the higher H2:CO feed ratio used to obtain the higher methane make (as dictated by the equation for the methane make) will cause the syngas conversion to increase (as dictated by the equation for the syngas conversion rate), and thus permit a higher space velocity to be used for the same overall 85 % syngas conversion.

Thus it can be seen that running the reactor with a high H2:CO ratio will ensure a desirably high space velocity, but will result in an undesirably high methane production rate.

The Independant Contractor decided to cost two cases. Case 1 would use a Union Carbide catalyst having a 1.6:1 usage ratio and a 2.68 specific activity, values which were considered readily achievable at the time. This catalyst would operate with a H2:CO feed ratio that would allow a high space velocity at the expense of a high (12.3 weight percent) methane make. Case 2 would use a Union Carbide catalyst having a 2.0:1 usage ratio (the increase in costs associated with the lower water gas shift activity was expected to be more than outweighed by the reduction of costs associated with the increased space velocity resulting from this higher usage ratio) and a 3.64 specific activity, values that were considered achievable over the course of an extended research effort. This higher

activity would operate at a leaner H2:CO feed ratio which would allow a low (7.8 weight percent) methane make at the expense of a lower space velocity (lower than would be required with a higher methane make). Case 2 would, in effect, use some of the anticipated increase in specific activity to reduce the methane make below that of Case 1.

When the Case 1 catalyst (having a usage ratio of 1.6:1 and a specific activity of 2.68) is located on Figure 79, the bottom and left hand ordinates indicate that the feed space velocity must be 300 vol./vol./hr. with a H2:CO feed ratio of 1.21:1. Similarly, when the Case 2 catalyst is located (having a usage ratio of 2.0:1 and a specific activity of 3.64) is located on Figure 79, the bottom and left hand coordinates indicate that the feed space velocity must be 360 vol./vol./hr. with a feed H2:CO ratio of 1.39:1.

Table 32 lists the compositions of the off-gas and liquid streams calculated by the FIXBD1 program for the two cases. Table 33 lists the characterization of the various components in the streams, for both cases.

It should be mentioned that the 0.11:1 and 0.17:1 H2:CO ratios in the off-gases of the cases shown in Table 32 are the ratios seen by the last section of the catalyst bed. These are far lower than the 0.68:1 and 0.39:1 ratios used in the correlations for the syngas conversion rate, methane make, and alpha. Consequently, the use of these

correlations in such extrapolations, particularly the one
predicting the methane make, is certain to lead to
significant errors.

It was assumed that such errors would be corrected in
future correlation work for new, more promising F-T
catalysts expected to be developed under a follow-up
contract.