3 EXPERIMENTAL SUMMARY

Three approaches for the conversion of synthesis gas to isobutylene or products that can be used as precursor to isobutylene have been investigated in this project. The preliminary work focussed on the evaluation of ZrO_2 and modified ZrO_2 catalysts for the direct conversion of CO/H_2 to isobutylene via the isosynthesis reaction. All of the catalysts and conditions evaluated in this work gave isobutylene yields of less than 4% which is far below that required for an economically viable process. A summary of the key results from this portion of the project is given in Section 3.6. In view of the poor performance of these catalysts and the lack any encouraging results from other research groups working in the isosynthesis area, this approach was abandoned in favor of approaches related to higher alcohols synthesis.

Conventional methanol synthesis catalysts can be modified to increase the selectivity to higher alcohols, particularly isobutanol, from synthesis gas. It has been proposed that alcohol condensation is catalyzed by a basic function on the catalyst surface. For example, alkali-modified Cu/Zn/Al catalysts have been commonly used. The isobutanol selectivities of the best catalysts to date remain below the level required for economic viability. Two problems that need to be overcome are to increase the isobutanol/methanol product ratio to at least 1.0 and overcome the loss in synthesis gas conversion activity that typically occurs on alkali modification. The second approach investigated in this program has been to combine a conventional methanol synthesis catalyst with an alternative sold base catalyst. The use of Metal Oxide Solid Solutions (MOSSs) derived from hydrotalcites as the solid base component has been investigated. However, these materials have too much residual acidity to afford clean higher alcohols products. The results of this testing are described in Section 3.1.2.

The generally accepted mechanism for higher alcohol formation involves the formation of methanol followed by its condensation to higher alcohols. Therefore, it should be possible to

combine a conventional methanol synthesis technology with a catalyst optimized for the condensation of alcohols to isoalcohols. In this process, the formation of the initial C-C bond is the most difficult step. The third approach for the production of higher alcohols pursued in this program has been to identify a catalyst and process for this reaction. Initial catalyst screening with a methanol-only feedstock gave very low conversions. Section 3.1.3 describes this work. In order to determine whether the lack of activity was due to poor catalysts or inappropriate selection of reaction conditions, a methanol/ethanol feedstock was employed. A promising catalyst formulation consisting of noble metal on a Zn/Mn/Zr mixed metal oxide support has been identified and mechanistic tests performed that suggest that this catalyst may be capable of methanol-only condensation. The effects of catalyst composition (Section 3.2) and process variables (Section 3.3) have been examined with this basic catalyst formulation. Finally, pilot plant demonstration runs with a methanol-only feed, at optimized conditions and with high H_2 co-feed have been completed (Section 3.4). A conceptual design of a combined methanol synthesis/higher alcohols synthesis process has been done and preliminary economic analysis completed (Section 3.5). Because of the low selectivity of the methanol conversion catalyst to isobutanol and the need to imported ethanol, the process is uneconomical. Considering the current performance limitations, this particular process for the conversion of lower alcohols to higher branched oxygenates cannot produce isobutanol at a price which would allow penetration into the gasoline market.

3.1 Catalyst Identification and Reaction Mechanism (Task 1)

The initial phase of this program has focussed on proof-of-principle testing to identify a catalyst for the conversion of synthesis gas to higher branched alcohols, particularly isobutanol. Due to poor results with a variety of catalyst for the direct conversion of CO/H_2, the direction of this project was shifted to investigate the conversion of light alcohols (methanol and ethanol) to higher oxygenates. A secondary objective of this task has been to obtain key reaction mechanism information to help understand the performance of the best

catalysts found.

In this section, the pilot plants used for catalyst testing are described, as well as blank runs performed to measure background activity in the stainless steel reactors. The screening of catalysts for the direct conversion of CO/H_2 to higher alcohols is described. The shift to a light alcohol feed initially focussed on the conversion of methanol only to higher alcohols. However, poor results were obtained. Therefore, a 10/1 methanol/ethanol blend has been used to develop a standard catalyst screening test. Noble metal on Zn/Mn/Zr oxide catalysts have been found to give the highest selectivity and productivity of higher branched oxygenates. Space velocity testing also suggested that this catalyst system might be capable of converting methanol alone to higher oxygenates. Therefore, this catalyst type has been investigated further in the latter tasks of this program.

3.1.1 Pilot Plant Descriptions

Pilot Plant 700, an existing Fischer-Tropsch fixed bed pilot plant, has been modified for the screening of catalysts for the production of isoalcohols from synthesis gas. Tables 1 and 2 give a listing of the runs that have been conducted for the conversion of CO/H_2 and light alcohols, respectively, to higher branched oxygenates.

3.1.1.1 Pilot Plant for CO/H_2 Conversion to Higher Alcohols

A diagram of Plant 700 as used for testing catalysts for the conversion of CO/H_2 to higher alcohols is shown in Figure 4. Several modifications were required to the plant prior to use in this program. These included the addition of a new capillary to the CO/H_2 feed system to allow control of feed rates from 0.1 to 1.0 scf/hr, a separate pressure regulator after the reactor and a by-pass line around the hot traps used to collect wax during Fischer-Tropsch operation. A new 5/8" ID, 316 stainless steel differential reactor was dedicated to the isoalcohols project, to avoid cross-contamination with Fischer-Tropsch catalyst and products. The catalyst (sized to 20-40 mesh) was contained within the reactor using stainless steel screens.

A dual GC system has been used to obtain a complete product analysis. The entire reactor effluent is maintained at 100°C and passed to a Total Hydrocarbon GC to detect all hydrocarbons and oxygenates from C_1 through about C_{15}. The product is then passed through a cold (0°C) trap to condense the liquid product. The overhead gas is sent to a Total Gas GC to analyze for CO, CO_2, H_2, Ar, N_2 and C_1-C_3 hydrocarbons and a dry ice (-78 °C) trap to condense any residual liquid product. Initially, this GC system was shared with another Fischer-Tropsch pilot plant with samples alternated hourly when both plants were operating. However, the shake-down runs demonstrated that cross-contamination in the hydrocarbon GC was a serious problem. Therefore, a separate Total Hydrocarbons GC, for use during isoalcohols testing only, was added to the plant.

3.1.1.2 Blank Runs with CO/H_2 Feed

A blank reactor test using silica gel only has demonstrated that back-ground activity of the stainless steel reactor, particularly for CO_2 formation, is negligible at 310°C. Table 3 shows that product gas analysis is virtually identical to the feed analysis. The change-over time of the feed system at the rates used is about 4 hours.

Catalyst testing at 450°C has also been done in this program. However, blank tests in the stainless steel reactor loaded with SiO_2 gel or alpha-Al_2O_3 have shown high yields of CO and light hydrocarbons indicative of non-catalytic reactions occurring on the walls of the reactor. In an attempt to minimize these reactions, the use of a ceramic-lined reactor has been evaluated. When the reactor filled with either alpha-Al_2O_3 or quartz chips, light hydrocarbons and CO_2 yields were still greater than 2%. An empty ceramic-lined reactor gave about a 50% reduction in the by-product yields, indicating that some of the by-products are formed on the packing material.

3.1.1.3 Pilot Plant for Conversion of Methanol and Methanol/Ethanol to Higher Alcohols

A diagram of Plant 700 as used for testing catalysts for the conversion of methanol and

methanol/ethanol mixtures to higher alcohols is shown in Figure 5. A liquid feed system with flow rates maintained with a controlled pressure drop across a capillary was added to the plant.

3.1.1.4 Blank Runs with Methanol and Methanol/Ethanol Feeds

The results of blank reactor tests with the 10/1/20 methanol/ethanol/N_2 feed at 350°C are summarized in Table 4. A 316 stainless steel reactor has been used. Two packing materials have been used to fill the reactor volume above and below the catalyst bed. Borosilicate glass beads show significantly less activity for methanol decomposition than alpha-Al_2O_3. This packing material has been adopted for all subsequent testing.

In order to conduct catalytic tests at temperatures greater than 350°C, a copper-lined stainless steel reactor has been fabricated. Table 5 shows that a blank reactor test using a ½ methanol/N_2 feed in the original stainless steel reactor gave acceptable methanol loss at 250°C and 350°C (0.2% and 5.9%), but decomposition became excessive at 450°C (35%) and 500°C (68%). CO and H_2 are the primary products, although CH_4 was also observed at the highest temperatures. In contrast, the copper-lined reactor gave less than 10% methanol decomposition at 350, 400 and 450°C. At 350°C, C_2 oxygenates (DME and methyl formate) are the major products, while carbon oxides, particularly CO become more predominant at higher temperatures.

3.1.2 Catalyst Screening for CO/H_2 Conversion to Higher Alcohols

The initial phase of catalyst screening in this program focussed on the conversion of synthesis gas to higher branched alcohols. One of the ideas for an improved catalyst has been to combine a conventional methanol synthesis catalysts with a basic metal oxide which might promote the aldol condensation step of light alcohols to the desired isobutanol. Several Pd/K on Zn/Mn/Zr oxide catalysts, based on reports by Keim and co-workers, have also been tested. However, none of these catalysts has shown promise for the conversion of CO/H_2 to isobutanol at the conditions used.

3.1.2.1 Methanol Synthesis Catalysts

Shake-down testing of the pilot plant has been done using low temperature (Cu/Zn/Al) and high temperature (Zn/Cr) methanol synthesis catalysts. Both laboratory prepared and commercial samples of the former material have been tested.

3.1.2.1.1 Comparison of Commercial and Lab Prepared Cu/Zn/Al Oxide Catalysts

In order to the establish the suitability of laboratory prepared Cu/Zn/Al oxide methanol synthesis catalysts for higher alcohol synthesis, they have been compared with two commercial Cu/Zn/Al oxide catalysts, a low temperature WGS catalyst (ICI 52-1) and a methanol synthesis catalyst (ICI 51-3). The results of reference runs of these materials at 310°C, 1100 psig, 2250 hr^{-1} CO GHSV and 1/1 CO/H_2 molar feed ratio are given in Table 6. These materials show comparable performances for methanol synthesis at 310°C. The lab prepared catalysts give slightly higher CO conversions, but also more DME and CO_2, than the commercial samples. The presence of some residual acidity in the laboratory prepared materials may be the explanation of the slightly lower selectivity. These results were deemed similar enough for catalyst screening purposes.

3.1.2.1.2 Zn/Cr Oxide High Temperature Methanol Synthesis Catalyst

A Zn/Cr co-precipitated catalyst has been prepared and tested in the pilot plant at 450°C. This catalyst showed very poor performance. The results are summarized in Table 7 and compared with the performance of a Cu/Zn/Al oxide catalyst. Light hydrocarbons and CO_2 were the primary products observed, virtually no alcohols were produced. Subsequent blank reactor runs at 450°C (see above) demonstrated that these products are due to reactions occurring on the reactor walls.

3.1.2.2 Cu/Zn/Al Oxide Catalysts with Basic Metal Oxide Co-Catalysts

One of the approaches that has been investigated to increase the production of higher, branched alcohols from synthesis gas has been the combination of conventional methanol synthesis catalysts, such as Cu/Zn/Al oxide, with a basic co-catalyst. There is strong evidence

in the literature that a base-catalyzed aldol condensation type mechanism leads to the selective formation of isobutanol in these systems. While the metal oxide support of the methanol synthesis catalyst can provide the basic functionality, particularly when impregnated with alkali, one of the objectives of this program has been to determine whether the addition of a stronger base component to the catalyst formulation as a physical mixture might lead to improved performance. Pilot plant evaluations of 5 wt. % K (as KOH) on Al_2O_3 and SiO_2 as basic co-catalysts for the promotion of isoalcohol formation in combination with a Cu/Zn/Al oxide catalyst are summarized in Table 8. Conversions and selectivities with the K/Al_2O_3 co-catalyst are nearly identical to those of the SiO_2 reference. Therefore, this material appears to be inert. Addition of K/SiO_2 to the Cu/Zn/Al oxide resulted in a significant decrease in conversion and increase in DME selectivity. Potassium migration could be a possible explanation for this observation, but further investigation has not been pursued.

Three mixtures of the Cu/Zn/Al methanol synthesis catalyst and basic metal oxide co-catalysts have been evaluated. The basic co-catalysts have consisted of two Mg/Al MOSS samples (one lab prepared and one commercial sample obtained from Alcoa) and MgO. Table 9 shows the results of these pilot plant tests. All of the tests using the basic co-catalysts show an increase in CO and H_2 conversion. However, DME is the new product. This undesired by-product does not lie on the pathway from methanol to isobutanol. It is well known that even mild acid catalysts, such as gamma-alumina, can dehydrate methanol to DME. Therefore, this result suggests the presence of some acid sites on the Mg/Al MOSS and MgO materials. In an attempt to eliminate these sites, an Al/Mg MOSS sample has been impregnated with 0.2-0.3 wt. % alkali (Na, K, and Cs) and evaluated in combination with the Cu/Zn/Al oxide catalyst. Table 10 shows that the addition of this level of alkali to the Mg/Al MOSS is not effective for reducing the formation of DME.

The addition of alkali to Cu/Zn/Al oxide methanol synthesis catalysts has been used to increase selectivity to higher branched alcohols. Therefore, 1.3% Cs has been added to a laboratory prepared Cu/Zn/Al oxide sample by impregnation with an aqueous Cs formate solution. Table

11 shows that this catalyst was active for methanol synthesis, with reduced selectivity to CO_2 compared with the non-cesium catalyst. However, the production of the desired branched higher alcohols was negligible.

3.1.2.3 Zn/Mn/Zr Oxide Based Catalysts

Keim and co-workers have reported that very high selectivity to isobutanol from synthesis gas can be obtained with the use of Zn/Mn/Zr oxide based catalysts [25, 26]. The best isobutanol selectivities are obtained at very high pressures (250 bar) that are commercially unattractive. The literature preparations of these catalysts have been reproduced in order to evaluate their performance at more realistic conditions. A typical catalyst preparation consisted of co-precipitating the Zn/Mn/Zr support by simultaneously adding a 1M aqueous KOH solution and a 1M solution of the mixed zirconium, manganese and zinc nitrates to a stirred bucket over 20-30 minutes while maintaining the pH of the mixture at 10 and temperature at 50-60°C. The precipitate was aged in the solution for up to 5 hours then washed with water until the pH of the effluent was 7. The solid was recovered by filtration, dried at 155°C and calcined at 327°C under air for 3 hours. The noble metal component (Pd or Pt), and optionally alkali (K), were added by impregnation using an aqueous solution of either the metal chloride or the metal nitrate. The material was then calcined for a final time at 450°C in air for 6 hours to afford the finished catalyst.

Six pilot plant tests have been conducted using the Pd/K on Zr/Zn/Mn oxide catalysts. The results of these tests are summarized in Table 12. The temperature, feed rate and H_2/CO feed ratio used in these tests are comparable with those used by Keim, but the pressure (1100 psig) is substantially lower than that reported in the literature. All tests conducted at 450°C gave primarily light hydrocarbons and CO_2 rather than alcohols due to reactions catalyzed by the stainless steel reactor walls. A single test at 350°C showed higher selectivity to methanol, but low conversion. In contrast to the literature report, only traces of higher alcohol products were observed in these tests. It is suspected that the poor performance of these catalysts is due to the low pressure used. However, failure to precisely reproduce the catalyst formulation

from the limited description available in the literature cannot be ruled out.

3.1.3 Methanol and Methanol/Ethanol Conversion

The goals of this program were reassessed in light of the failure to identify any promising catalysts for the direct conversion of synthesis gas to higher alcohols. The problematic step in the conversion of either synthesis gas or methanol to higher alcohols is the coupling of two C_1 species to give a C_2 compound. Further condensation, ending with a branched C_4 oxygenate, is well precedented. Since the current commercial methanol synthesis process utilizing a Cu/Zn/Al oxide catalyst is more active for the conversion of CO/H_2 than any of the modified higher alcohols catalysts tested in this program or described in the literature, it appears that an indirect two-step process might have advantages over the direct synthesis gas to higher alcohols process. First, an optimized methanol synthesis process can be used to maximize the activity and selectivity for CO hydrogenation. Secondly, a completely different catalyst composition, that does not need CO hydrogenation activity, can be utilized for the methanol condensation. Finally, the conditions of the condensation can be separated from those of methanol synthesis allowing the use of high temperatures and lower pressures. Therefore, catalyst screening in this program was re-directed to evaluate catalysts for the conversion of light alcohols to higher branched oxygenates. Initial testing was done using a methanol only feed, but very low conversions were obtained. The use of 10/1 methanol/ethanol feed mixture was adopted in order to screen catalysts. The reaction mechanism of the condensation reaction has been probed by conducting tests at varying space velocities.

3.1.3.1 Screening of Catalysts for the Conversion of Methanol to Isoalcohols

A variety of mixed metal oxide catalysts have been evaluated for the conversion of methanol to higher alcohols at a standardized set of conditions similar to those used for conventional methanol synthesis (250°C, 1100 psig, 2 hr^{-1} methanol WHSV). Table 13 shows that all catalysts afforded very low conversions of methanol. DME, rather than higher alcohols, was the primary product in all cases. The initial runs employed a N_2 diluent. However, switching

to H_2, to ensure catalyst reduction, did not result in any improvement in performance.

3.1.3.2 Screening of Catalysts for the Conversion of Methanol/Ethanol to Isoalcohols

It is well known that the reaction of methanol with ethanol to give isobutanol is significantly easier than that of methanol with itself. In fact, several recent literature reports have appeared describing the production of iso-C_4 oxygenates from methanol and ethanol [34, 36]. Since it was not clear whether the poor results obtained in the methanol only testing were due to inadequate catalysts or improper selection of conditions, testing with a methanol/ethanol feedstock has been used to identify suitable catalysts and conditions for the production of higher branched oxygenates.

3.1.3.2.1 Mg/Al Moss Catalysts - Establishment of a Catalyst Screening Test

The development of a catalyst screening test for the conversion of a mixed methanol/ethanol feed to higher oxygenates has been done using a Mg/Al MOSS catalyst. The effects of temperature, pressure and space velocity on performance with a 10/1 methanol/ethanol mixture are summarized in Table 14. At 250°C with an H_2 co-feed, methanol conversions were negligible. However, a small amount of aldehydes were observed in the product at 100 psig. At higher pressure (1100 psig) only DME was observed. Since the desired aldol condensation step for C-C bond formation may require the presence of aldehyde intermediates, the use of low pressure and elimination of the H_2 co-feed was pursued. Increasing temperature to 350°C gave a significant increase in conversion, while further reduction in pressure to 30 psig increased selectivity to C_{3+} alcohols. A final run at low space velocity afforded higher conversion, but selectivity to DME and C_{2+} hydrocarbons also increased suggesting that dehydration and hydrogenation reactions were becoming more dominant. Based on this work, conditions of 350°C, 30 psig, 2 hr^{-1} MeOH WHSV and 1/0.1/2 MeOH/EtOH/N_2 molar feed ratio have been adopted for catalyst screening.

3.1.3.2.2 Methanol Synthesis Type Catalysts

A Cu/Zn/Al oxide low temperature methanol synthesis catalyst gives almost complete

conversion of both methanol and ethanol at the screening test conditions developed with the Mg/Al MOSS catalyst. CO, CO_2 and DME are the major products, but C_4 oxygenates are also observed including isobutanol, isobutyraldehyde and methylisobutylether (Table 15). The productivities for isobutanol and total C_{3+} oxygenates in this test are 25 and 76 g/kg catalyst/hr which remain below the targets for an higher alcohol production process.

The use of lower temperatures with the Cu/Zn/Al oxide catalyst has been evaluated. Higher C_{3+} oxygenates selectivity (31.8%) and productivity (121 g/kg cat/hr) are obtained at 300°C, but methanol conversion is substantially reduced. At 250°C, methanol and ethanol conversions are lowered further and selectivity and productivity to the desired oxygenate products are also reduced. The results are summarized in Table 15. In view of the performance of this catalyst it has been selected as a baseline material for comparison with new catalysts developed in this program.

Low Cu content Cu/Zn/Al oxide and Cu/Zn/Mn oxide catalysts are less active than the baseline catalyst, but have superior selectivity and productivity to the desired C_4 oxygenates (Table 16). However, comparison of the 350°C performances of these materials with that of the baseline catalyst at 300°C, where conversions are comparable, show similar productivities. It is also unlikely that these materials would be significantly more active for the C_1-C_1 coupling needed for methanol only conversion than the baseline catalyst. Zn/Cr and Zn/Al mixed metal oxide materials, based on high temperature methanol synthesis catalysts, have substantially lower activity and productivity of the desired higher oxygenate products.

3.1.3.2.3 Noble Metal/Zn/Mn/Zr Oxide Type Catalysts

Catalysts consisting of Pd impregnated on a Zn/Mn/Zr mixed metal oxide support prepared by co-precipitation of metal nitrates with KOH have been claimed to have high selectivity for isobutanol from synthesis gas [24, 25]. However, severe conditions (high temperatures and very high pressures) are required to achieve attractive conversion levels. One interpretation of these results is that this catalyst is active for the condensation of light alcohols to higher

alcohols with high selectivity to isobutanol, but requires severe conditions for CO hydrogenation. If this is the case, these materials would be promising catalysts for a methanol to higher alcohols process.

The ability of bifunctional materials to catalyze the conversion of light alcohols to higher branched alcohols can be rationalized in the following way. The aldol coupling reaction, which presumably is the C-C bond forming step in this system, likely requires the presence of aldehyde as a target for nucleophilic attack. This suggests that the rate of condensation might be increased if the concentration of aldehyde species in the feed can be raised. Noble metal catalysts are well known to catalyze the dehydrogenation of alcohols to aldehydes. For example, silver metal is used commercially for the conversion of methanol to formaldehyde. Therefore, the addition of a noble metal function to a catalyst support capable of promoting the aldol condensation reaction should lead to a superior catalyst.

Catalysts prepared by impregnating a representative Zn/Mn/Zr metal oxide support with 0, 0.2 and 2 wt. % Pd using a $PdCl_2$ solution have been evaluated using the methanol/ethanol screening test. These materials show lower activity than the baseline Cu/Zn/Al oxide catalyst, but significantly higher selectivity to isobutanol, isobutyraldehyde and total C_{4+} oxygenates (Table 19). In spite of the lower conversions, the Pd containing catalysts give higher productivities to the desired products than the baseline catalyst.

A variety of mixed metal oxide supports containing Zn, Mn, Cr, Cu, Ce, La and Al have been prepared by the co-precipitation of a mixed metal nitrate solution with KOH at constant pH. These supports, after drying and calcining, have been impregnated with both 2 wt. % Pd and 2 wt. % Pt and tested in the standard pilot plant screening test for the conversion of a 10/1 (molar) methanol/ethanol blend. Table 18 summarizes the testing results of the Pd containing catalysts, while Table 19 summarizes results with Pt containing materials. In the case of Pd, the Zn/Mn/Cr oxide support affords the highest isobutanol selectivity and productivity. The Zn/Mn/Zr oxide support gives comparable selectivity, but at a slightly lower activity level.

This material also shows lower CO_x selectivity due to reduced CO. The other supports tested all show lower selectivity to the desired isobutanol product than the best catalysts. The Zn/Mn/Zr oxide supports (1/1/1 and 1/1/0.2 molar ratio of metals) give the best Pt containing catalysts, with the Zn/Mn/Ce oxide a close second. In contrast with the Pd findings, Pt on the Zn/Mn/Cr support gives poor selectivity to isobutanol and total C_{4+} products and high selectivity to CO_x. The Zn/Mn/Cu and Zn/Mn/La oxide supports, as well as several bimetallic oxide supports, give lower isobutanol selectivity.

The effect of varying the noble metal has been investigated using the best two supports, Zn/Mn/Zr and Zn/Mn/Cr. The Pd or Pt addition clearly increases the activity of these catalysts for methanol/ethanol conversion (Table 20). Catalysts with either no noble metal or Ag (either impregnated or physically mixed), give much lower conversion levels. This suggests that the dehydrogenation of alcohol to aldehyde is an important, and perhaps rate limiting, step in the condensation process. On the other hand, isobutanol selectivity is relatively independent of the identity or presence of the noble metal in the case of Zn/Mn/Zr oxide. This suggests that oxygenate selectivity may be primarily a function of the basic metal oxide support. Therefore, variations of this support composition would be a reasonable approach for improving isobutanol selectivity. Table 21 shows an overall summary of the selectivities to all identified products observed with the Pt on Zn/Mn/Zr oxide and Pd on Zn/Mn/Zr oxide catalysts on a CO_x included basis. All of these catalysts show higher selectivity to isobutyraldehyde than to isobutanol. This is probably due to the low pressure (30 psig) used in this testing, where equilibrium favors the dehydrogenated product. The presence of substantial amounts of methyl isobutyrate, the ester derived from methanol and butyric acid, suggests that either further oxidation to the carboxylic acid or condensation of iC_4 aldehyde and methanol is also occurring. Acid catalyzed etherification of methanol to DME appears to be minimal, except for the Pd on Zn/Mn/Zr oxide catalyst, but light ester formation, presumably by the reaction of methanol with formaldehyde and acetaldehyde intermediates, occurs at about 3% selectivity. The Pd containing catalysts show twice as much CO formation as the Pt samples, which is highly undesirable since it represents the reverse of the met

synthesis process.

The reproducibility of the preparations of noble metal on mixed metal oxide catalysts has been evaluated by making new samples of Zn/Mn/Zr and Zn/Mn/Cr oxide supports following the same co-precipitation, washing and calcination procedures used previously. Table 22 summarizes the pilot plant results obtained with catalysts prepared by the impregnation of these supports with Pd and compares them with earlier catalyst samples. In the case of the Zn/Mn/Zr support, a first reproduction shows very comparable performance to the earlier sample. However, another sample prepared by a separate Pd impregnation on this second Zn/Mn/Zr oxide support showed substantially lower activity and selectivity to isobutanol. Differences in performance between two Pd impregnations on the same support are also seen with the original Zn/Mn/Cr oxide support. In this case, activities were similar but selectivities to isobutanol and total C_{4+} products were different. A second co-precipitation of the Zn/Mn/Cr oxide support afforded a very poor catalyst with low activity and selectivity to isobutanol.

Better catalyst preparation reproducibility has been obtained with two Pt containing catalysts made on Zn/Mn/Zr and Zn/Mn/Cr oxide supports. Table 22 compares the pilot plant results of these catalysts with earlier samples. The Pt on Zn/Mn/Zr oxide sample shows good reproducibility with the previous material, while the Pt on Zn/Mn/Cr catalyst shows lower activity and higher selectivity to total C_{4+} products than the original sample. It should be noted that the poor performances of these Zn/Mn/Cr catalysts is similar to that of the Pd catalyst prepared using the second Zn/Mn/Cr oxide support. In general, the reproducibility of noble metal on Zn/Mn/Zr oxide catalysts has been superior to that of the Zn/Mn/Cr formulations. A possible explanation for this observation may be that the co-precipitated supports may have differing amoiunts of Aisolated@ metals that can affect the noble metal function. Chromium is know to attentuate noble metal functions while zirconium ussually does not.

3.1.3.2.4 Other Catalysts

The performances of catalysts consisting of Pt on several pure metal oxide supports is shown in Table 23. In the case of ZnO, the oxide powder was bound with 50% SiO_2 to obtain a material with a particle size sufficient for use in the pilot plant. While the ZnO sample shows some activity and selectivity for isobutanol formation, the MnO_2 and ZrO_2 samples have virtually no activity. Finally, Pt on MgO, TiO_2 and a Zn/Mg mixed oxide support (also bound with SiO2) show high activity for methanol conversion, but low selectivity to isobutanol and total higher products. Instead, CO, CO_2, and light hydrocarbons are the major products observed.

A series of catalysts consisting of Cu and Mo on TiO_2, Mg/Al MOSS, and polyvinylpyridine polymer supports have been tested. The performances of these material are summarized in Table 24. The Cu on metal oxide samples give isobutanol and total C_{4+} product selectivities that are comparable with those obtained with the best Pt catalysts, but activity is substantially lower. The Mo containing catalysts have higher methanol and ethanol conversions, but poorer selectivities to the desired products. The polyvinylpyridine supported catalysts all show very low conversion and no production of either isobutanol or CO_x.

A variety of commercial and lab prepared MnO_2 catalysts have been evaluated in the standard methanol/ethanol pilot plant test. These catalysts all show very low activity and selectivity to isobutanol (Table 25). The negative ethanol conversions suggest that some methanol is being converted to ethanol over these catalysts, but the levels are very low. Two commercial MnO_2 samples have also been tested with 2% Pt and 2% Pd added by the standard aqueous metal chloride impregnation technique. These catalysts show substantially higher methanol and ethanol conversions, but also higher selectivity to CO_x (primarily CO). Selectivities to isobutanol are very low. Thus, alcohol decomposition appears to be the primary reaction over these materials.

3.1.3.3 Space Velocity Testing to Determine Reaction Pathways with Methanol/Ethanol

One of the primary mechanistic questions in the production of branched C_4 oxygenates from methanol is the relative rates of the C_1-C_1, C_1-$C_{2,3}$ and C_2-C_2 condensation steps. The latter condensations are sufficient for the production of higher alcohols from a methanol/ethanol feed blend. However, the C_1-C_1 coupling step is necessary for the primary goal of this project, the condensation of methanol only to higher alcohols. In order to evaluate the extent of C_1-C_1 coupling occurring over experimental catalysts, tests have been conducted to determine the dependence of product yields on space velocity. At conditions where ethanol conversion is high, an increase in the yields of isobutanol and other higher oxygenates as WHSV is decreased suggests that the desired products are being formed from methanol only.

The aldol condensation of two C_2 species is expected to yield straight chain C_4 products. However, the C_4 oxygenate products observed with the best catalysts identified in screening with a methanol/ethanol feed are highly branched. This suggests that their formation occurs by sequential C_1 aldol condensations to C_2 and C_3 intermediates and that C_1-$C_{2,3}$ coupling is substantially favored over C_2-C_2 condensation. In view of the dehydrogenation equilibrium constants at 327 °C of 0.03 for methanol to formaldehyde + H_2 and 1.12 for ethanol to acetaldehyde + H_2, it appears that branched C_4 compounds are formed by the condensation of methanol with acetaldehyde and propionaldehyde intermediates.

Based on these findings, subsequent research has been focussed on the Zn/Mn/Zr support. Further tests with a methanol-only feedstock will be described in section 3.4.1 to characterize the ability of this catalyst system to affect the desired C_1-C_1 condensation step.

3.1.3.3.1 Cu/Zn/Al Oxide Catalyst

The methanol, ethanol and total carbon conversions for the Cu/Zn/Al oxide baseline catalyst as a function of space time at 300°C and 30 psig are shown in Figure 6. At space times between 0.5 and 1.0 hr, ethanol conversion exceeds 90%, while methanol and total carbon conversions increase from about 70% to near 90%. However, isobutanol and total C_{4+} oxygenates yields

(on a % of total carbon basis) are essentially flat (Figure 7). Only CO yield shows an increase comparable with the total carbon conversion rise. This suggests that the additional conversion occurring in this portion of the catalyst bed is due to methanol reforming to CO rather than aldol condensation. Therefore, it appears that Cu/Zn/Al oxide material is a poor catalyst for the C_1-C_1 condensation required for the production of higher oxygenates from methanol alone.

3.1.3.3.2 Pd on Zn/Mn/Zr Oxide

The 2% Pd on Zn/Mn/Zr oxide catalyst appears to be capable of condensing methanol alone to higher alcohols. Figure 8 shows methanol, ethanol and total carbon conversions as a function of space time. This data shows that ethanol conversion exceeds 80% at space times greater than 0.15 hr and reaches 95% at 0.50 hr. Figure 9 shows that over this range of space times the yields for the desired products, isobutanol and total C_{4+} oxygenates, increase 2-3 fold. The substantial rise in the yields of higher oxygenates after the near complete conversion of ethanol suggests that these products are formed by the reaction of methanol with itself or with another reaction intermediate.

3.1.3.3.3 Pt on Zn/Mn/Zr Oxide

The large scale 2% Pt on Zn/Mn/Zr oxide catalyst described in Task 2.2 has also been evaluated at varying space velocities. Figures 10-12 summarize the results of these runs. This data shows that the yields of C_{4+} oxygenates, particularly isobutanol and isobutyraldehyde, continue to increase as contact time is increased past the point of complete ethanol conversion (space times greater than 0.3 hr). Figure 11 shows that all three of the major C_4 oxygenate products (isobutanol, isobutyraldehyde and methyl isobutyrate) have increasing yields in this region. The major by-products that can be produced from methanol only (methyl formate and DME) are also increasing (Figure 12). These results suggest that the additional higher alcohol product may be arising from the conversion of methanol alone. However, other side-reactions involving methanol or formaldehyde only also appear to become more important at higher space times.

3.1.3.3.4 Pd on Zn/Mn/Cr Oxide

Similar testing with a 2% Pd on Zn/Mn/Cr oxide catalyst at low space velocities shows that at space times where ethanol conversion is complete (greater than 0.2 hr), the yield of isobutanol and total C_{4+} products is flat (Figure 13). This indicates that the additional methanol converted is going to other products, mainly CO and CO_2. Thus, the Zn/Mn/Cr support appears less active for methanol only conversion than the Zn/Mn/Zr oxide. In addition, comparison of the CO yields in Figures 9 and 13 shows that the Zn/Mn/Cr support is much more active for the decomposition of the light alcohols.

3.2 Catalyst Development and Optimization (Task 2)

Noble metal (Pt or Pd) on co-precipitated Zn/Mn/Zr oxide supports have been identified as promising catalysts for the synthesis of higher branched alcohols from a methanol/ethanol feed in the catalyst screening portion of Task 1 of this program. The highest selectivity and productivity for isobutanol and total C_{4+} products has been obtained with 2 wt.% Pt or Pd on a Zn/Mn/Zr oxide support. In Task 2 the effects of key compositional variables have been investigated. Metal oxide support composition and noble metal loading have been the variables examined. Table 26 summarizes analytical data on the Pt and Pd on Zn/Mn/Zr oxide catalysts that have been prepared in this task. Elemental compositions, apparent bulk densities (ABD) and surface areas, pore volumes and average pore diameters from N_2 BET porosimetry are included. Finally, a 300g batch of the best catalyst formulation, 2% Pt on Zn/Mn/Zr (60/20/20 mole ratio) oxide, has been prepared for use in process variable studies (Task 4) and demonstration runs (Task 3).

3.2.1 Support Composition

The mixed metal oxide support presumably provides the solid base functionality that catalyzes the condensation of lower aldehydes (formaldehyde and acetaldehyde) formed by alcohol dehydrogenation to higher oxygenates. The basicity of the support is expected to have a large

impact on the activity and selectivity the catalyst for this condensation. Varying the composition of the mixed metal support is one approach for modifying this catalyst property. The standard pilot plant test using a methanol/ethanol blend feed has been used to measure the effects of composition on performance for alcohol condensation.

A series of 2% Pt or 2% Pd on Zn/Mn/Zr oxide catalysts have been prepared using the co-precipitation and noble metal impregnation techniques. The ratios of the three major support components have been varied systematically between 10-60% to sample the composition space of the ternary mixed metal oxide. Table 27 summarizes the pilot plant testing results for the Pt containing catalysts. The key results are also shown in Figures 14 and 15 as a function of the metal oxide support composition. Figure 14 gives methanol and ethanol conversion as well as selectivities and productivities to the desired oxygenate products. Figure 15 shows the selectivities of some of the key by-products; methyl formate and methyl acetate which are presumably formed by the Cannizzaro reaction of the formaldehyde and acetaldehyde intermediates and CO_x. This data shows that a wide variation of the composition of the ternary metal oxide has only a small affect on catalyst performance. However, all three components appear to be important since single and dual oxide supports all have inferior performance to the ternary supports. A performance trend toward higher selectivity to isobutanol and isobutyraldehyde with increasing Zn and decreasing Zr contents can be seen in Figure 14. In addition, the support with the lowest Zn content gives the highest amount of Canizzarro by-products and CO. Based on these results a support composition with $>33\%$ Zn and $<33\%$ Zr appears to most preferable for higher alcohol production.

The results for Pd containing catalysts prepared on the same ternary Zn/Mn/Zr oxide supports used above are summarized in Table 28 and Figure 16. All of these materials show lower selectivities to isobutanol and isobutyraldehyde products than the Pt catalysts. Overall selectivities and productivities to total higher products are comparable with the Pt containing catalysts, but selectivities to the desired C_4 oxygenates are substantially lower.

3.2.2 Nobel Metal Loading

The noble metal loading on the alcohol condensation catalyst will have a major impact on the cost of the catalyst and, therefore, the economic viability of the process. In addition, independence of the catalytic performance on the noble metal loading would suggest that alcohol condensation, rather than dehydrogenation to aldehydes, is the rate determining step in this process. If this is the case, the development of an improved catalyst needs to focus on the basic mixed metal support rather than the noble metal function.

Table 29 summarizes the pilot plant results obtained by impregnation of the Zn/Mn/Zr (60/20/20) oxide support from the support composition series with 0.5%, 1%, 2% and 5% Pt using the standard aqueous H_2PtCl_6 impregnation procedure. It can be seen that the highest selectivities to the desired C_4 oxygenates are obtained with the 2% Pt catalyst. However, all of the other catalysts gave higher alcohol conversion, as well as lower selectivities. Therefore, the selectivity differences could be due to catalyst activity rather than intrinsic catalytic performance. In order to properly compare these materials, a more through testing procedure, using varied space velocities to determine selectivity versus conversion relationships, is required. In contrast with the C_4 oxygenates, other by-products show clear trends with changing noble metal loadings. Increasing Pt decreases the levels of DME and CO, but increases the amount of Canizzarro products (methyl formate and methyl acetate). The latter observation suggests that more light aldehydes, particularly methyl formate, that can be condensed over the basic metal oxide via the Canizzarro reaction are produced with higher Pt catalysts.

In order to obtain a better comparison of catalysts with different noble metal loadings, a more thorough testing procedure has been utilized. Catalysts consisting of 0.5% and 2% Pt on Zn/Mn/Zr (60/20/20) oxide have been tested at methanol space velocities of 2, 3 and 4 hr^{-1} over 16 hour intervals to obtain data over a range of conversion levels. In contrast to the earlier results, these catalysts show little difference in activity. Figure 17 shows that the plots of methanol, ethanol and overall conversions versus space time are similar. Both samples

show lower activity on return to the initial conditions indicating that some catalyst deactivation occurred over the test. However, the loss in activity is less than that obtained with the space velocity changes. Figure 18 shows that the 2% Pt catalyst affords higher selectivity to the desired iC_4 oxygenated products (isobutanol, isobutyraldehyde and methyl isobutyrate). Overall selectivities are summarized in Table 30 which indicates that the improved performance of the 2% Pt catalyst is due to a reduction in the amount of methyl formate, CO and other C_{4+} by-products. The C_1-C_2 Cannizzaro reaction product, methyl acetate, increases with higher Pt.

The observed shift in oxygenate selectivity from methyl formate to methyl acetate and iso-C_4 oxygenates with increased Pt loading suggests that the extent of dehydrogenation affects the relative rates of C_1-C_1 and C_1-C_2 condensation. Aldol condensations (Reaction 1) are required for the production of the desired iso-C_4 oxygenates, while Cannizzaro condensations (Reactions 2 and 3) give rise to light ester products. In each of these reactions, aldehydes formed by alcohol dehydrogenation are key intermediates. At the high methanol/ethanol feed ratio used in the pilot plant testing, a high dehydrogenation activity catalyst (i.e. high Pt) would be expected to give a higher acetaldehyde concentration and, therefore, favor Reactions 1 and 2 over Reaction 3.

$$CH_3OH + CH_3CHO \text{ (from } CH_3CH_2OH) \text{ --> } CH_3CH_2CH_2OH \qquad (1)$$

$$CH_3OH + CH_3CHO \text{ (from } CH_3CH_2OH) \text{ --> } CH_3COOCH_3 \qquad (2)$$

$$CH_3OH + HCHO \text{ (from } CH_3OH) \text{ --> } HCOOCH_3 \qquad (3)$$

3.2.3 Catalyst Scale-up

The catalyst formulation studies have indicated that a catalyst composition of 2% Pt on a

60/20/20 (molar) Zn/Mn/Zr oxide support affords the best performance for higher oxygenate production. Therefore the preparation of this catalyst has been scaled-up from 30 g to 200 g. Pilot plant testing of the new material has shown that the methanol/ethanol conversion performance of this material is comparable with previous samples of the same nominal composition (Table 31). This large supply of catalyst has been used for all of the process variable studies of Task 4 and the demonstration runs of Task 3.

3.3 Process Variable Study (Task 4)

The effects of temperature, pressure and methanol/ethanol molar feed ratio on the performance of the 2% Pt on Zn/Mn/Zr Oxide catalyst has been evaluated in a series of pilot plant tests. The results of these runs are summarized in Table 32. Based on these findings a set of optimized conditions have been identified for the 2% Pt on Zn/Mn/Zr (60/20/20) oxide catalyst. A demonstration test at these conditions has been conducted under Task 3 of the program. The effects of co-feeding H_2, CO and CO_2 with the methanol/ethanol feed on catalyst performance have also been examined.

3.3.1 Temperature

Increasing temperature from 325°C to 375°C increases alcohol conversion, but reduces selectivity and productivity to the desired branched C_4 oxygenates. CO and light hydrocarbons production is substantially greater at the higher temperature, while CO_2 and methyl acetate (presumably from Cannizzaro condensation) formation is lower. Higher temperature also shifts the C_4 oxygenates product ratio toward isobutyraldehyde from isobutanol and methyl isobutyrate. Based on these results, it appears that lower temperature, with the use of lower space velocity to maintain conversion, is the preferred operating condition.

3.3.2 Pressure

The major effect of higher pressure operation is to shift the product ratio from isobutyraldehyde to isobutanol. CO selectivity is also increased, which is surprising considering that the thermodynamics of methanol decomposition to CO and H_2 should be disfavored by raising pressure. Operation at 300 psig affords the highest productivities of isobutanol and iC_4 oxygenates observed with a 10/1 methanol ethanol feed. The combination of higher pressure and lower temperature may allow these better oxygenate selectivities and productivities to be obtained while reducing the amount of CO produced.

3.3.3 Methanol/Ethanol Feed Ratio

Variation of the methanol/ethanol feed ratio has been used to gain a understanding of the mechanism of alcohol coupling. Decreasing the feed ratio from 10/1 to 7/1 increases methanol conversion as well as selectivity to each of the iC_4 oxygenates. CO_x selectivities are also slightly reduced. However, further reduction of the methanol/ethanol feed ratio to 4/1 does not give additional improvement as light esters, presumably arising from base-catalyzed Cannizzaro reactions, and unidentified heavy by-products increase. At a 1/1 feed ratio branched higher alcohol products are substantially reduced and light ester products dominant. The highest productivity of I-C_4 oxygenates has been obtained at a 7/1 methanol/ethanol feed ratio. This indicates that an excess of methanol is required to prevent other base catalyzed coupling reactions (such as the Cannizzaro reaction) from occurring over this catalyst.

3.3.4 H_2, CO and CO_2 Co-Feeds

Co-feeding H_2 at a 2/1 H_2/MeOH feed ratio had very little effect on the performance of the Pt on Zn/Mn/Zr oxide catalyst (Table 33). Methanol conversion is higher and selectivity shifts from isobutyraldehyde to isobutanol giving an slightly higher overall productivity for isobutanol. It has been speculated that the dehydrogenation of methanol and ethanol to the corresponding aldehydes is a key first step in the coupling mechanism. The presence of an H_2 co-feed might be expected to inhibit the formation of these intermediates and hinder the formation of higher alcohols. However, it appears that this is not a problem to the low H_2