V. TASK 1 STUDIES

Microporous Catalysts Without Metal Component Using Methanol or Propylene as Feed

The objective of Task 1 was to evaluate the most promising shape selective catalysts for their efficacy in converting low molecular weight liquid hydrocarbons (representative of the primary Fischer-Tropsch synthesis products) to the desired hydrocarbon fuels - gasoline, turbine, and diesel fuel. Those which performed best in terms of product quality and stability were to serve as a basis for the work in Task 2. Testing began with methanol and switched to propylene. A chronological listing of all of these runs is presented in Table 29.

A. Shape Selective Catalyst Preparation and Characterization

It has been shown that methanol and syngas can be converted to gasoline by the use of a catalyst system based on the use of the Mobil ZSM-5 material. This zeolite, because of the size and shape of the pore structure, converts methanol to liquid fuels in the gasoline boiling range with high efficiency. The products are free of oxygenates and have a high aromatic content. The largest aromatic produced is durene which can present a problem, namely, that this material can foul carburetors and thus, the concentration must be kept low.

The object of the contract's work was to evaluate a variety of molecular sieves for use in catalyst systems to convert syngas to liquid hydrocarbon fuels (LHF), with some preference placed on the kerosine and diesel products. Thus, the effect of the molecular sieve composition, structure, acidity level and strength, and polarity was investigated to determine their impact on the LHF product yield and composition.

A number of proprietary materials used during the course of this contract, were coded "UCC-XXX" and were not disclosed in the quarterly or annual reports. Their descriptions are now given below:

UCC-101 is a hydrophobic Y zeolite (UHP-Y) prepared as described in U. S. Patent 4,652,538.

UCC-103 is the acid extracted version of UHP-Y.

UCC-104 is SAPO-11 prepared as in example 15 of U. S. Patent 4,440,871.

UCC-106 is a hydrophobic Y but not as severely steamed as UCC-101.

UCC-107 is LZ-210 zeolite (described in U.S. Patents 4,503,023 and 4,610,856) with a Si/Al2 ratio of 8.3

UCC-108 is SAPO-11 prepared as in example 17 of U. S. Patent 4,440,871

UCC-109 is SAPO-5.

References to the Quarterly and Annual reports for synthesis details are given in Table 28. A list of Task 1 runs with reference to the Quarterly reports is given in Table 29.

B. Methanol Series

A preliminary run was first performed (Run 9502-1), using methanol feed over a medium-pore high silica zeolite catalyst (LZ-105-6). Although it yielded products in the gasoline boiling range, these were unsatisfactory because of the presence of multi-methylated aromatics, which are solid at room temperature. Methanol is suspected of forming these products when it coexists with reaction intermediates, whereas the intermediate products of a syngas feed are believed to be mainly small olefins and free of methanol. It seemed questionable from the outset that methanol conversion would be a sufficiently relevant probe for evaluating SSC components.

Ten test runs were conducted in this series (Runs 9710-1 through 10), using four different catalysts (LZ-105-6, ZSM-5, Y-82, and UCC-101). The LZ-105-6 material is the acid form of UCC aluminosilicate which has a structure that is similar to ZSM-5, but is synthesized in an organic free form. Y-82 is a strongly acidic form of stabilized Y zeolite. UCC-101 was described above. The catalyst charge in each case was approximately 20 grams. The feed was a methanol-nitrogen mixture of approximately 63:37 mole ratio. The nitrogen was included to facilitate control of the reactor pressure. The mixture of methanol and nitrogen was fed to the reactor for seven hours a day, during the daytime while the equipment was attended. During the remaining 17 hours, only nitrogen was fed to the reactor. The methanol feed rate was about 1 WHSV (weight hourly space velocity: grams methanol per hour per gram of catalyst).

Most of the runs were made at 300 psig and 370 C. Because of the excessive amount of solids present in the product, two of the later runs were made at reduced pressures (50 and 25 psig), and in part at a higher temperature (408 C), to determine whether by such means the liquid hydrocarbon yield might be improved and the solid product reduced. Samples of both liquid and gaseous products were collected daily.

The liquid product was a mixture of three phases - aqueous liquid, hydrocarbon liquid, and hydrocarbon solids. These were separated by centrifugation and then analyzed. The results are presented in Table 1. In the first three runs (Runs 9710-1, 2, and 3, at 1.0 WHSV, 300 psig, 370 C) the catalysts were LZ-105-6 and ZSM-5, active catalysts of medium pore size with anticipated reasonable life. The hydrocarbon products were mostly solid crystals with some oil. The solids were found to be highly methylated aromatics, primarily durene (m.p. 79 C) as well as other tetramethyl benzenes, toluene, xylenes, and trimethyl benzenes. The solids plugged the pressure control valves and the product lines necessitating numerous shutdowns.

The next six runs (Runs 9710-4 through 7 at 1 WHSV, 300 psig, 370 - 400 C and Runs 9710-8/9 at 1 WHSV, 25 psig, 370 - 408 C) were made using UCC-101 and Y-82. Since the former is less active than LZ-105-6 or ZSM-5, and the latter deactivates rapidly, the hydrocarbon yields were low, and the pentane plus yield not only small but mostly solid. For these reasons no FIA data could be obtained. In the last run (Run 9710-10) the catalyst was ZSM-5. The methanol feed rate was varied from 1 to 3 WHSV, the methanol:nitrogen ratio was 0.63:0.37 molar, the pressure 25 psig, and the temperature successively 370, 410, and 448 C. At 370 C the products were mixtures of crystalline solid and oily liquid and at the two higher temperatures only a liquid product was obtained. Even at the highest temperature the oily liquid product was highly aromatic (72.8 percent), but contained enough lighter hydrocarbons to dissolve the tetramethyl benzenes.

Each of the four catalysts performed fairly well in the conversion of the methanol, but they differed widely in stability and product selectivity.

The LZ-105-6 and ZSM-5 were highly stable and active throughout the testing. They converted from 90 to 100 % of the methanol, almost all of it to hydrocarbons, of which 50 to 67 % were C3 and heavier.

The UCC-101 and Y-82 deactivated rapidly, especially the Y-82. Although the methanol conversion remained fairly steady at 71 to 78%, after a few hours the product shifted mainly to dimethyl ether, and further conversion to hydrocarbons dropped steeply with additional time on stream. Even the production of C3's and C4's fell off to the point where nothing was produced but methane. Data for these observations are plotted in Figures 3, 4, and 5. The details of the material balances and product distributions are presented in Table 1.

The distillation ranges of the condensed hydrocarbon products were characterized by simulated distillations and presented in Figures 6 through 23. With a zeolite catalyst, using methanol feed in the Berty reactor, most of the products are poly-methylated aromatics. These will appear as distinct peaks on a derivative plot of the distillation curves. Plots for the intermediate pore size zeolites LZ-105-6 and ZSM-5 show peaks for toluene, xylenes, and trimethylbenzenes. Those for the larger pore catalysts Y-82 and UCC-101 show peaks for pentamethylbenzene (b.p. 232 C), hexamethylbenzene (b.p. 265 C), and decamethylbiphenyl. For LZ-105-6 and ZSM-5 the distillation plots terminate around 410 F. For the Y-82 and UCC-101 they start at 380 F and terminate at about 710 F, the desirable range for turbine and diesel fuel.

From these ten runs, the following conclusions can be drawn as to the effects of process variables:

1. Higher pressure makes heavier products.
2. Higher temperatures make lighter products.

3. Higher space velocity makes lighter products.

The runs also demonstrated that methanol's unacceptably high production of poly-methylated aromatics, uncharacteristic for syngas conversion, disqualifies it as a simulated reaction intermediate in Fischer-Tropsch synthesis. Propylene was used as feed in the remaining Task 1 efforts, and was found to be a considerable improvement.

C. Propylene Series

1. Screening Runs in Fixed Bed Micro-Reactor System

Five catalysts were screened for activity in a small fixed bed micro-reactor system (5/8 " O.D. and 5 " long). These were LZ-105-6, which was used as a reference, and four variations of LZ-Y-62, (NaY-62, 10% HY-62, 40% HY-62, and 97% HY-62). The undiluted catalyst charge in each test was 7 grams, the feed a mixture of hydrogen and propylene in a 2:1 molar ratio, a propylene feed rate of 1 WHSV, the pressure at 150 psig, and the temperature 340 C. The tests were run for two days with propylene fed during the daytime hours and only hydrogen at night. These runs yielded little except that the LZ-105-6 gave the most liquid product and that the liquid yield increased dramatically on the Y-62 catalyst as the acidity was increased from zero to 97% HY-62.

2. Catalyst Synthesis for Propylene Runs

A series of catalysts were prepared for study. A catalyst designated UCC-101, a large pore catalyst of moderate acidity was prepared with an alumina binder. Modifications of this material by ion exchange with potassium provided another material with reduced acidity. An additional variation was obtained by acid extraction of the UCC-101.

Lewis acid sites are created by ion exchange of zeolites with polyvalent cations. These sites offer a source of potential activity and their inclusion in the screening testing in Task 1 was planned. To this end, calcium and rare earth exchanged Y-62 materials were prepared.

Other shape selective zeolites were also provided for testing. Two silicalites with different levels of aluminum and sodium impurities were prepared, as were several LZ-105's. A ZSM-5 type material was synthesized with a SiO2/Al2O3 of 35, ammonium exchanged and prepared as a catalyst. Likewise, a ZSM-5 with a SiO2/Al2O3 of 80 was synthesized, ammonium exchanged and prepared as a catalyst.

3. Test Results on Propylene in the Berty Reactor

Twenty seven runs were made in this series on fourteen different shape selective catalysts. The tables cited list the experimental data, conversion, selectivity, and product characterization. The key findings will be highlighted in this section.

a. Run 9710-11. Catalyst LZ-105-6 (Table 2, Fig. 24)

The conversion of propylene began to drop at around 50 hours on stream from 77 to 57 %. At this point the continuous feeding of propylene was interrupted while the hydrogen was continued. Subsequent operation was to feed the propylene during the day and feed only hydrogen at night. Over the next few days, the conversion had recovered back to 72 %. However, the production of aromatics did not recover, and the hydrocarbon product was mainly olefinic. This indicates that the activities which recovered following the hydrogen purge were polymerization and isomerization. This was encouraging, since in Fischer-Tropsch synthesis with syngas feed there will be an excess of hydrogen over the catalyst when a metallic hydrogenating component is present. Thus, the deactivation phenomenon observed here would be expected to be less significant in actual syngas runs.

b. Runs 9710-12,13 Cat. LZ-105-6 (Table 3,4-Fig 25,26).

Although there were slight differences in operating conditions between these two runs, they show a clear pattern of gradual deactivation. Conversion fell from nearly 100 % at the start to below 50 % by the time 60 hours had been logged. Even before this occurred, it was evident from the product distribution that a decrease in aromatics and an increase of olefins was occurring. In the early stages, the high aromatics production was accompanied by a high yield of propane and butane. This reconfirms the known characteristic of strongly acid zeolites - their facility in promoting hydrogen redistribution among the hydrocarbons:

olefins -> aromatics + paraffins

When the catalyst deactivates, and presumably the strongly acid sites are deactivated by coking, then this is the first activity to decline. The catalysts skeletal isomerization activity fell off as well.

c. Runs 9710-14 to 17.Cat. UCC-101 (Table 5-8,Fig.27-33)

This proprietary large pore catalyst deactivates more rapidly than LZ-105-6. In all four runs the conversion was low, from 15 to 31 %, and proportional to operating temperature. Also, with an increase in temperature, the production of light hydrocarbons and aromatics increased.

Run 9710-15 had different operating conditions. The propylene was more dilute, and both the feed rate and pressure were lower. This extended the catalyst life somewhat and the initial activity was somewhat higher than under the standard conditions.

A comparison of the relative boiling ranges of the condensed liquid hydrocarbons produced by the intermediate pore size zeolite LZ-105-6 with those of the larger pore zeolite UCC-101 can be found from the differences in their simulated distillation curves (Figures 29, 30, and 31 vs. 32 and 33). The operating conditions were the same. The plots for LZ-105-6 products after deactivation (Fig. 30 and 31) and for the UCC-101 were almost equally smooth, denoting predominantly olefinic products. However, when the LZ-105-6 catalyst was fresh (Fig.29) and showed considerable aromatics production, the curve was segmented and the plateaus were associated with individual aromatic boiling points. Finally, the UCC-101 catalyst yielded a higher boiling point product than the LZ-105-6 which is consistent with the concept of shape selective catalysts.

These findings pointed to the potential for UCC-101 to convert syngas to the desired higher boiling point products provided that more optimum operating conditions were provided. Also, the poor stability of UCC-101 on propylene may be significantly improved by the presence of water in the feed, which would more nearly simulate the Task 2 (and anticipated commercial) environment.

d. <u>Run 9972-1.Catalyst LZ-105-6</u> (Table 9,Fig. 34-35)

Since this catalyst had demonstrated good stability, this run included the evaluation of a wide range of process conditions. The sequence was as follows: at 150 psig a temperature study from 280 C to 310 to 340 to 370 and back to 280 C, then at 280 C a pressure study at 150, 75, and 300 psig, and finally a pressure study at 300, 150, and 50 psig at 370 C. The conversion was high throughout, between 78 and 98 percent. The effect of temperature on conversion, product distribution, and hydrocarbon type is shown in Figure 34. The effect of pressure on these same factors is shown in Figure 35. In summary, raising the temperature led to increased butane and lighter hydrocarbons and lighter liquids in the product. Also, the product distillation curves become more irregular as the temperature is increased with an increase of individual toluene, xylene, and C9 aromatics becoming evident. As expected, this is accompanied by an increase in the refractive index of the product and an increase in the propane and butane yield, which are products of hydride transfer.

Increasing pressures caused an increase in the C1-C4 cut (particularly at 370 C), a decrease in the C5-420 F cut (particularly at 370 C), and a small or negligible increase in the 420+ F cut (at 280 C and 370 C respectively).

e. Run 9972-2.Catalyst LZ 105-6 (Table 10, Fig. 36)

A Mobil patent disclosed that the presence of steam did not affect the stability of ZSM-5, alleviated hot spots, improved product distribution, reduced coking (as expected) and lowered the fraction of C10 and C11 aromatics. This run was made at the same conditions as Run 9710-13 except for the addition of steam in the feed.

The conversion in the presence of steam was very high and stable during this run, never falling below 96 % through 79 hours. The great bulk of the product was saturated, which increased over time; a smaller amount was aromatic, which decreased with time; and a small amount was olefinic. The carbon number distribution, which was also comparatively stable, was predominantly C4's, liquid products, and propane. The C1 and C2 products were negligible.

The results of 9710-13 were initially almost identical, but there the similarity ends. The product distribution shifted strongly with time from saturates and aromatics to olefins and from C1 to C5's to higher liquids. The conversion dropped from an initial 97 % to less than 11 % after less than 98 hours on stream.

Unlike Mobil's experience in a fixed bed reactor with ZSM-5, this run shows that the major effect of steam on LZ-105-6 in a Berty reactor is to stabilize the catalyst's conversion activity. The changes in product selectivity are secondary and modest.

f. Run 9972-3,4. Catalyst UCC-101(Table 11-12,Fig.37-39)

These two runs were made to test the effect of steam addition to the UCC-101 catalyst. Although the addition of the steam did improve the stability compared to Runs 9710-14,16,and 17, both the conversion and stability were worse than LZ-105-6. The initial conversion increased with temperature but was much lower than that of LZ-105-6. Over the temperature range studied (278 to 408 C) the conversion increased from 11 to 50 percent while the selectivity to C5+ decreased from 55 to 45 percent. Here again, the liquid product has a considerably higher boiling range than that obtained from the LZ-105-6 catalyst.

g. Run 9972-5.Catalyst AlPO4-11 (Table 13)

A new class of aluminophosphate molecular sieves were discovered by Union Carbide. One of these is a medium pore size (about 6 Angstrom) material called AlPO4-11. As synthesized, this material has a net zero framework charge, and thus, has no cation exchange capacity, a requirement for acid catalytic capability. Therefore, it has little or no capacity to oligomerize small olefins. It was included for testing to ascertain its potential for syngas catalysis.

The catalyst was almost totally inactive. As noted above, the charge balanced structure implies the inability to oligomerize olefins. This, by itself, does not rule out its use in syngas. The small amount of converted products was attributed to the alumina binder used in forming the catalyst.

h. <u>Runs 9972-6,7.Cat. UCC-104</u> (Fig.40-42,Tables 14,15)

These two runs were made on UCC-104 catalyst with hydrogen/propylene feed, with and without steam. Without steam the initial conversion was a good 70 % at 280 C and an excellent 96 % at 340 C. With steam present the initial conversion was lower (49 and 64 %, respectively at 280 and 340 C) but with a reduced deactivation rate. The lower activity could be the result of the steam moderating the acidity of the catalyst or it could be due to the lower residence time which accompanies the addition of the steam to the feed. This effect upon conversion on the addition of steam was not observed in the case of LZ-105-6 or UCC-101.

Only negligible quantities of C1 through C5 hydrocarbons were produced. These are the products of cracking reactions. The catalyst also showed a low selectivity to propane. The total C1 to C4 products were less than 10 % without steam and even less when steam was present. The steam had little effect on the C1 to C4 distribution. The simulated distillation data for the products from the three catalysts (LZ-105-6, UCC-101, and UCC-104) are compared in Figure 42. It shows that the product from the UCC-104 had a boiling range similar to that of the LZ-105-6 and not UCC-101. Also, the UCC-104 has plateaus in the distillation curves at the boiling points of the C6, C9, and C12 hydrocarbons. The material balances show that the selectivity for the C6 hydrocarbons ran from 60 % to over 80 % during these runs and that the C9 hydrocarbons ranged from 3 % to 15 % of the total product. All of this indicates that UCC-104 is a mild acid. It does not have the strength for cracking or hydride transfer reactions. It simply dimerizes and trimerizes the propylene feed. For this reason it is very selective. This milder acidity may also explain why its activity was more heavily influenced by the presence of steam than UCC-101 and LZ-105-6.

UCC-104 is an excellent catalyst for propylene oligomerization. It has a very high selectivity to C5+ products (over 95%), with nearly all the C5+ in the gasoline range. The good conversion and desirable selectivity make UCC-104 the best catalyst tested so far. It is a promising candidate as a shape selective component in Task 2.

i. <u>Run 9972-8. Catalyst UCC-103</u> (Fig.43, Table 16)

By this time, a standard catalyst test had been developed. Specifically, the propylene was introduced to the reactor at 0.5 WHSV in a 1:1:2 $H_2:C_3H_6:H_2O$ molar ratio feed composition. The reactor was maintained at 150 psig. A minimum of two reaction temperatures were used, 280 and 340 C. Additional temperatures of 250 and 370 C were also included depending on the activity of the catalyst being tested. Generally the catalyst was tested for two days at each temperature. This time was reduced if the catalyst exhibited low activity or rapid deactivation.

UCC-103 was prepared by the acid extraction of UCC-101, with the intention of reducing its acid activity still further while maintaining its molecular sieve character and to compare the performance with that of the UCC-101. The activity was very low (10.6 % conversion at 280 C and 13.2 % at 340 C) and deactivation occurred. In this regard the performance was similar to UCC-101. However, there were major differences in product selectivity. Due to the reduced acidity and the subsequent reduced hydride transfer activity, the UCC-103 product contained less of the light saturates, thus, a higher fraction of C5+.

j. <u>Run 9972-9. Catalyst UCC-106</u> (Fig. 44, Table 17)

UCC-106 is a new, large pore molecular sieve of moderate acidity, similar in this respect to UCC-101 and 103. The initial conversion was a poor 17 %, although better than either UCC-101 or UCC-103. The deactivation rate was higher than either of the other two catalysts. The product selectivity was intermediate between the UCC-101 and UCC-103. In contrast to both UCC-101 and UCC-103, the C5+ yield did not decrease upon raising the reactor temperature to 340 C. UCC-106 was not a candidate for Task 2 testing.

k. Run 9972-10. Catalyst CaY-62 (Fig.45, Table 18)

This catalyst was prepared by the calcium exchange of the sodium back-exchanged form of the Y-62 zeolite. Standard conditions were employed for this test. The initial activity was low and deactivated steadily with time. Raising the temperature only accelerated the deactivation rate. The product quality was poor as well. The poor performance was ascribed to the catalyst's strongly acidic nature.

l. Run 9972-13. Catalyst LZ-105-6 (Fig.46, Table 19)

This catalyst had been extensively tested in previous runs on methanol and propylene. However, once a standard set of run conditions had evolved, it was necessary to retest this catalyst at those conditions. This was a long run (seven days). A comparable run was 9972-1 which studied pressure and temperature variables but had no steam added to the feed.

The initial conversion at 280 C was almost 97 % and a little higher than 9972-1. The deactivation was slow and gradually dropped to 85 % at the end of the run (172.7

hours). Significant changes in selectivity were observed during the course of this run. They were most evident at 280 C and decreased with increasing temperature. The concentration of butenes increased constantly throughout the run to the point that their concentration approached that of propylene. Butane was high initially, propane somewhat less so: both dropped quickly and then rose with increasing temperature. Since these paraffins are products of hydride transfer to corresponding olefins, changes in their concentrations are related to changes in rates of hydride transfer and are reflected in changes in concentrations of liquid aromatics.

As the production of propane and butane decreased, that of the C5+ rose. At 280 C the C5+ fraction was as high as 89 percent of the total hydrocarbons and at 370 C it had decreased to 69 %.

Variations in the composition of the liquid samples showed up in the refractive indexes. The initial product of this run contained about 50 % aromatics as against less than 20 % in Run 9972-1. The last sample taken at 280 C was down to less than 20 % ; the corresponding sample from 9972-1 was down to less than 15 %. At 280 C the presence of water increased the aromatics content but did not arrest the deactivation of the aromatization activity. At 340 C, while the first sample was about half aromatics, the last sample was down to about 30 %. When comparing these results with

9972-1, it can be stated that the effect of water in the feed on retarding deactivation was more pronounced at 340 C than at 280 C and at 370 C it was almost complete. The price of the improvement was a loss of activity.

These trends are confirmed by the simulated distillations, which showed xylenes and C9 aromatics in Sample 1; a smoother curve with no signs of xylene in Sample 5; xylenes and trimethyl benzenes in Sample 6 after the temperature increase; some xylenes and toluene , but no C9 aromatics in Sample 12; and the same aromatics along with apppreciable toluene in the last sample (Sample 15). The liquid fraction of the last sample contained mostly secondary products of propylene oligomerization, lacking the C6, C9, and C12 olefins which showed up in earlier samples.

LZ-105-6 was shown to be an excellent catalyst for the oligomerization of propylene, even at 280 C, with high activity and good selectivity for liquid products. At the lower temperatures its conversion deactivated in spite of the presence of steam in the feed. While it was less selective to C5+ than UCC-104 (Runs 9972-6 and 7), it was more active.

m. <u>Run 9972-14. Catalyst UCC-107</u> (Fig. 47, Table 20)

UCC-107 was a new proprietary molecular sieve of large pore size. It was tested at standard conditions at 280,340, and 370 C over a period of 145 hours. The conversion was initially quite low (13 %) and dropped within two days to around 3 %. Each time the temperature was raised, a slight recovery occurred followed by a further decline in performance.

Two of the major products, propane and butenes, remained constant throughout the test, independent of both time and temperature. The total production of C5+ varied from 69 % initially to 61 % at the end of the run, but the composition varied considerably over time.

UCC-107 was shown to be a poor catalyst for propylene oligomerization. Since its production of propane and butenes remained constant in the face of rapid overall deactivation, the mechanism by which the deactivation occurs must be different than that of the other catalysts studied.

n. <u>Run 9972-15. Catalyst REY-62</u> (Fig. 48, Table 21)

This material was prepared by the cation exchange of Y62 using trivalent rare earth salts. The purpose was to introduce acidity.

The standard test conditions were employed and temperatures of 280, 340, and 370 C were studied over a period of 102 hours. The performance was poor, with low activity and rapid deactivation. Propane was a major product which increased with deactivation at 280 C, then decreased when the temperature was raised. Production of butenes increased with rising temperature.

The performance of REY-62 was even poorer than that of CaY-62, the initial conversion was about the same but the deactivation was much more rapid.

o. <u>Run 9972-16. Catalyst Silicalite</u> (Fig.49, Table 22)

The Silicalite used for this test had a trace of alumina impurity present. The test was run under standard conditions for 2 days each at 280 and 340 C, and three days at 370 C. This catalyst showed low conversion at 280 C; however, this catalyst did not show signs of deactivation. In addition, the temperature increase to 340 C increased the conversion by a factor of seven. A further increase to 370 C yielded no additional conversion. Almost no C1 or C2 hydrocarbons were formed and the catalyst also showed a low selectivity to propane. Butane also remained low. The low butane was unusual considering that the butenes were high, up to 20 %. The C5+ yield was fairly constant throughout the run (80 % at 280 C and 75 % at 370 C). As temperature was increased the C5+ product became more aromatic (from 5 % at 280 C to 25 % at 370 C) and the average boiling point decreased. The aromatization process resulted in no deactivation as had been observed with other catalysts.

The Silicalite is a good catalyst for propylene oligomerization. Although the activity was low at 280 C, the activity at 340 C was good and the catalyst did not deactivate. The C5+ product contained a good amount of aromatics without the usual propane and butane yields.

p. <u>Run 9972-17. Catalyst Silicalite</u> (Fig. 50, Table 23)

This catalyst had a greater alumina impurity than the previously tested material. Pressure control problems were encountered during the course of this run which limits the conclusions which can be drawn. The conversion stabilized at 6 % at 250 C and increased to 89 % at 340 C. The C5+ liquid product became lighter with an increase in reactor temperature. The catalyst showed no deactivation. This catalyst was more active than the previously tested silicalite.

q. Runs 9972-18 & 20.Cat. ZSM-5 (Fig.51-54,Tables 24,25)

Since ZSM-5 is well known as a catalyst for conversion of methanol and small olefins to gasoline range products, it was the catalyst of choice to serve as a reference standard. For this purpose, two synthesis preparations of ZSM-5 were made; one with a silica/alumina ratio of 35 and the other with a silica/alumina ratio of 85. They were both tested extensively at standard conditions. The LZ-105-6, tested previously (Run 9972-13), also had a silica/alumina ratio of 35, and will be included in the discussion.

In all three cases the catalysts were stable at 340 C, in both conversion and selectivity. The ZSM-5 with the higher silica/alumina ratio deactivated at 280 C.

At these conditions, neither of the ZSM-5 materials produced the quantities of propane and butane that the LZ-105-6 did. The C4's that were produced by the ZSM-5 materials were olefins and likely the products of cracking of larger hydrocarbons. The gasoline yield was high (over

80 %). The gasoline range material was predominantly olefinic with low levels of aromatics.

There was little difference in the selectivities of the two ZSM-5 materials and the LZ-105-6. The ZSM-5 materials are good reference catalysts for this work.

r. Run 9972-19. Catalyst LZ-Y82 (Fig. 55, Table 26)

This material is the strong acid form of ultrastable Y zeolite. It showed little activity for propylene conversion. The activity was limited by the rapid coking of the strongly acidic sites. Very little of the product was condensed to liquid. The liquid contained significant amounts of aromatics. This is not an important Task 1 catalyst.

s. Run 9972-22. Catalyst UCC-108 (Fig.56-57, Table 27)

UCC-108 is a new Union Carbide proprietary catalyst, which is related to UCC-104 (Run 9972-6) and should be considered as a more active version of that material.

This was an excellent catalyst for the conversion of propylene to gasoline range products. The conversion was higher than was achieved by UCC-104, a little lower than that achieved by the 35 silica/alumina ratio LZ-105-6 and ZSM-5, and higher than that of the 85 silica/alumina ratio ZSM-5. In addition, the conversion did not significantly increase with the increase in temperature from 280 to 340 C.

The products were almost entirely hydrocarbons in the gasoline range. There was little propane or butane. The liquid product was olefinic rather than aromatic. The catalyst showed little sign of deactivation. The end of run product is very similar to the start of run product. The UCC-108 catalyst acted primarily as a dimerization catalyst with some trimerization activity. It had little cracking or aromatization activity. This proved to be a superior catalyst for propylene conversion and represents an important candidate for Task 2 testing.

t. Run 9972-21. Catalyst Modified AlPO4-11

AlPO4-11, a new molecular sieve recently announced by Union Carbide, was found to have no activity for propylene oligomerization. Subsequently, this material was modified to introduce acidity into the structure. The modification had no effect on the activity. The AlPO4-11 seems to have little capability to oligomerize olefins.

u. Run 10112-1. Catalyst UCC-109

UCC-109 is a new proprietary molecular sieve with a large pore structure. It was tested at the standard conditions. This catalyst had a very low activity for converting propylene. The catalyst coked quite rapidly. This suggests that UCC-109 is a strong acid.

UCC-109 is not an important catalyst for propylene oligomerization, but some aspects of its chemistry are of interest. The liquid product was almost entirely aromatic and a wide spectrum is represented from toluene through poly-alkylated aromatics. The catalyst exhibits little shape selective control. However, this high acidity may be useful for isomerizing the products of Fischer-Tropsch synthesis in Task 2.

v. Run 10112-3. Catalyst 97% HY-62

The 97 % HY-62 was synthesized by extensive exchange of NaY with ammonium cation followed by calcination to remove ammonia. Standard test conditions were employed. The activity was too low to warrant any further consideration.

D. Summary of Task 1

Task 1 was initiated during the Fifth Quarter of the contract (March through May 1982), and successfully concluded during the Eighth Quarter December 1982 through February 1983). All its objectives have been achieved.

Principal among these was the identification of UCC-108 as a superior catalyst. A comparison of UCC-108 with other catalysts considered as good candidates for Task 2 testing is given in the following table:

Propylene Oligomerization (280 C, $H_2:C_3H_6:H_2O$ = 1:1:2)

Catalyst	LZ-105-6	ZSM-5 (1)	ZSM-5 (2)	UCC-108
Conversion	97-90	90-85	84-44	74-60
C_3H_8	10-2	6-2	6-3	2.5-2.3
C_5+	72-89	79-90	81-87	95.5-96.5
Refr.Index	1.454-1.425	1.441-1.423	1.436-1.428	1.421-1.419

(1) Silica/alumina = 35 (2) Silica/alumina = 85

All of these catalysts have high conversions. The high silica/alumina ratio ZSM-5 showed the highest deactivation.

None of the catalysts made much propane at these conditions. LZ-105 produced the most initially and UCC-108 the least, with LZ-105 also having the most consistent selectivity over the course of the run. The catalysts all produce mostly C5+ hydrocarbons. Here again, UCC-108 produces the most and shows the least sign of deactivation. The refractive indexes indicate that the products are mostly olefinic. The UCC-108 is clearly superior to the others.

Task 1 yielded other potentially useful results as well. Aspects of molecular sieve activity were discovered, for example, which indicate that some SSC's, although inferior for Task 1 purposes, might prove useful in Task 2 when certain types of chemical reactions are indicated. Thus, UCC-101, while not very active, did yield some products in both the gasoline and diesel fuel ranges. UCC-109 and LZ-Y-82, which were highly acidic, might be of use in some circumstances, as when paraffinic hydrocarbons are produced by the metal component. AlPO4-11 might be useful in elucidating the chemistry of a pore system which lacks acid activity.

There are many catalysts that have been identified that may be useful in Task 2 depending upon the desired properties. However, UCC-104 and its active modification UCC-108 appear to be the most promising candidates.