3. EXPERIMENTAL SUMMARY

3.1 INTRODUCTION

The catalysts prepared during this work were screened in a fixed-bed pilot plant. Their performance was compared to a reference catalyst which resulted from two earlier DOE contracts to Union Carbide Corporation. A drawing of this plant is in Figure 3. Most of these screening runs were performed according to the conditions outlined in Figure 4. These conditions were adopted early in this work when it was found that the initial catalysts were not very active at the condition used to evaluate the reference catalyst (Condition 1). The second two conditions are more strenuous than the first insuring some high conversion data to allow assessing methane and ethane selectivity at reasonable conversions.

In the fixed bed runs 13 g of catalyst were loaded with 160 g of quartz sand diluent. The large mass of diluent was needed to facilitate heat removal from the reactor since the F-T reactions are very exothermic. During the fixed-bed runs reactor bed temperatures were measured by means of an internal sliding thermocouple.

A few of the most promising catalysts were evaluated in a slurry autoclave pilot plant (drawing: Figure 5, simplified schematic: Figure 6). The benefits of such testing are several-fold. First of all a heavy oil is added to the autoclave reactor at startup to aid maintenance of a constant reaction temperature which promotes catalyst stability. Secondly, the run length is longer than in the fixed bed screening tests which allowed determination of catalyst stability.

Regardless of the test method, the feed was always a blend of hydrogen, carbon monoxide and argon with a hydrogen to carbon monoxide molar ratio of two. A typical feed composition (mole percent) was: hydrogen = 64, carbon monoxide = 31, argon = 5. Although the feeds were quite pure, they were pretreated through molecular sieves and hot alumina to remove any remaining impurities.

3.2 REVERSE MICELLE CATALYSTS

The reverse micelle method was shown in a previous DOE contract to UOP to be capable of forming 50-100 Å ruthenium aggregates on a support. In the current work this method was used to prepare cobalt and cobalt-ruthenium catalysts on a variety of supports. Preparation and evaluation of these catalysts are discussed in Section 4; they were not very active and were only screened in the fixed-bed pilot plant.

3.3 Y-ZEOLITE SUPPORTED CATALYSTS

Catalysts were prepared on two different samples of steamed Y-zeolite. The preparation methodology was similar to that used during two previous DOE contracts to Union Carbide (prior to the Union Carbide/UOP joint venture). Some changes to the original catalyst preparation method were investigated. A few of these catalysts were more active than the reference catalyst, these were evaluated in the autoclave pilot plant as well as the fixed-bed plant. Most of these catalysts were only evaluated in the fixed-bed pilot plant, their preparation and evaluation are covered in Section 5.

During both the screening and autoclave runs light gas analyses were performed by an on line gas chromatograph. These on line analyses were used to calculate conversions and selectivities (CO_2 and $C_1 -> C_4$) via the calculation method in the Appendix which is based on the feed internal standard (argon).

4. DEVELOPMENT OF REVERSE MICELLE CATALYSTS

This section contains a brief summary of the UOP-developed reverse micelle method for preparing catalysts with uniformly-sized ruthenium aggregates. Also summarized is the work done during the current contract toward development of reverse micelle type cobalt and cobalt/ruthenium catalysts.

The cobalt and cobalt/ruthenium catalysts were screened in the fixed-bed pilot plant. None were active enough at the first of the three test conditions to warrant further testing in the slurry autoclave pilot plant. All catalysts were at least evaluated at the first condition of the three condition test described in Section 3 (Figure 4). Most were evaluated at all three conditions.

4.1 BACKGROUND

Depositing uniformly-sized aggregates of metal onto supports via reverse micelles and subsequently using such composites as catalysts for F-T synthesis was first demonstrated by H. Abrevaya at UOP during the previous DOE Contract DE-AC22-84PC70023. This impregnation method was based on previous work by Stenius, et. al.[6] who developed a way to prepare small, regularly-sized (30-50 Å), metal aggregates using surfactant molecules. In this methodology, the aqueous core (Figure 7) of a reverse micelle is used to carry metal salt(s) to the catalyst surface. The catalyst preparation method developed by Abrevaya uses metal-containing reverse micelles for support impregnation followed by the steps of calcination and reduction with hydrogen.

The ruthenium-only catalysts from the above contract were very active but would be costly to

produce. The original objective of the current contract was preparation of reverse micelle catalysts containing mainly cobalt, but with a small amount of ruthenium as, hopefully, an activity promoter.

4.2 CATALYST PREPARATIONS

All reverse micelle catalysts were impregnated in the same way. First a mixture was made of n-hexane and Berol 050, a surfactant from Berol Kemi, Stenungsund, Sweden. After standing overnight the mixture was filtered and an aqueous solution of salts of the metals to be impregnated was added. This admixture was shaken and added to a set of vials. Enough metal salts were present in each vial to impregnate two grams of support. After addition of support the vials were intermittently swirled for four minutes. After the support settled the liquids were pipetted out and the impregnated support was allowed to dry overnight at room temperature. The dried samples were separately analyzed for metals, those with similar metals levels were combined. STEM analyses were performed on some of the combined samples. Catalysts were calcined at 300° C then reduced at 380° C for four hours under hydrogen before they were evaluated in the fixed-bed pilot plant.

Control catalysts were prepared on the supports via simple evaporative impregnation of aqueous solutions of metal salts.

The reference catalyst was one prepared during a previous DOE contract to Union Carbide Corp. via a pore-filling method which uses a solution of metal salts in an organic solvent and a modified Y zeolite support.

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4.3 CATALYST SUPPORTS

Examples of reverse micelle and aqueous impregnated catalysts were prepared on each of these supports: magnesium oxide, carbon and alumina-titania.

4.4 CATALYST PERFORMANCE

Screening test results from the various catalysts are summarized below. None of the experimental catalysts were promising enough vs. the reference catalyst to warrant further testing.

4.4.1 REFERENCE CATALYST PERFORMANCE

The reference catalyst was supported on a sample of steamed and acid-washed Y zeolite. Steaming causes large (50-100 Å diameter) amorphous pores to form within the crystalline framework of the Y zeolite crystallites. After the acid wash which removes residual, steaming-derived, amorphous alumina from the crystalline channels, the new large pores are accessible via the crystalline channels of the remaining Y zeolite. The large pores can support cobalt crystallites of the size required for effective F-T catalysis, namely 50-100 Å. Catalysts with cobalt crystallites much below 50 Å become quite selective for methane. During the previous development it was found that small amounts of manganese and zirconium are beneficial for lowering light ends selectivities and stabilizing catalyst activity.

The reference catalyst was evaluated in Run 65, plots of conversions and selectivities vs. hours on

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stream from this run are attached as Figures 8 to 14. It was a longer run than the screening runs with experimental catalysts below. This catalyst appeared to reach a line out in activity and selectivity by fifty hours on stream. In comparing its performance to that of the experimental catalysts below, the fifty hour conversions and selectivities will be used. After extended use at other feed rates, the catalyst was returned to the starting conditions at three hundred and fifty hours on stream. The activity had diminished during the time at the other conditions, for instance, the carbon monoxide conversion between fifty and one hundred hours on stream was forty percent whereas after return to the initial conditions it was twenty percent.

4.4.2 PERFORMANCE OF CATALYSTS SUPPORTED ON MAGNESIUM OXIDE

The first reverse micelle catalysts made under this contract were inactive. The first active ones were supported on a very pure sample of magnesium oxide which was particularly noteworthy in containing very little sulfur. Previous magnesium oxide samples had failed to produce active catalysts.

Three catalysts from this pure magnesium oxide support were evaluated. Two resulted from aqueous impregnation and one from reverse micelle impregnation. The metals content of these catalysts and a brief overview of their performance appear in Figure 15. The reverse micelle impregnated catalyst seemed to be slightly more active and less selective to methane than the two catalysts resulting from aqueous impregnation. However, all three were less active than the reference catalyst of Run 65.

Plots of conversions and selectivities vs. hours on stream for the three runs with magnesium oxide-

supported catalysts are attached as Figures 16 to 32. Run 63 used a reverse micelle catalyst. This run was performed before the three condition test was being used, however, the start up conditions were the same as condition 1 of the three condition test. The carbon monoxide conversion seemed to be stabilizing at or slightly above seventeen percent by fifty-five hours on stream at which time the temperature was increased. A carbon monoxide conversion of about twenty percent resulted when the temperature was increased to 224° C. The methane selectivity was about ten percent at 211° C and twelve percent at 234° C; this selectivity is known to increase as temperature increases. Problems with the on line gas chromatograph caused most of the ethane and ethylene selectivity data to be lost. The propane and propylene selectivities are in Figure 17.

The two catalysts prepared via aqueous impregnation were evaluated by the three condition screening test in Runs 69 and 72. The catalyst of Run 69 was less active (Figure 20) than that of Run 72 (Figure 25). Furthermore, the Run 69 catalyst lost activity during the entire one hundred hour run whereas that of Run 72 appeared to approach an activity line out; by one hundred hours on stream it was much more active than the Run 69 catalyst. One difference between the two catalysts was the lack of manganese in the Run 69 catalyst. Both catalysts produced the lowest level of methane at the last condition. The Run 72 catalyst achieved 80% carbon monoxide conversion at the last condition but exhibited a high methane selectivity of 27 mole %.

Composition-wise the Run 72 catalyst was the one most similar to the Run 63 reverse micelle catalyst, however, at condition one it was less active (6 vs. 17% carbon monoxide conversion and produced much more methane than the Run 63 catalyst (24 vs. 10 mole %). Thus with magnesium oxide support the reverse micelle method did produce a more active/less methane selective catalyst, however, the activity and selectivity were not as good as the previously developed zeolite catalyst.

Two catalysts were prepared on Carbotrap B carbon, one via reverse micelle impregnation and one by aqueous impregnation. These two catalysts only contained cobalt and ruthenium. They are compared to the reference Y zeolite catalyst in summary fashion in Figure 33. Neither of these catalysts was as active as the reference. Of the two, the one resulting from aqueous impregnation was more active. Both of these catalysts were more selective to methane than the reference catalyst.

Plots of conversions and selectivities vs. hours on stream for the two runs with carbon-supported catalysts are in figures 34 to 44. Both catalysts lost activity throughout the two short runs. The aqueous impregnated catalyst became more selective for methane as the run progressed (Figure 40) whereas the reverse micelle impregnated one produced less methane and was more stable with regard to methane production. Both catalysts were similar in ethane selectivity (Figures 36 and 41). The Run 67 catalyst was slightly more selective to propane + propylene than the run 77 catalyst, (Figures 37 and 42).

Although the reverse micelle catalyst did seem to be more promising than the aqueous catalyst for low methane selectivity, the fact that the reference catalyst was so much more active caused the work on carbon-supported catalysts to be stopped.

4.4.4 PERFORMANCE OF CATALYSTS SUPPORTED ON ALUMINA-TITANIA

Metals content and performance overview of the two catalysts prepared on alumina-titania support are in Figure 45. More detailed performance data from the two screening runs with these two catalysts are in the conversion and selectivity plots vs. hours on stream in Figures 46 to 57. The Run 68 catalyst was prepared via the reverse micelle route whereas the Run 73 catalyst was prepared via aqueous impregnation. Both of these catalysts contained only cobalt and ruthenium. Neither was as active as the reference catalyst, of the two the aqueous impregnated one was most active.

The reverse micelle impregnated catalyst was less selective to methane than the aqueous impregnated one, although it was still much more selective to methane than the reference catalyst.

4.5 STEM ANALYSES

STEM analyses were performed on pre-reduced samples of reverse micelle and aqueous impregnated catalysts. Six catalysts were so studied, one of each impregnation type on each of the three supports. Additionally, a STEM analysis was performed on the reference catalyst.

REFERENCE CATALYST. STEM analysis of this material was done with difficulty. The zeolite particles were not very transparent, however, the crystallites that could be observed were in the 50-100 Å range, elemental analyses were performed on eleven crystallites and are reported in Figure 58.

MAGNESIA-SUPPORTED CATALYSTS. Fresh samples of pre-reduced catalysts used in Runs 63 and 69 were analyzed. Elemental analyses of individual crystallites from each of these catalysts are attached as Figures 59 and 60. The Run 63 (reverse micelle) crystallites contained, on the whole, less ruthenium than those of the Run 69 crystallites (aqueous), suggesting that ruthenium was more likely to exit as small, undetectable, crystallites in the reverse micelle catalysts..

The Run 63 sample had detectable crystallites ranging in size from 60 to 300 Å whereas the Run 69 material exhibited crystallites in the range 50 to 350 Å with most being 100 to 200 Å. Thus the crystallite size ranges from reverse micelle and aqueous impregnation were about the same.

The amounts of manganese and zirconium in the crystallites of the Run 63 catalyst are summarized in Figure 59. The levels of these two metals in the crystallites were very irregular compared to their levels in the reference catalyst (Figure 58).

CARBON-SUPPORTED CATALYSTS. The two carbon-supported materials exhibited different crystallite size ranges. The Run 67 material (reverse micelle) exhibited mainly 20-40 Å crystallites, however, some as large as 60 Å were observed. The Run 77 catalyst (aqueous), on the other hand, had many in the 300 to 500 Å range with most in the 100-300 Å range. With this support the reverse micelle method did seem to produce a narrow crystallite size range close to that desired. However, once again the reverse micelle cobalt crystallites contained less ruthenium than those from aqueous impregnation (Figures 61 and 62).

ALUMINA-TITANIA-SUPPORTED CATALYSTS. The two catalysts on this support were reasonably active but highly selective for methane. Crystallites were hard to locate on these

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materials, the cobalt was probably, therefore, highly dispersed with most crystallites below the limit of detection by STEM. Small crystallites are known to be selective for methane. Individual crystallites that could be discerned were analyzed for cobalt and ruthenium. Once again it was the crystallites from the aqueous impregnation which contained ruthenium whereas the ones from reverse micelle impregnation usually contained little or no ruthenium (Figures 63 and 64).

4.6 SUMMARY

None of the reverse micelle-impregnated catalysts were active enough to satisfy the goals of this work. .

All seven of the experimental catalysts contained ruthenium, and were, in fact, less active than the reference catalyst resulting from previous DOE contracts to the Union Carbide Corporation for development of a ruthenium-free, Y-zeolite supported, cobalt-based F-T catalyst. In some cases it appeared to have been well incorporated into the cobalt crystallites (aqueous impregnations), in other cases it wasn't (reverse micelle impregnations). Since all of these catalysts were of low activity compared to the ruthenium-free reference catalyst no cobalt-free catalysts were prepared. Rather, the focus of this work was shifted to the previously-developed method of catalyst preparation utilizing a Y-zeolite support. This work is summarized in the following section.

5. DEVELOPMENT OF HIGH ACTIVITY Y-ZEOLITE SUPPORTED CATALYST

This section summarizes further development of a Y zeolite-supported catalyst.

5.1 BACKGROUND

As originally developed under DOE contracts to Union Carbide Corp. this catalyst contained 8 wt % cobalt. In the current work much more active catalysts were prepared which contained as much as 28 wt% cobalt. The activity per mole of contained cobalt was about the same as the earlier catalyst indicating that even at very high levels the individual atoms of cobalt were still accessible as catalyst, i. e., little cobalt, at best, was deactivated by being covered over with other cobalt atoms. The new catalysts were more active on a total catalyst volume basis, such activity is very critical for use in a LPFT reactor. In such a reactor the liquid (wax) phase is the major phase, for efficient operation the catalyst should comprise 20 % or less of the total reactor volume.

In the original Union Carbide catalyst of the mid 1980's manganese and zirconium were found to be useful adducts for control of, respectively, selectivity and stability. In the current work ruthenium was also added to some catalyst formulations to determine whether it could be useful for enhancing catalyst activity.

The original Union Carbide catalyst was supported on an unbound zeolite powder. This catalyst resulted from a pore-filling type of impregnation utilizing an ethylene glycol solution of salts of cobalt, manganese and zirconium. Pre-steaming of the support resulted in formation of roughly

50-100 Å amorphous pores within the crystalline structure of the Y-zeolite. X-Ray analysis after steaming showed that the crystalline nature of the remaining Y-zeolite was largely intact. The acid wash serves the purpose removing extraneous amorphous alumina from the crystalline channels of the Y-zeolite framework. This alumina originates during the steaming process and its loss from the crystalline zeolite structure is what causes formation of the large pores. Removal of the amorphous alumina increases the rate of diffusion of reactant and product molecules during catalysis and also facilitates introduction of metals into the large pores during catalyst preparation. Acid-washing is accomplished with little loss in crystallinity.

The large pores were desired in the support to dimensionally stabilize the cobalt as 50- 100 Å crystallites, i. e., the crystallites would be resistant to agglomeration. This size crystallite is considered optimal for F-T catalysis, small crystallites are very selective for methane and, in addition, are prone to form volatile ruthenium carbonyls which can exit the catalysis zone with the gas effluent. In the current work with very high cobalt loadings at least some of the cobalt is present external to the zeolite as >100 Å crystallites.

In the present work, except for the catalysts in Sections 5.2.1 and 5.2.2 below, the Y-zeolite supported catalysts were prepared according to the preparation method outlined in Figure 65. In the exceptional cases water replaced ethylene glycol as impregnation solvent. The new catalysts are discussed below in terms of how they compare to each other and to the reference catalyst from the previous Union Carbide DOE contracts.

5.2 PREPARATION AND EVALUATION OF CATALYSTS

5.2.1 AQUEOUS IMPREGNATIONS, STEAMED BUT NOT ACID-WASHED Y-ZEOLITE SUPPORT

Four catalysts were prepared on a sample of steamed, but not acid-washed Y-zeolite. This material was later used as a support for other catalysts after acid-washing. Metals were impregnated from aqueous solutions of their salts, unlike the reference catalyst which used an ethylene glycol solution. All four catalysts were evaluated in the fixed-bed pilot plant according to the three condition test. The amounts of metals present on these catalysts and an overview of catalyst performance compared to the reference catalyst are in Figures 66 to 68. The amount of cobalt on each of these catalysts was about the same as on the reference catalyst. The new catalysts were all of about the same activity. However, this activity was lower than that of the reference catalyst.

Of the four new catalysts, the one which incorporated a small amount of ruthenium was the most selective to methane + ethane. Since this catalyst did not evince superior activity, the presence of ruthenium was in no way beneficial and was, in fact, a detriment to the desired catalyst performance.

The manganese and zirconium adducts did not facilitate superior catalyst performance compared to the Run 80 catalyst which only contained cobalt.

5.2.2 AQUEOUS AND REVERSE MICELLE IMPREGNATED CATALYSTS, STEAMED AND ACID-WASHED Y-ZEOLITE SUPPORT

Five catalysts were prepared on three samples of steamed and acid-washed Y-zeolite. Each acid washing was under a separate set of conditions, each used a separate aliquot of the steamed Y-zeolite used for the catalysts in Section 5.2.1. The washing conditions are in Figure 69 along with properties of the washed material and amounts of metals impregnated onto the support.

Nitric acid was used for all of the washes. The first sample resulted from a thirty-six hour wash with 2M nitric acid. Two catalysts were prepared from this support. The second wash also lasted thirty-six hours but used 3M nitric acid. One catalyst was prepared from this support. The final wash again used 3M nitric acid but the length of the wash was seventy-two hours. Two catalysts were prepared from this support.

One of the two catalysts prepared on the seventy-two hour washed material was prepared via reverse micelle impregnation. The other four catalysts were prepared by aqueous impregnation.

These catalysts were not all of the same activity. Catalyst activity increased as the severity of the washes increased. Activities and selectivities are summarized in Figures 70 and 71.

The surface area, as determined by nitrogen porosimetry, did not change much as the washes became more severe. The washes did seem to eventually cause a slight increase in the pore volume (Figure 69). Plots of fractional pore volume vs. pore radius from nitrogen porosimetry are attached

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as Figure 72; there was at best a slight change in the pore distribution as the washes became more severe. However, the amount of aluminum did decrease continually as the severity of the washes increased. It is possible that channels open to nitrogen when the aluminum content was high were not yet open to the metal salts used in the impregnation step, and/or were not yet fully capable of allowing product molecules to diffuse out.

The most active catalyst was the one evaluated in Run 87. It was prepared on a support that had been acid-washed for seventy-two hours. It was initially more active than the reference catalyst but lost activity throughout the time it was operated at Condition 1. The methane and ethane selectivities were low compared to the other four new catalysts but slightly higher than obtained with the reference catalyst. Run 87 was continued past the normal shut down time for the screening runs to allow a return to the original conditions (Figures 73 to 78). The activity loss observed at Condition 1 had continued throughout the run; the conversions upon return to Condition 1 were lower. This activity loss was no doubt accelerated by Conditions 2 and 3 at 231° C. The methane and ethane selectivities were also slightly higher at the end of the run. This could have been due in part to the lower conversions since with cobalt catalysts methane and ethane are known to be conversion dependent with higher selectivities resulting at lower conversions. One question not resolved is whether zirconium would have stabilized the catalyst. The above work illustrates that the most extensively nitric acid-washed supports provided the most active catalyst.

The reverse micelle catalyst evaluated in Run 86 was less active than the aqueous catalyst prepared from the same support (Run 87). It also did not exhibit the low methane + ethane selectivity of the Run 87 catalyst. this was the last reverse micelle catalyst evaluated in this work.

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5.2.3 ETHYLENE GLYCOL IMPREGNATIONS, STEAMED AND ACID-WASHED Y-ZEOLITE SUPPORT

Solutions of metals in ethylene glycol were used to impregnate supports in the original Union Carbide work. A "pore filling" approach was used, namely enough ethylene glycol solution was added to the support powder to barely wet it. There are no residual impregnation liquors; the impregnated support is dried and calcined.

The first ethylene glycol impregnated catalyst was evaluated in Run 95. The support was from the second batch of seventy-two hour washed Y-zeolite. The properties of this material were slightly different than those of the initial batch (Figure 79). The catalyst prepared from this material contained minor amounts of manganese, zirconium and rhenium, the amounts of which are also in Figure 79. After reduction this catalyst was screened in the fixed-bed pilot plant. It was maintained at Condition 1 until the rate of loss of activity from the initially high activity had slowed appreciable (Figures 80 to 85). The carbon monoxide conversion decreased from 100% to 61% during this period. The methane selectivity increased from 9 to 12 mole %. The conversions at the apparent line out were similar to those of the reference catalyst but the methane selectivity was higher. For this run since the catalyst was quite active, the first condition change was a feed rate reduction to allow assessment of selectivities at higher conversion. The feed rate was halved resulting in a carbon monoxide conversion of 85% and a lowered methane selectivity (11 mole %). The final condition change was a temperature increase to 221° C. This resulted in an initial carbon monoxide conversion of 98%, but strong indication of a faster rate of catalyst deactivation. The temperature increase also resulted in an increase in methane selectivity, even though the catalyst

was operating at a much higher conversion. This was probably due to the higher temperature since a conversion increase alone should result in lower methane selectivity.

Bench experiments indicated that the extensively washed Y-zeolites could adsorb greater quantities of metals than present on the reference catalyst. Furthermore, it was shown that short washes with hydrochloric acid could replace the long nitric acid washes, a considerable savings in time and, ultimately, cost. Long hydrochloric acid washes result in destruction of the Y-zeolite crystallinity resulting in formation of amorphous silica.

A high cobalt catalyst was prepared on a support resulting from three hours of wash with 3.87 M hydrochloric acid. The properties of the earlier seventy-two hour nitric acid-washed zeolites and the three hour hydrochloric acid-washed one are compared in Figure 86. The surface area after hydrochloric acid wash was 582 m^2/g, a strong indication that no loss in crystallinity resulted from the acid wash since the prewashed steamed Y-zeolite had a similar high surface area (591 m^2/g). The three hour hydrochloric acid wash removed more aluminum than the seventy-two hour nitric acid washes.

The high cobalt catalyst contained 17.6 wt% cobalt, double the amount on the earlier catalysts including the reference catalyst. The surface area and pore volume of the material after impregnation of metals and calcination were 313 m^2/g and 0.33 cc/g compared to 329 m^2/g and 0.36 cc/g for the Run 95 material. After reduction this catalyst was evaluated in Run 97 and was so active that the evaluation was only at Condition 1. Plots of conversions and selectivities vs. hours on stream are attached as Figures 87 to 93. At the end of the one hundred and thirty hour run the catalyst appeared to be reaching a carbon monoxide conversion line out of about 73%. This is

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about 10% higher than the conversion at a comparable time during Run 95. The selectivities, however, were the same in these two runs with the exception that in Run 97 the butene selectivity was slightly lower than in Run 95. The methane selectivity started at 10 mole % and appeared to be lining out between 12 and 13 mole % at the end of the run.

With the lower activity catalysts the inlet temperature was very close to the catalyst bed maximum temperature, however, with the high activity catalyst the catalyst bed maximum temperature was initially about 20° C above the inlet temperature. This is illustrated by the temperature profiles in Figure 94. This means that the catalyst was operating *de facto* at a much higher temperature than desired, and, therefore, that the large amount of quartz sand diluent was not enough to remove all the heat generated at the top of the catalyst bed. The slurry autoclave reactor operates with more diluent (290 g of wax) and since it is *stirred* there are no appreciable differences between the temperatures at different points within the reactor. The very active high cobalt catalyst was thus evaluated in the slurry autoclave reactor.

5.2.4 BOUND CATALYST: FIXED-BED AND SLURRY AUTOCLAVE EVALUATIONS

The overall objective of this work was development of a cobalt-ruthenium catalyst for LPFT. The activity and selectivity of the high cobalt catalyst was promising enough to warrant a determination of its potential as such a catalyst. For a commercial application binding will be necessary to furnish catalyst shapes large enough to be separated from the F-T product wax by mechanical means since the zeolite alone is a very fine mesh powder.

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Binding was accomplished by making a mull with Ludox followed by drying, calcination and crushing of the large pieces. Ludox is an aqueous solution of a silica precursor which reverts to silica when heated. It is a common material for binding catalyst powders. The zeolite to silica weight ratio in the bound catalyst was 75:25. The metals analyses before and after binding are in Figure 95.

The bound catalyst was first evaluated in the fixed-bed pilot plant as Run 99. Enough was loaded so that the amount of zeolite in the reactor was the same as in Run 97. The feed rate per gram of cobalt in the reactor was the same in Runs 95 and 97.

Plots of conversions and selectivities vs. hours on stream are attached as Figures 96 to 102. Once again the entire run was performed at one test condition, Condition 1 of the three conditions of the screening test. As in Runs 95 and 97, the initial conversions were very high followed by a period of activity loss. By run's end the carbon monoxide conversion appeared to be near line out at about 55%. This is less than resulted from the unbound version of this catalyst. It is not unexpected to find some loss in conversion due to binding, since the binder can block access to some of the catalyst active sites.

The selectivities also appeared to approach line out by the end of the run. The near line out conversions and methane, ethane and ethylene selectivities from Runs 97 and 99 are compared in Figure 103. The C_1 and C_2 selectivities were quite close as were the propane and butane selectivities. However, the bound catalyst was less selective to propylene and butylene:

ALKENE	SELECTIVITIES, MOLE %	
	RUN 97	RUN 99
PROPYLENE	2.1	4.1
BUTYLENE	1.7	3.1

Temperature profiles for Run 99 are included in Figure 104. In spite of the somewhat lower activity than Run 97, there was still a noticeable exotherm in the catalyst bed.

A fresh sample of the run 99 catalyst was evaluated in the slurry autoclave pilot plant (Run 61). The catalyst was reduced at 350° C in flowing hydrogen in a tube reactor before being loaded into the slurry autoclave reactor. The initial conditions during this run were 211° C and feed rate = 4.9 NL/hr · g cobalt. Plots of conversions and selectivities vs. hours on stream for Run 61 are attached as Figures 105 to 112.

Since this was the first slurry autoclave run with a cobalt catalyst from this contract, several conditions were studied. Catalyst activity loss had slowed appreciably by 80 hours on stream when the first condition change was made. At this time the carbon monoxide conversion also appeared to be approaching line out at 10 mole %. The other light gas selectivities were also approaching line out at this time.

The first condition change at 80 hours on stream was made so that the catalyst would operate at

a temperature closer to the that of Run 99 which utilized a 211° C inlet but had a noticeable exotherm meaning the actual operating temperature was higher than the inlet temperature. Thus the temperature was increased to 221° C, after which it was apparent that the catalyst deactivation was still occurring, although slowly. Deactivation rates generally increase as the temperature increases. Performance at this set of conditions is compared to that during Run 99 in Figure 103. The conversions in the two runs were about the same among the selectivities only that of methane is noteworthy, it being slightly lower in Run 61.

By the end of the run the temperature had been increased to 241° C. Additional catalyst deactivation had occurred by then and, as might have been expected, the catalyst was very selective for methane (20 mole %) at this high temperature.

Near the end of the run potassium was added to the reactor as a solution of potassium laurate in isopropanol/heptane. During work being done simultaneously on a DOE contract for development of an iron-based LPFT catalyst it had been found that so-added potassium can increase conversion and decrease the selectivities to light gases. In this case no change in the light hydrocarbon selectivities was noted. At best a small decrease in conversions and a small increase in carbon dioxide selectivity occurred.

5.2.5 EFFECT OF CHANGING THE CATALYST REDUCTION TEMPERATURE

Two runs were performed with catalysts that were reduced at 325° C and 375° C instead of the normal 350° C. The catalysts for these two runs resulted from separate fresh samples of catalysts containing 18.5 wt% of cobalt. These resulted from impregnation of the washed Y-zeolite resulting

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from the second three hour hydrochloric acid wash which earlier provided the support for the Run 101 catalyst. Properties of the support and final metals levels are in Figure 86. Run 102 utilized catalyst from a 375° C reduction whereas Run 104 utilized one from a 325° C reduction. Both of these runs were performed under conditions identical to those of the earlier Run 97. In each the initial fast rate of change of conversions and selectivities had slowed appreciably by run's end. Both of the runs were approximately 100 hours long, a tabular summary of catalyst performance during them and the earlier Run 97 is in Figure 113. The 375° C reduction temperature resulted in the least active catalyst, the 325° C and 350° C reductions produced catalysts of about the same activity. The selectivities during all three runs were nearly the same. The 325° C reduced catalyst was a little less selective to methane and a little more selective to carbon dioxide than the other two. Based on this an even lower activation temperature was investigated.

A 27 wt % cobalt catalyst was reduced at 300° C for two hours, it resulted from work outlined in the following section of this report. It was evaluated in a similar fashion to the Run 110 catalyst (350° C reduction) including use of a 6.5 rather than 13 G loading of catalyst. This run is not summarized because except for somewhat lower conversions (carbon monoxide + hydrogen = 80%, carbon monoxide = 75%) the performance was the same as the Run 110 catalyst. So far the low temperature reductions produce slightly inferior catalysts. Additional 300° C reductions might be warranted, perhaps a longer reduction period is needed.

Low reduction temperatures are of interest because the LPFT reactor will almost certainly not allow an _in- situ_ reduction at temperatures much above the F-T processing temperature (<300° C). Thus for a high temperature reduction costly equipment will be required for an _ex-situ_ reduction.