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HETEROGENEOUS CATALYTIC PROCESS FOR ALCOHOL FUELS FROM SYNGAS

DOE Contract No. DE-AC22-91PC90046
Pittsburgh Energy Technology Center

Final Technical Report

Prepared by B. D. Dombek

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1. Contract Objectives

Alcohols have been used as transport fuels ever since the invention of the automobile, although inexpensive gasoline held a near-total domination of this market for many years following World War II. The development of synthetic transportation fuels based on domestic fossil fuel reserves, particularly coal, remains a mid-term goal of the U.S. government; the objective is to reduce our dependence on imported petroleum. More recently, however, it has been environmental concerns that have stimulated the interest of industry in developing oxygenated fuels. In particular, the restrictions on gasoline Reid vapor pressures (i.e., butane reductions) and lead phase-out have created an octane number shortage in most domestic refinery gasoline pools, while clean air regulations have heightened the need for cleaner burning fuels. Oxygenates afford a solution to meet both the octane and clean air demands. Most alcohols and ethers have very high octane numbers (>95) and burn to produce largely carbon dioxide and water. At the present, a substantial portion of the unleaded gasoline sold in the United States contains oxygenates, mainly ethanol and MTBE. These oxygenates could be used directly as transport fuels, but their direct use as fuels requires extensive modification of engines, fuel delivery systems, and storage and distribution facilities. It is probable that in the near to medium term the most important contribution of oxygenates to the fuels area will continue to be their use as gasoline octane enhancers and as emission reducing additives.

Overall, two approaches have been followed in developing the use of oxygenated fuel additives — the use of alcohol mixtures blended with gasoline, and the addition of ethers to gasoline. In both cases, the oxygenated additive replaces up to 10 to 20% of the gasoline, and no modification of engines or delivery systems is required.

Ethers, in particular methyl tertiary-butyl ether (MTBE), have become a very significant player in the U.S. fuel market. An analogue of MTBE, ethyl tertiary-butyl ether (ETBE) has also received recent attention. Much of the unleaded gasoline today contains MTBE as an octane enhancer. An advantage of MTBE is that it has good solubility characteristics in gasoline, requiring no co-solvents. The methyl portion of this molecule is obtained from methanol, and the t-butyl fragment is derived from isobutylene, a petroleum-derived fraction. As a result, MTBE production is feedstock limited.

The primary objective of this project has been the pursuit of a catalyst system which would allow the selective production from syngas of methanol and isobutanol. It is desirable to develop a process in which the methanol to isobutanol weight ratio could be varied from 70/30 to 30/70. The 70/30 mixture could be used directly as a fuel additive, while, with the appropriate downstream processing, the 30/70 mixture could be utilized for MTBE synthesis. The indirect manufacture of MTBE from a coal derived syngas to methanol and isobutanol process would appear to be a viable solution to MTBE feedstock limitations.

To become economically attractive, a process for producing oxygenates from coal-derived syngas must form these products with high selectivity and good rates, and must be capable of operating with a low-hydrogen-content syngas. This was to be accomplished through extensions of known catalyst systems and by the rational design of novel catalyst systems.

2. Project Organization

This contract for the study of alcohol production for fuels from syngas was conducted at Union Carbide's South Charleston Technical Center, South Charleston, West Virginia 25303.

Program Manager / Principal Investigator was Dr. B. Duane Dombek. Contributors to the project include:

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3. Project Summary

3.1 Approaches Pursued

Synthesis gas can be converted into mixtures of methanol and higher alcohols by use of alkali-modified methanol synthesis catalysts known for many years. Interest in higher alcohol synthesis from syngas has stemmed from the desire to use the alcohol mixtures as high-octane blending stock for gasoline. Refining modifications and the use of oxygenated petrochemicals such as methyl tert-butyl ether (MTBE) have been implemented as alternatives. The production of a mixture of methanol and isobutanol is of interest due to its possible use as a feedstock in the production of other oxygenates such as MTBE and related ethers.

Previously known catalysts for Higher Alcohol Synthesis (HAS) can be divided into the following classes based on the alcohol product distribution.

<u>Modified Fischer-Tropsch (FT) and Group VIII Metal-Based Catalysts.</u> Traditional Fischer-Tropsch catalysts can be made to produce appreciable amounts of oxygenates (alcohols, aldehydes, acids, ketones and esters) by addition of alkali. Typical FT metals include Fe, Co, Ni, and Ru. The products observed follow an Anderson-Schulz-Flory (ASF) distribution, characteristic of the linear condensation polymerization mechanism. Molybdenum sulfide catalysts promoted with alkali also produce the ASF product distribution. Rh-based catalysts are similar, but produce more C_{2+} oxygenates.

<u>Modified Methanol or Iso-Alcohol Catalysts.</u> These consist of Methanol Synthesis catalysts modified with alkali promoters, forming significant quantities of branched primary alcohols. These can be divided into two classes:

(a) The "high-temperature" (~ 400°C operating temperature) catalysts, which are essentially alkali-modified ZnCrO and ZnMnCrO systems. The major products are methanol and iso-butanol, but small amounts of ketones, secondary alcohols, ethers and hydrocarbons are also observed. The formation of higher alcohols is maximized by operating under hydrogen lean conditions (syngas ratio of $H_2/CO = 1$). The operating catalyst is thought to consist of a microcrystalline $ZnCr_2O_4$ spinel oxide phase. Manganese can be substituted for chromium to reduce the acidity of the spinel, thus decreasing the amounts of ethers and hydrocarbons formed. The presence of alkali is thought to be essential to promote HAS.

(b) "Low-temperature" catalysts, which are generally alkali-modified copper-containing catalysts, based on low-temperature methanol catalysts.

The reaction over these iso-alcohol catalysts is believed to proceed by a combination of hydrogenation and carbon-carbon bond formation via aldol condensation. The result of this is the formation of branched alcohols with a non-ASF product distribution. This should be contrasted with the modified FT catalysts which proceed by a classical polymerization mechanism.

We chose to investigate catalysts of the iso-alcohol type because of the greater possibility of forming a product mix in the range of most interest. Catalysts from both the high-temperature and low-temperature class were studied, but our efforts soon became focused largely on the high-temperature class of catalysts, where significant progress has been made in catalyst formulation and overall performance.

3.2 Summary of Progress

Work at Union Carbide under a previous contract (DE-AC22-86PC90013) on a methanol-isobutanol catalyst used consecutive Hyper-Greco-Latin Squares to identify and bracket levels of important variables in catalyst formulation and preparation. Catalysts with good isobutanol selectivities were developed, but the overall alcohol rate was low. Work under the present contract was focused on improving catalyst performance through studies of both catalyst formulation and catalyst preparation techniques. Process variables such as reaction conditions and product/feed recycle were also investigated.

The work completed under this contract has shown that catalysts based on ZnCrMn oxides are effective HAS catalysts, particularly when promoted with alkali metals such as potassium or cesium. Cesium is generally a more effective promoter than potassium for higher alcohol synthesis. Catalysts were prepared under various conditions, and it was found that a high precipitation pH and low calcination temperature gave catalysts with the highest surface areas.

Substitution of manganese for chromium in the spinel lowers the overall activity of the catalysts, although it improves the alcohol selectivity. The difference is not due to changes in relative surface areas of the two spinels. The Mn-containing catalysts also require less cesium promoter, consistent with manganese substitution lowering the overall spinel acidity.

The Zn/Cr/O catalysts prepared by our procedures are actually Zn/Cr spinel oxides containing excess zinc oxide. The performance of potassium-promoted Zn/Cr/O spinel oxide catalysts and potassium promoted ZnO catalysts is inferior to potassium promoted Zn/Cr/O spinel oxide catalysts containing excess ZnO. The combination of the two components performs better than each of the individual parts. The presence of excess zinc oxide has a beneficial effect on the performance of Zn/Cr spinel oxide catalysts (a) promoted with cesium and (b) promoted with both cesium and palladium. The presence of the excess zinc oxide results in a more active and selective catalyst to total alcohols and increased isobutanol rates.

Palladium addition to the cesium-promoted Zn/Cr spinel oxide containing excess zinc oxide catalyst allows operation at only 1000 psi with good selectivities to total alcohols (> 80%), good isobutanol productivities (> 150 g/kg-hr) and with a methanol/isobutanol mole ratio of 0.58: this is our best overall performance to date.

Surface science studies have shown that the surface of these catalysts is predominately ZnO and alkali. With use, the ZnO is reduced to Zn metal, and Cr migrates to the surface giving increased surface acidity. Mn addition tends to lower the overall acidity.

Operation at temperatures above 440°C results in a further increase in the isobutanol rate, a further decrease in the methanol rate, but a marked increase in the hydrocarbon rate. Promoter optimization may be necessary for successful operation in this higher temperature regime. The combination of high temperature and high pressure optimizes the yields of higher alcohols. Lower space velocities and low H_2/CO ratios (<1) increase the relative proportion of higher alcohols, but at the expense of catalyst productivity.

Potassium addition promotes higher alcohol synthesis on a commercial Zn/Cr spinel oxide methanol synthesis catalyst. Incremental potassium levels (1, 3 and 5 wt%) result in an increase in total alcohol selectivity, while isobutanol rates are maximized at 1 wt% potassium. Rates greater than 100 g/kg-hr are achievable with this formulation. The commercially prepared catalyst promoted with potassium is slightly less active for isobutanol synthesis and less selective to total alcohols when compared with our spinel formulation promoted with potassium and containing excess ZnO.

Product/feed recycle studies show that the recycle of methanol is ineffective with this catalyst system. The recycle of ethanol and isopropanol was marginally effective, and addition of n-propanol gave significantly enhanced yields of isobutanol. Recycle of water and carbon dioxide increases the effective CO_2 concentration over the catalyst via the water gas shift reaction, and results in inhibition of higher alcohol synthesis. Presumably, the CO_2 occupies basic catalyst sites involved in the base-catalyzed aldol condensation steps responsible for higher alcohol synthesis.

3.3 Conclusions and Prospects for Future Work

After several years of work on spinel oxide-based catalysts for the synthesis of higher alcohols from syngas, we now have a significantly better understanding of the catalyst system and conditions of operation. Our progress on catalyst preparation, catalyst composition, catalyst operation and product recycle, taken together with detailed surface science and other analytical measurements suggest the following directions for future work:

1. Use high temperature catalysts to control selectivity among the alcohols

Higher alcohol formation increases with increasing temperature, due to two complementary kinetic and thermodynamic processes.

- Higher alcohol synthesis proceeds in a stepwise fashion from lower molecular weight building blocks; thus a higher proportion and absolute amount of higher alcohols are made as the rates of these consecutive reactions increase with increasing temperature.
- The thermodynamics of the methanol equilibrium disfavor methanol formation at higher temperatures. In this case, high temperature operation is actually an advantage, as methanol is best made separately (with high selectivities and yields) by conventional methanol catalysts; in higher alcohol synthesis, methanol formation should be minimized.

The overall result of high temperature operation is that less of the undesired methanol is made and the amount that is made is more rapidly converted to higher alcohols.

However, a temperature ceiling, where hydrocarbon formation becomes the thermodynamically favored product, is reached much above 450°C. This defines the operating window in the range 400-450°C.

2. Use higher pressures to increase reaction rate

The largest handle on overall reaction rate is pressure, not temperature. Increasing pressure results in an increased selectivity to total alcohols vs. hydrocarbons and in methanol production over higher alcohols.

3. Use a combination of higher temperatures and higher pressures to maximize higher alcohol yield

Based on the above discussion, the *combination* of higher temperatures and higher pressures will maximize higher alcohol yield.

4. Use inert high surface area conventional supports for higher activity catalysts

Higher alcohol production rates (and CO conversion) still fall below commercial targets. Surface science results show that the surface of the catalysts consists of alkali/zinc oxide supported on the spinel. Zinc oxide/alkali catalysts do show activity for higher alcohol synthesis, but are relatively inactive due to their correspondingly low surface area versus the spinels.

It is not unreasonable to suggest that supporting alkali/zinc oxide or palladium/alkali/zinc oxide on an inert, high surface area conventional support such as silica, alumina or titania would be equally as effective as supporting these materials on a spinel. Care should be taken to choose the support to be as non-acidic as possible to mitigate hydrocarbon formation.

5. Use basic supports

The proposed mechanism for branched higher alcohol synthesis over the high temperature catalyst is via base-catalyzed aldol condensation. The use of basic supports, such as magnesium oxide, or a lanthanide oxide, might provide additional help for this chemistry. The use of a basic support should also lower overall catalyst acidity, thus increasing alcohol selectivity over hydrocarbon formation. This will, in turn, allow higher catalyst operating temperatures.

6. Palladium is beneficial; other metals also may be useful

Palladium has been found to be a beneficial promoter, increasing higher alcohol production and allowing lower pressure operation. The use of other metals similar to palladium (near neighbors in the periodic table) might provide equivalent or better performance, e.g., ruthenium, rhodium, iridium or even platinum.

7. Recycle of alcohols for isobutanol synthesis is unlikely to be practical

Based on the alcohol feed/recycle experiments, n-propanol can be used as a feedstock or could be recycled to boost higher alcohol synthesis, but ethanol recycle is less successful. Note that *methanol* feed/recycle is NOT effective over our catalysts at high temperatures (>400°C).

4. Experimental Data

4.1 Copper-Containing Catalysts

We have investigated a family of copper-based low-temperature higher alcohol catalysts, which could be suitable for use in slurry reactors. We prepared the spinel oxide, $Co_xCu_{1-x}Cr_2O_4$, where x ranges from 0 to 1, using a coprecipitation method. It was hypothesized that the introduction of a Fischer-Tropsch metal such as Co to the Cu induces a classical ASF chain growth mechanism with primary alcohols as the main products. Unfortunately, this also gives rise to the parallel production of hydrocarbons. The active site for alcohol formation is thought to be highly divided Cu-Co clusters that are formed under reaction conditions.

A designed set of these copper/cobalt/chromium catalysts was tested at 275°C, 1000 psi, syngas ratio = 1:1, GHSV = 12,000. The materials consisted of a basic spinel structure AB_2O_4 where A = Cu/Co and B = Cr and are promoted with potassium. The Cu/Co ratio and the addition of palladium, platinum and silver were examined in a statistical design outlined in Tables 4.1-1 and 4.1-2. These formulations contain a good methanol synthesis metal (Cu) and a Fischer-Tropsch metal (Co) to promote carbon-carbon bond formation and chain growth. The expectation was that Cu/Co metal clusters are generated upon reduction that should catalyze the synthesis of higher alcohols.

Catalyst test results showed that these catalysts were very selective for methanol at 350°C and below (96-99%) and produced hydrocarbons and small amounts of higher alcohols at 400°C and above. These observations are consistent with a supported copper metal-based methanol catalyst operating at the lower temperatures and a spinel oxide support acting as the catalyst at the higher temperatures.

The hydrocarbon production follows a regular Anderson-Schulz-Flory distribution, indicating that Fischer-Tropsch chemistry is responsible for hydrocarbon formation. The catalysts deactivate rapidly, even at 275°C, probably due to sintering of the copper metal. A typical product profile is shown in Figure 4.1-1.

These materials were designed to produce higher alcohols at temperatures at or below 300°C. Detailed examination of the data (see Table 4.1-2) shows that the catalysts display a range of activities at 275°C, from completely inactive to up to 139 g/kg-hr of methanol. No higher alcohols were observed at this temperature.

Table 4.1-1. Designed Set to Examine Effect of Promoters on Cu/Co/Cr Catalysts.

Reference	Formula	KNO_3 wt% K	$Pd(NH_3)_4(NO_3)_2$ wt% Pd
10DAN103	$Co_1Cr_2O_4$	3	2.5
10DAN104	$Co_{0.25}Cu_{0.74}Cr_2O_4$	3	2.5
10DAN105	$Cu_1Cr_2O_4$	3	2.5

Reference	Formula	KNO_3 wt% K	$Pt(NH_3)_4(NO_3)_2$ wt% Pt
10DAN109	$Co_1Cr_2O_4$	3	2.5
10DAN107	$Co_{0.25}Cu_{0.74}Cr_2O_4$	3	2.5
10DAN108	$Cu_1Cr_2O_4$	3	2.5

Reference	Formula	KNO_3 wt% K	$AgNO_3$ wt% Ag
10DAN113	$Co_1Cr_2O_4$	3	2.5
10DAN111	$Co_{0.25}Cu_{0.74}Cr_2O_4$	3	2.5
10DAN112	$Cu_1Cr_2O_4$	3	2.5

Raising the temperature to 400°C results in an overall drop in total alcohol activity (70 – 80 g/kg-hr) and the production of small quantities of higher alcohols. Hydrocarbon production now becomes a serious inefficiency, with selectivities to alcohols only in the 16-69% range. Isobutanol comprises only a maximum of 19% of the alcohol product at a rate of around 12 g/kg-hr (Run 19, Table 4.1-2). Lowering the temperature back down to 275°C results in resumption of methanol production, but at rates reduced by as much as an order of magnitude, indicative of massive sintering of the copper.

One silver-promoted material (10DAN113) is an outstanding methanation catalyst at 400°C, producing 3597 g/kg cat-hr of total hydrocarbons with an ASF distribution at 90% syngas conversion (see Table 4.1-3). The formulation consists of a cobalt/chromium spinel promoted with 2.5 wt% silver and 3.0 wt% potassium. Industrial methanation to produce synthetic natural gas (SNG) is usually conducted with a nickel on alumina catalyst at 300-400°C and 200-400 psi.

Because these results were not as promising as our results with other families of catalysts, the study of copper-containing catalysts was not pursued further under this contract.

Table 4.1-2. Catalyst Results for Cu/Co Catalysts

Run #	Catalyst	Temp (°C)	ROH Sel (mol%)	ROH Act (g/kg-hr)	i-BuOH Act (g/kg-hr)	C3-C4 / Tot ROH*	i-BuOH / Tot ROH*
1	10DAN103	275	73	3	0	0	0
2		275	100	2.56	0	0	0
3		275	100	2.57	0	0	0
4	10DAN104	275	100	25.3	0	0	0
5		275	100	15.23	0	0	0
6		300	98.1	33.7	0	0	0
7		350	94.9	70.6	0.9	0.032	0.012
8		400	54.7	27.6	1.4	0.192	0.051
9		450	24.6	37.3	11.4	0.829	0.098
10	10DAN105	275	98.6	136.9	0	0	0
11		275	98.4	94.4	0	0	0
12		300	98.3	205.8	0	0	0
13		350	89.8	259.1	2.2	0.026	0.008
14		400	52.9	84.1	1.9	0.23	0.089
15		450	15.5	29.9	3.31	0.407	0.111
16	10DAN107	275	95.5	139.1	0	0	0
17		275	94.7	81.7	0	0	0
18		350	59.3	106	4.58	0.068	0.021
19		400	16.8	61	11.7	0.399	0.192
20		275	86.9	21.5	0	0	0
21	10DAN108	275	98.4	112.3	0	0	0
22		275	98.2	86.1	0	0	0
23		350	90.1	228.7	2.49	0.029	0.01
24		400	48.4	68.3	5.67	0.1935	0.09
25		275	100	10.6	0	0	0
26	10DAN109	275	0	0	0	0	0
27		350	13.7	20.6	0.7	0.23	0.035
28		400	50.6	73.9	6.15	0.237	0.083
29		275	92.5	20.6	2.33	0.455	0.113
30	10DAN 111	275	0	0	0	0	0
31		350	18.4	20.1	0	0.219	0
32		400	12.1	73.3	0	0.515	0
33		275	0	0	0	0	0
34	10DAN112	275	100	99.5	0	0	0
35		275	100	77.3	0	0	0
36		350	90.4	148.7	2.91	0.046	0.02
37		400	53	46.4	5.26	0.236	0.113
38		275	100	2.9	0	0	0
39	10DAN113	275	0	0	0	0	0
40		275	0	0	0	0	0
41		350	9.7	151.5	10	0.551	0.066
42		400	5	244.6	33.3	0.842	0.136
43		275	0	0	0	0	0

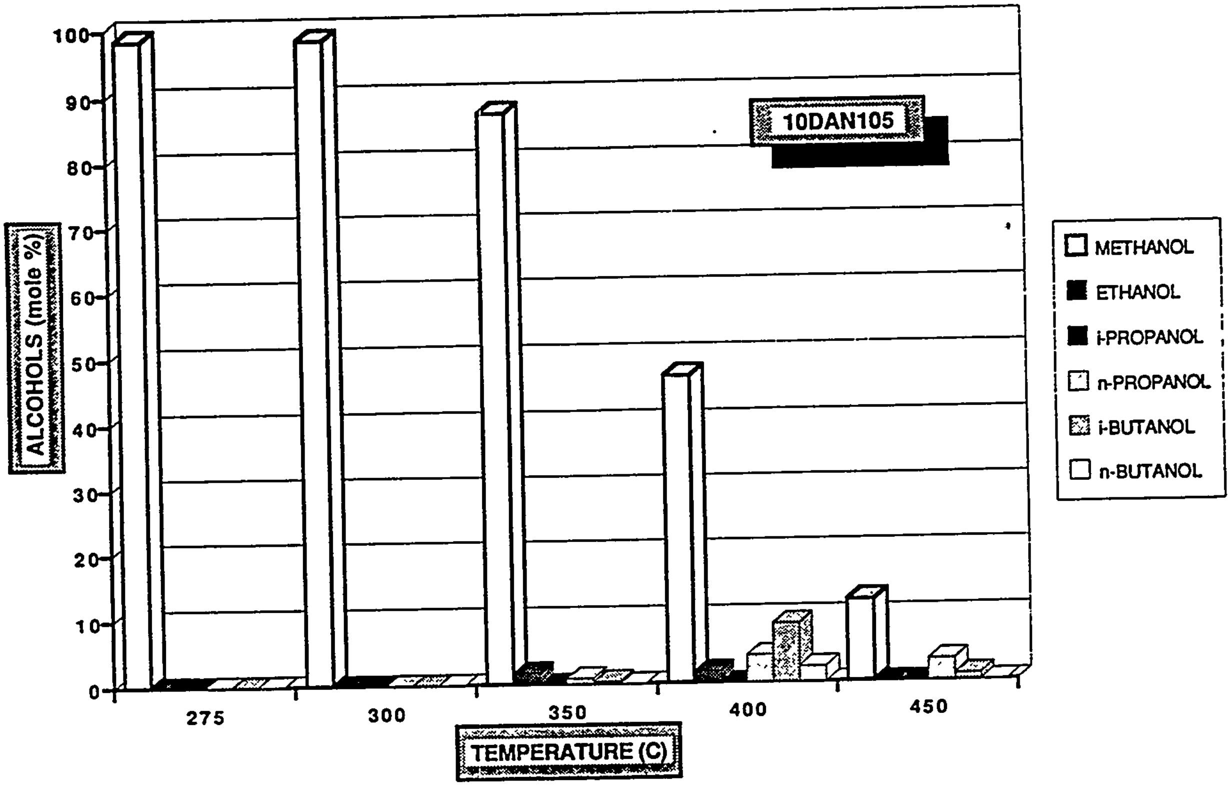
* By weight. Conditions: 1000 psig, $H_2/CO = 1$, GHSV 12000

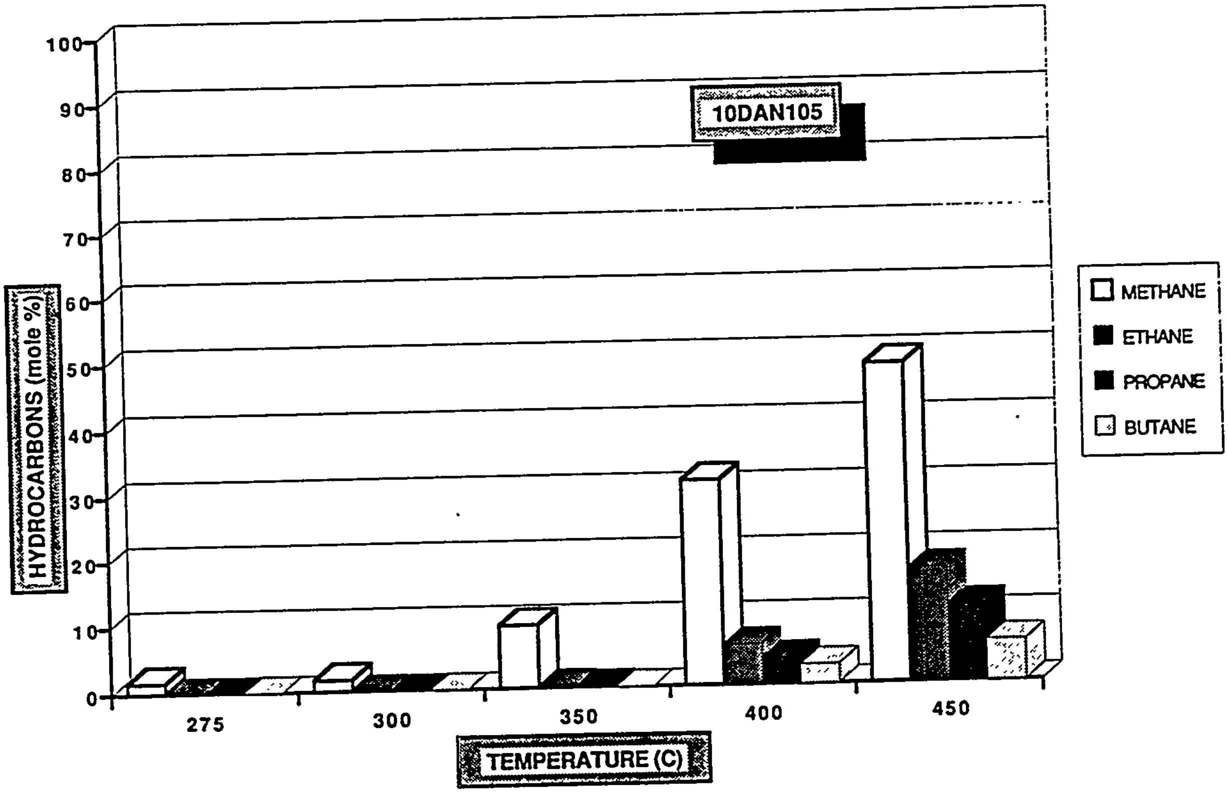
Table 4.1-3. Catalyst Results for Cu/Co Catalyst 10DAN113

Run #	Catalyst	Temp (°C)	HC Sel (mol%)	HC Act (g/kg-hr)	CH4 Sel (wt%)	C2H6 Sel (wt%)	C3+ Sel (wt%)
39	10DAN113	275	100	30	62	15.4	22.6
40		275	100	26.4	64.1	14.9	21
41		350	90.3	1026.6	61.2	10.8	28
42		400	95	3596.6	69.3	12.4	18.3
43		275	100	5.6	67.9	19.2	12.9

Conditions: 1000 psi, $H_2/CO = 1$, GHSV 12000

Figure 4.1-1. Product Selectivities for a Cu/Co/Cr Catalyst (10DAN105).





4.2 Isobutanol Catalyst Synthesis - Design #1

An area of research that we identified as having potential for further progress was that of modified "high-temperature" (~ 400°C operating temperature) methanol catalysts, which are essentially alkali-modified ZnCrO and ZnMnCrO systems. The major products are methanol and iso-butanol, but small amounts of ketones, secondary alcohols, ethers and hydrocarbons are also observed.

Our initial investigations on these catlysts focused on the catalyst preparation, and particularly on the influence of precipitation pH on surface area, porosity, and thermal characteristics of the resulting precipitate. Potentiometric titrations during coprecipitation were conducted to aid in improving this catalyst preparation technique. Potentiometric titrations were carried out during coprecipitation from aqueous solutions containing zinc, chromium, and manganese nitrates. Titration curves of pH versus CO_3^{2-}/total M^{n+} have shown, for example, that if a coprecipitation is to be carried out at a constant pH of 9, the rate of addition for the respective solutions should be such that the CO_3^{2-}/total metal ratio is 1.7.

Variables in catalyst preparation were examined by a fractional factorial designed experiment. The effect of precipitating pH, calcination temperature and time on surface area, porosity, and powder x-ray diffraction pattern were examined in a preliminary 3x3 designed set (#1). The immediate goal was to map the response surface of the crucial variables using fractional factorial experimental designs.

The 3x3 design was carried out to determine best values for the precipitating pH and the range for calcination temperature and time to obtain high surface area and porosity. The designed set as well as the analytical results are shown in Table 4.2-1.

The analytical data clearly showed that the BET surface area is dependent on the calcination temperature as expected. The pH has a very strong effect on the surface area. These two parameters are the main factors influencing the resulting surface area within this design. This is graphically shown in Figure 4.2-1.

Statistical analysis of the data yielded a model for the BET surface area, pore volume, and pore diameter in terms of pH and temperature. Importantly, calcination time was not a significant factor in any model. Numbers in parentheses below the equations are t-ratios, which indicate the relative significance of the corresponding term in the model.

$$\text{BET Surface Area} = 71.19 + \underset{(4.6)}{11.72(\text{pH}-9.33)} - \underset{(4.5)}{0.198(\text{Temp} - 400)} - \underset{(3.0)}{7.6(\text{pH}-9.33)^{**}2}$$

$$R^{**}2 = 0.922 \qquad RSD = 10.7$$

$$\text{Pore Volume} = \underset{(15.4)}{0.373 + 0.085(\text{pH}-9.33)} - \underset{(3.4)}{0.000317(\text{Temp} - 400)} - \underset{(4.3)}{0.0232(\text{pH}-9.33)^{**}2}$$

$$R^{**}2 = 0.922 \qquad \text{RSD} = 10.7$$

$$\text{Pore Diameter} = 24.86 + \underset{(4.3)}{0.057(\text{Temp} - 400)}$$

$$R^{**}2 = 0.722 \qquad \text{RSD} = 3.27$$

Therefore from these models (see Figures 4.2-2 and 4.2-3) the optimal pH to achieve the maximum surface area would be around 10.0-10.3. Calcination time is not a factor in these models and therefore could be removed as a variable in the fractional factorial design.

Table 4.2-1. Designed set (#1) and analytical results for the $Zn_{1.25}Mn_{0.16}Cr_{0.47}O_{2.1}$ catalyst.

Sample Reference	pH	Temp (°C)	Time (hr)	BET S.A. (m2/g)	Pore Volume (cc/g)	Pore Diameter (nm)
3DAN79	7.5	300.0	4.0	36.6	0.19	20.9
3DAN79	7.5	400.0	11.0	16.1	0.10	25.1
3DAN79	7.5	500.0	18.0	20.2	0.13	26.1
3DAN69	9.5	300.0	18.0	98.2	0.41	16.6
3DAN69	9.5	400.0	4.0	74.7	0.39	20.9
3DAN69	9.5	500.0	11.0	46.0	0.36	31.1
3DAN75	11.0	300.0	11.0	97.9	0.49	20.0
3DAN75	11.0	400.0	18.0	63.0	0.45	28.5
3DAN75	11.0	500.0	4.0	47.8	0.41	34.5

Figure 4.2-1. Surface area of the $Zn_{1.25}Mn_{0.16}Cr_{0.47}O_{2.1}$ catalyst as a function of precipitation pH and calcination temperature.

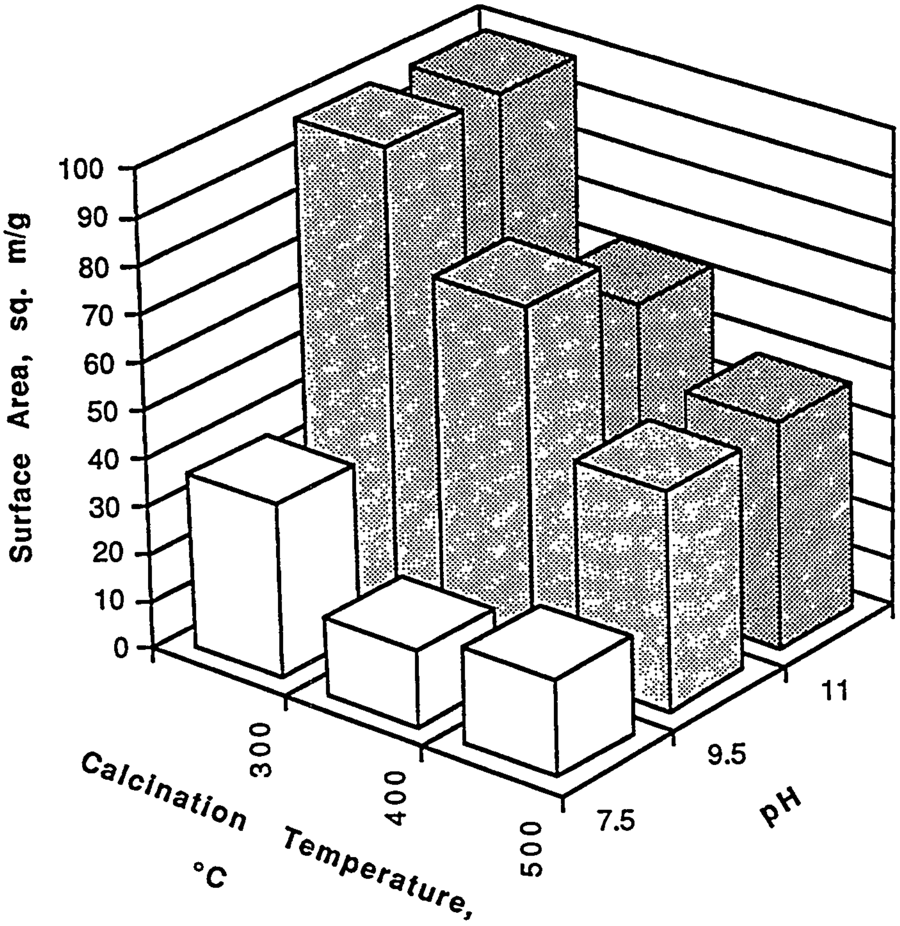


Figure 4.2-2. Effects of precipitation pH and calcination temperature on BET surface area of the $Zn_{1.25}Mn_{0.16}Cr_{0.47}O_{2.1}$ catalyst.

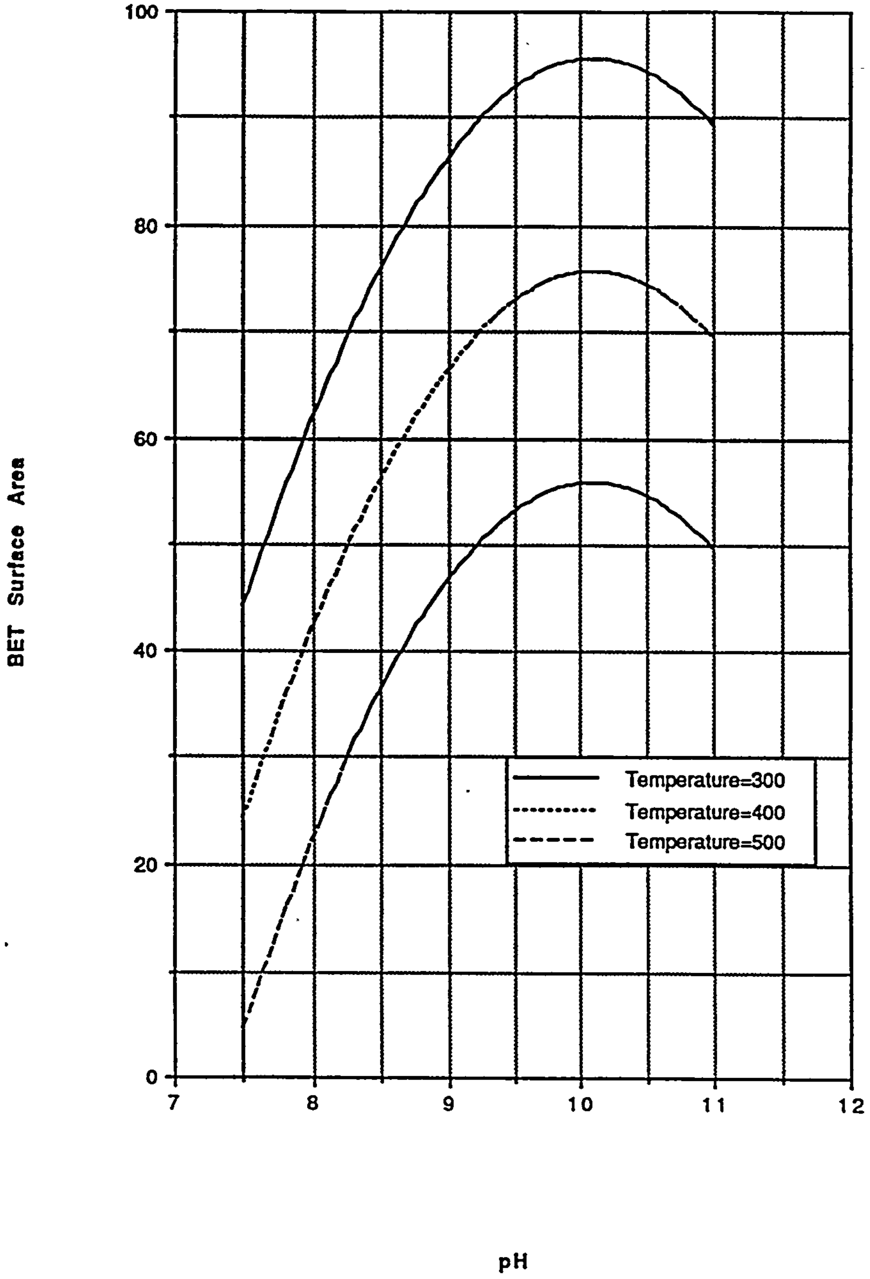
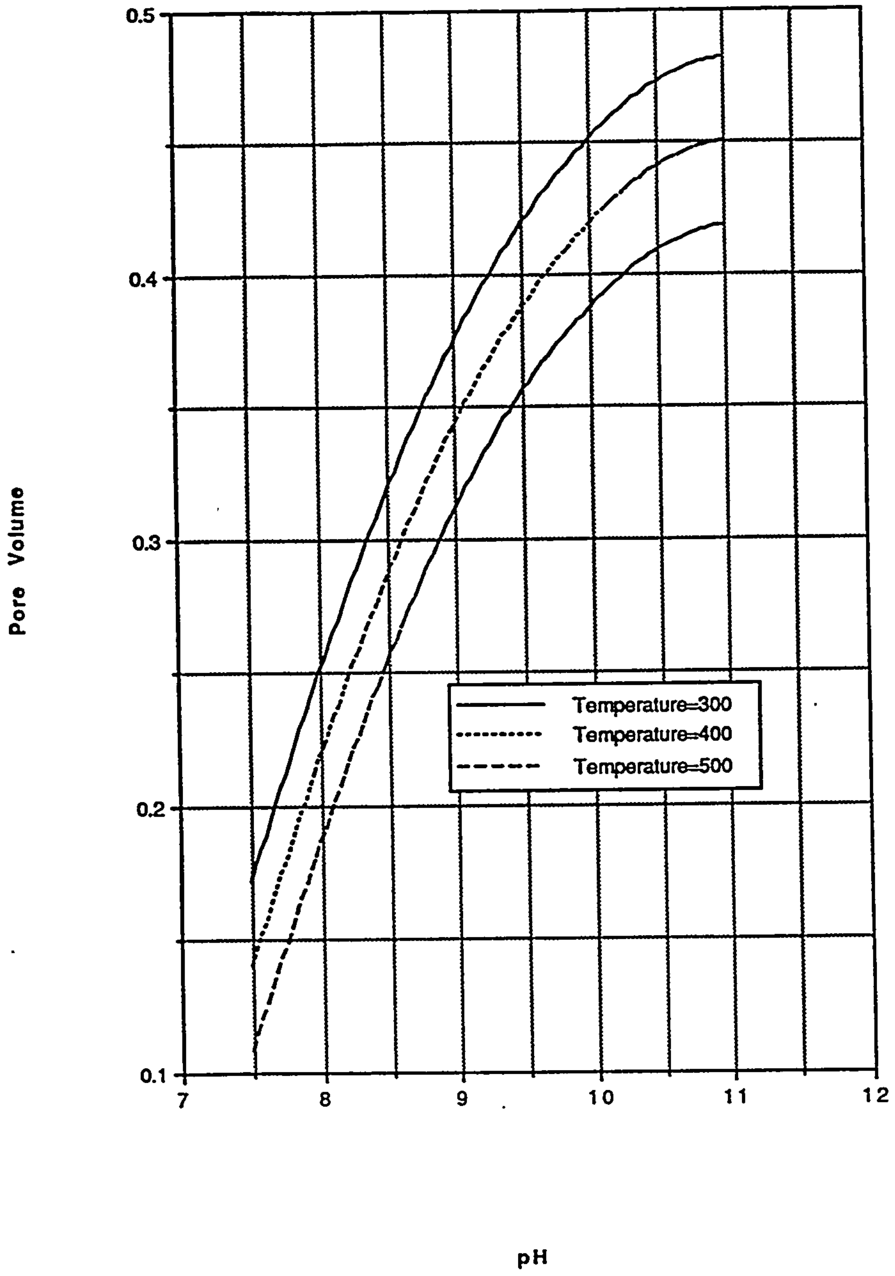


Figure 4.2-3. Effects of precipitation pH and calcination temperature on pore volume of the $Zn_{1.25}Mn_{0.16}Cr_{0.47}O_{2.1}$ catalyst.



4.3 Isobutanol Catalyst Formulation and Preparation - Design #2

The catalysts we chose to focus much of our effort on comprised a spinel oxide support (general formula AB_2O_4, where $A = M^{2+}$ and $B = M^{3+}$) promoted with various other elements. The spinel itself consists of the traditional zinc/chromium oxide formulation, modified by the partial substitution of chromium by manganese in the octahedral sites in the oxygen lattice. This reduces the overall acidity of the spinel (Mn^{3+} is less acidic than Cr^{3+}) and should reduce hydrocarbon formation, which is acid-catalyzed.

HAS requires at least two complementary, yet competing reactions: carbon-carbon bond formation and hydrogenation. In the copper metal-based, low-temperature system, carbon-carbon bond formation is thought to occur via a classical CO insertion mechanism, followed by hydrogenation. In contrast, the high-temperature catalysts utilize an aldol condensation mechanism to form the carbon-carbon bonds. The aldol reaction can proceed via acid or base catalysis. Clearly, in HAS, the base-catalyzed route will be preferred, as acid sites will promote hydrocarbon formation. Basic components included in the design are alkali (specifically potassium) and ceria (the rare earth oxides are basic materials).

The hydrogenation components necessary to produce higher alcohols included in this design are palladium and excess zinc. Copper metal cannot be used, as it sinters rapidly above 300°C. A fractional factorial design was constructed to determine the importance of each catalyst component.

A 16-run, 8-variable fractional factorial design (#2) was set up to study the variables in the catalyst formulation and preparation of an isobutanol catalyst system. Various metals were added to the standard spinel in the design: potassium, palladium and cerium, all thought to be beneficial for HAS. The addition of manganese (at the expense of chromium) and excess zinc in the make-up of the spinel itself was also examined. Other preparation variables included drying temperature, drying time, etc.

Our initial attempts to impregnate the $Zn_aCr_bMn_cO_x$ with K, Pd, and Ce were complicated by an incompatibility between $KHCO_2$ and $Ce(NO_3)_3$. In water the Ce^{3+} rapidly reacts with the HCO_2^- anion to form an insoluble salt. Upon seeing this, we looked up solubility constants of cerium salts and found that cerium oxalate is only very slightly soluble in water. This prevents using these materials for a simple one-step co-impregnation, but suggested the possibility of doing a sequential impregnation in which the salts are precipitated within the pores during the impregnation. This was tried on one sample in which the $Ce(NO_3)_3$ was first impregnated onto the support, followed by a second impregnation of the $KHCO_2$. The resulting catalyst visually looked fine, although there were areas of the metal oxide that were covered with a white powder. Other complicating issues in the original impregnation method were discovered and it was decided that a new impregnation method was needed.

Our new method still used the aqueous incipient wetness technique, but KNO_3, $Ce(NO_3)_3$ and $Pd(NH_3)_4(NO_3)_2$ were used. Due to the limited solubility of KNO_3, both the impregnating solution and the metal oxide are heated to slow down KNO_3 precipitation during the impregnation and drying steps.

The initial samples using potassium formate were submitted for catalyst performance testing. The catalysts were used to test for diffusional limitations by testing different mesh sizes of the catalyst. These results show that there are diffusional limitations but they are not large.

Data on the compositions and preparation procedures for these catalysts are listed in Tables 4.3-1 and 4.3-2.

Table 4.3-1 Catalyst Support Compositions

Chemical Formula of Support	Sample Reference (pH/Temp.°C/Time.Hr)	Zn	Mn	Cr	O	Zn / Mn+Cr	Mn / Cr	pH	Temp (°C)	Time (hr)	BET S.A. (m2/g)	Pore Volume (cc/g)	Pore Diameter (nm)
Zn2.0Mn.33Cr.67O3.5	10DAN60(9.0/400/11)	2	0.33	0.67	3.5	2.00	0.49	9.0	400.0	11.0	79.9	-.-	-.-
Zn3.0Mn0.50Cr0.50O4.5	3DAN134 (9.0/500/18)	3	0.5	0.5	4.5	3.00	1.00	9.0	500.0	18.0	35.6	0.250	24.4
	10DAN19(9.0/500/4)	3	0.5	0.5	4.5	3.00	1.00	9.0	500.0	4.0	55.3		
	10DAN19(9.0/300/18)	3	0.5	0.5	4.5	3.00	1.00	9.0	300.0	18.0	112.4		
	3DAN134 (9.0/300/4)	3	0.5	0.5	4.5	3.00	1.00	9.0	300.0	4.0	69.4	0.460	18.0
Zn3.0Cr1.0O4.5	10DAN22 (9.0/500/18)	3	0	1	4.5	3.00	0.00	9.0	500.0	18.0	39.0	0.097	26.1
	10DAN22(9.0/500/4)	3	0	1	4.5	3.00	0.00	9.0	500.0	4.0	43.0		
	10DAN22(9.0/300/18)	3	0	1	4.5	3.00	0.00	9.0	300.0	18.0	90.2		
	10DAN22 (9.0/300/4)	3	0	1	4.5	3.00	0.00	9.0	300.0	4.0	127.6	0.234	16.0
Zn2.0Mn.33Cr.67O3.5	3DAN132(9.0/400/11)	2	0.33	0.67	3.5	2.00	0.49	9.0	400.0	11.0	80.1		
Zn1.0Mn.50Cr.50O4.5	10DAN24 (9.0/500/18)	1	0.5	0.5	4.5	1.00	1.00	9.0	500.0	18.0	35.3	0.243	26.8
	3DAN127(9.0/500/4	1	0.5	0.5	4.5	1.00	1.00	9.0	500.0	4.0	43.6		
	3DAN127(9.0/300/18	1	0.5	0.5	4.5	1.00	1.00	9.0	300.0	18.0	96.2		
	10DAN24 (9.0/300/4)	1	0.5	0.5	4.5	1.00	1.00	9.0	300.0	4.0	114.1	0.240	8.5
Zn1.0Cr1.0O2.5	11DAN42 (9.0/500/18)	1	0	1	2.5	1.00	0.00	9.0	500.0	18.0	1.6	.0.005	11.7
	11DAN42(9.0/500/4)	1	0	1	2.5	1.00	0.00	9.0	500.0	4.0	3.3		
	10DAN26(9.0/300/18)	1	0	1	2.5	1.00	0.00	9.0	300.0	18.0	63.7		
	10DAN26 (9.0/300/4)	1	0	1	2.5	1.00	0.00	9.0	300.0	4.0	77.4	0.027	5.4
Zn2.0Mn.33Cr.67O3.5	10DAN28 (9.0/400/11)	2	0.33	0.67	3.5	2.00	0.49	9.0	400.0	11.0	77.1		

Table 4.3-2. Catalyst Composition and Metal Loadings

Catalyst	Chemical	Support	K Loading	KNO3	Pd Loading	Pd(NH3)4(NO3)2	Ce Loading	Ce(NO3)3	Reduction
Reference	Formula of Support	Reference	(umole/m2)	(g/5g cat)	(umole/m2)	(g/5g cat)	(umole/m2)	(g/5g cat)	Temp
		(pH/Temp.°C/Time.Hr)							
10DAN66	Zn2.0Mn.33Cr.67O3.5	10DAN60(9.0/400/11)	6.65	0.26872	2.5	0.29827	8.3	1.44038	450
10DAN53	Zn3.0Mn0.50Cr0.50O4.5	3DAN134 (9.0/500/18)	13.3	0.23957	5	0.26592	16.6	1.28414	600
10DAN47		10DAN19(9.0/500/4)	13.3	0.37179	0	0.00000	0	0.00000	300
10DAN54		10DAN19(9.0/300/18)	0	0.00000	5	0.83887	0	0.00000	300
10DAN52		3DAN134 (9.0/300/4)	0	0.00000	0	0.00000	16.6	2.50197	600
10DAN65	Zn3.0Cr1.0O4.5	10DAN22 (9.0/500/18)	0	0.00000	5	0.29098	16.6	1.40520	300
10DAN58		10DAN22(9.0/500/4)	0	0.00000	0	0.00000	0	0.00000	600
10DAN48		10DAN22(9.0/300/18)	13.3	0.60653	5	0.67323	0	0.00000	600
10DAN49		10DAN22 (9.0/300/4)	13.3	0.85776	0	0.00000	16.6	4.59776	300
10DAN50	Zn2.0Mn.33Cr.67O3.5	3DAN132(9.0/400/11)	6.65	0.26918	2.5	0.29878	8.3	1.44285	450
10DAN59	Zn1.0Mn.50Cr.50O4.5	10DAN24 (9.0/500/18)	0	0.00000	0	0.00000	0	0.00000	600
11DAN45		3DAN127(9.0/500/4	0	0.00000	5	0.32540	16.6	1.57139	300
11DAN44		3DAN127(9.0/300/18	13.3	0.64649	0	0.00000	16.6	3.46535	300
10DAN51		10DAN24 (9.0/300/4)	13.3	0.76746	5	0.85186	0	0.00000	600
3DAN90	Zn1.0Cr1.0O2.5	11DAN42 (9.0/500/18)	13.3	0.01076	0	0.00000	0	0.00000	300
10DAN67		11DAN42(9.0/500/4)	13.3	0.02190	5	0.02431	16.6	0.11739	600
10DAN56		10DAN26(9.0/300/18)	0	0.00000	0	0.00000	16.6	2.29582	600
10DAN55		10DAN26 (9.0/300/4)	0	0.00000	5	0.57766	0	0.00000	300
10DAN57	Zn2.0Mn.33Cr.67O3.5	10DAN28 (9.0/400/11)	6.65	0.21565	2.5	0.28771	8.3	1.38938	450

Basis for Design #2

The designed set consisted of a total of 22 separate runs divided into a center-point formulation, whose preparation was repeated three times (catalysts 10-DAN-50, 10-DAN-57 and 10-DAN-66), repeat tests of two of these center-point preparations (10-DAN-50R and 10-DAN-57R) and sixteen different catalyst formulations. The results are displayed in Table 4.3-3.

Center-Point Catalysts

The center-point formulations have all the promoters present in intermediate amounts and show reasonable agreement for two out of the three: 10-DAN-57 and 10-DAN-66. In contrast, 10-DAN-50 is less active and produces a significant amount of C_3 products. This C_3 split contains significant quantities of both the normal and branched products (n-propanol and isopropanol), suggesting some difference in the preparation. A likely scenario is incomplete incorporation of all of the promoters; 10-DAN-50 was made early in the campaign and may have suffered as a consequence of the learning process.

Alcohol activities for the two "good" catalysts are 6-7 lb/ft^3-hr (96-112 g/kg-hr),with selectivities, on a carbon dioxide-free basis, of 57-67%. The amount of isobutanol produced on a wt% basis is 18-20% of the total alcohols (11% on a mol% basis), giving isobutanol productivities of 17-22 g/kg-hr.

Scope of the Design

The results are summarized in Table 4.3-3. The alcohols produced are almost exclusively methanol and isobutanol. The isobutanol is believed to be formed because the HAS proceeds predominately via an aldol condensation mechanism over the promoted spinel oxide catalysts. The condensation occurs via beta-addition; thus the reaction terminates at the branched 2-methyl-1-propanol (isobutanol) product. A wide range of activities (0.39-10.9 lb/ft^3-hr, 6-174 g/kg-hr), total selectivities to alcohols (26-95%) and specific selectivities to isobutanol (0-34%) are observed. A number of the catalysts tested are highly selective to total alcohols (85-95%) with between 25 and 40% of the alcohols being C_2's or higher. Isobutanol selectivities of 19-34% are common. This indicates that the design limits chosen were wide enough to give meaningful models.

Design Models

The models derived from this set (see Table 4.3-4) are of variable quality. The model for C_4 alcohols (isobutanol) selectivity is the best of the group and the models for activity and selectivity to C_3+C_4 alcohols follow the same trend, thus giving a reasonable indication of promoter trends. All three models show the beneficial effect of palladium addition and the deleterious effect of potassium and cerium *at the levels added.* The presence of manganese in the parent spinel promotes the formation of isobutanol. A higher catalyst calcination temperature has a weak, negative effect on isobutanol selectivities and selectivities to C_3+C_4 alcohols.

Alcohol Product Distribution

Twelve of the 22 catalysts make significant quantities of isobutanol (14 wt% or greater). Four catalysts (highlighted in Table 4.3-3) have been selected for illustrative purposes. The alcohol distributions for these catalysts appear in Figures 4.3-1 – 4.3-4.

- 3-DAN-90: (see Figure 4.3-1). This catalyst is the most active of the set and the least selective for total alcohols, producing hydrocarbons instead. The formulation consists of the basic zinc/chromium spinel support with added potassium and gives a unique alcohol distribution, with the major components being the propanols (isopropanol and n-propanol). The ratio of branched to normal product is also unusual, with nearly a 1:1 split between iso- and n-propanol. The usual split is roughly 10:1.

- 10-DAN-47 and 10-DAN-52: (see Figures 4.3-2 and 4.3-3). These two formulations consist of a zinc/chromium/manganese spinel with excess zinc as the basis. Additionally, 10-DAN-47 has potassium and 10-DAN-52 has cerium. Both exhibit lower activities than the mean, are very selective to alcohols (93-94%), and produce relatively large quantities of methanol as the major alcohol product. Notice once more that potassium addition appears to favor products in the C_2-C_4 range (contrast this with 10-DAN-52).

- 10-DAN-54: (see Figure 4.3-4). This formulation is identical to 10-DAN-47 and 10-DAN-52, except palladium is the additional promoter instead of potassium or cerium. The catalyst is more active than its two counterparts, slightly less selective to total alcohols (but still a very respectable 86%) and the most selective of the whole design for isobutanol (34 wt%).

The results of the designed set indicate that the presence of potassium was not an important factor in the selectivity of the catalysts. This surprising result led us to wonder if there was alkali metal contamination in these catalysts. Indeed, X-ray fluorescence showed that there was potassium in the Zn-Cr-Mn oxide that had not been impregnated with potassium. Due to the usual matrix effects, quantitative numbers could not be determined with this technique. The rather insoluble nature of the finished catalysts complicated initial ICP analyses. Therefore, three unfired samples of the Zn-Cr-Mn oxides were used in ICP-OES measurements. These ICP-OES analyses showed that the Zn-Cr-Mn oxides contained 0.9 to 2.5% bulk potassium.

This presence of the potassium impurity explains the lack of strong dependence in the selectivity and activity on potassium loadings of the catalysts. The large variation in the levels of the potassium contamination could also explain why the catalytic data were so difficult to model. Even with the error that the uncontrolled levels of potassium contamination introduced in our results, statistical analysis of the data showed that Pd increased the total alcohol production and selectivity to C_3 and C_4 alcohols.

To further clear up the effects of K, Pd, and Ce on the activity and selectivity of these catalysts, $Zn_3Mn_{.5}Cr_{.5}O_{4.5}$ and $Zn_1Cr_1O_{2.5}$ were prepared using ammonium hydroxide in the coprecipitation step. Four catalysts — $Pd_bZn_3Mn_{.5}Cr_{.5}O_{4.5}$, $Pd_bZn_1Cr_1O_{2.5}$, $K_aPd_bCe_cZn_3Mn_{.5}Cr_{.5}O_{4.5}$, and $K_aPd_bCe_cZn_1Cr_1O_{2.5}$ —were prepared from this alkali-free material. The first two catalysts are repeats of the best two catalysts in the fractional factorial design, based on rate and selectivity to total alcohols. Results of tests on these catalysts are reported in the following section.

Table 4.3-3. Catalyst Formulation Designed Set (#2) Results

CATALYST SAMPLE	ACTIVITY [1]	SELECTIVITY TO ALCOHOLS [2]	C1 (wt%)	C2 (wt%)	C3 (wt%) [3]	C4 (wt%)[4]
10DAN50	4.79	87.88	55.32	0.00	16.34	16.22
10DAN50R	3.63	70.11	52.14	0.00	11.60	6.37
10DAN57	6.77	93.53	67.32	0.00	3.72	20.09
10DAN57R	6.74	83.99	65.74	0.00	1.76	16.09
3DAN90	***10.86***	***26.00***	***4.64***	***3.50***	***13.50***	***4.37***
11DAN45	5.93	91.44	64.43	0.53	2.65	23.83
11DAN44	0.85	65.00	47.86	0.00	9.09	8.05
10DAN47	**3.69**	**94.78**	**81.32**	**1.62**	**6.55**	**5.29**
10DAN54	**6.89**	**85.59**	**41.87**	**1.51**	**5.08**	**34.38**
10DAN49	0.39	69.78	57.79	0.00	11.99	0.00
10DAN55	7.96	89.93	55.34	1.65	9.32	23.61
10DAN52	**3.05**	**93.62**	**81.92**	**0.00**	**1.97**	**9.72**
10DAN53	4.87	79.28	70.01	0.00	0.00	9.26
10DAN48	4.20	80.80	54.07	0.00	9.22	17.52
10DAN51	6.33	80.51	57.77	0.00	1.85	19.01
10DAN56	5.72	96.31	71.17	0.00	3.46	19.25
10DAN24	3.81	92.61	63.31	0.00	4.43	24.88
10DAN66	6.66	78.43	57.69	0.00	2.00	18.20
10DAN65	4.45	74.61	64.53	0.00	1.82	8.26
10DAN58	2.79	49.67	32.32	0.00	6.46	10.89
10DAN59	5.90	65.06	49.11	0.00	1.73	14.22
10DAN67	3.23	85.95	72.94	0.00	8.23	4.78

[1] ACTIVITY= lbs/ft3-hr

[2] SELECTIVITY= wt%

[3] product is almost exclusively n-propanol

[4] product is almost exclusively iso-butanol

Table 4.3-4. Design Models from Catalyst Design #2

$$\text{Activity} = 4.59 - \underset{(2.5)}{0.127*\text{K}} + \underset{(3.3)}{0.447*\text{Pd}} - \underset{(1.9)}{0.0773*\text{Ce}}$$

$R^2 = 0.542$

Total Alcohols = No Model Found

$$\text{C3+C4 Alcohols} = 38.9 - \underset{(2.3)}{0.555*\text{K}} + \underset{(1.9)}{1.181*\text{Pd}} - \underset{(2.6)}{0.48*\text{Ce}} - \underset{(2.3)}{0.0354}*(\text{Calcination Temperature})$$

$R^2 = 0.561$

$$\text{C1+C2 Alcohols} = 54.7 + \underset{(2.0)}{0.687*\text{Ce}}$$

$R^2 = 0.174$

C3 Alcohol = No Model Found

$$\text{C4 Alcohol} = 27.0 - \underset{(4.1)}{0.8*\text{K}} + \underset{(3.2)}{1.61*\text{Pd}} - \underset{(2.5)}{0.378*\text{Ce}} + \underset{(2.2)}{11.4*\text{Mn}} - \underset{(2.3)}{0.029}*(\text{Calcination Temperature})$$

$R^2 = 0.726$

Figure 4.3-1. Product Distribution for 3DAN90 (Spinel Support plus Potassium)

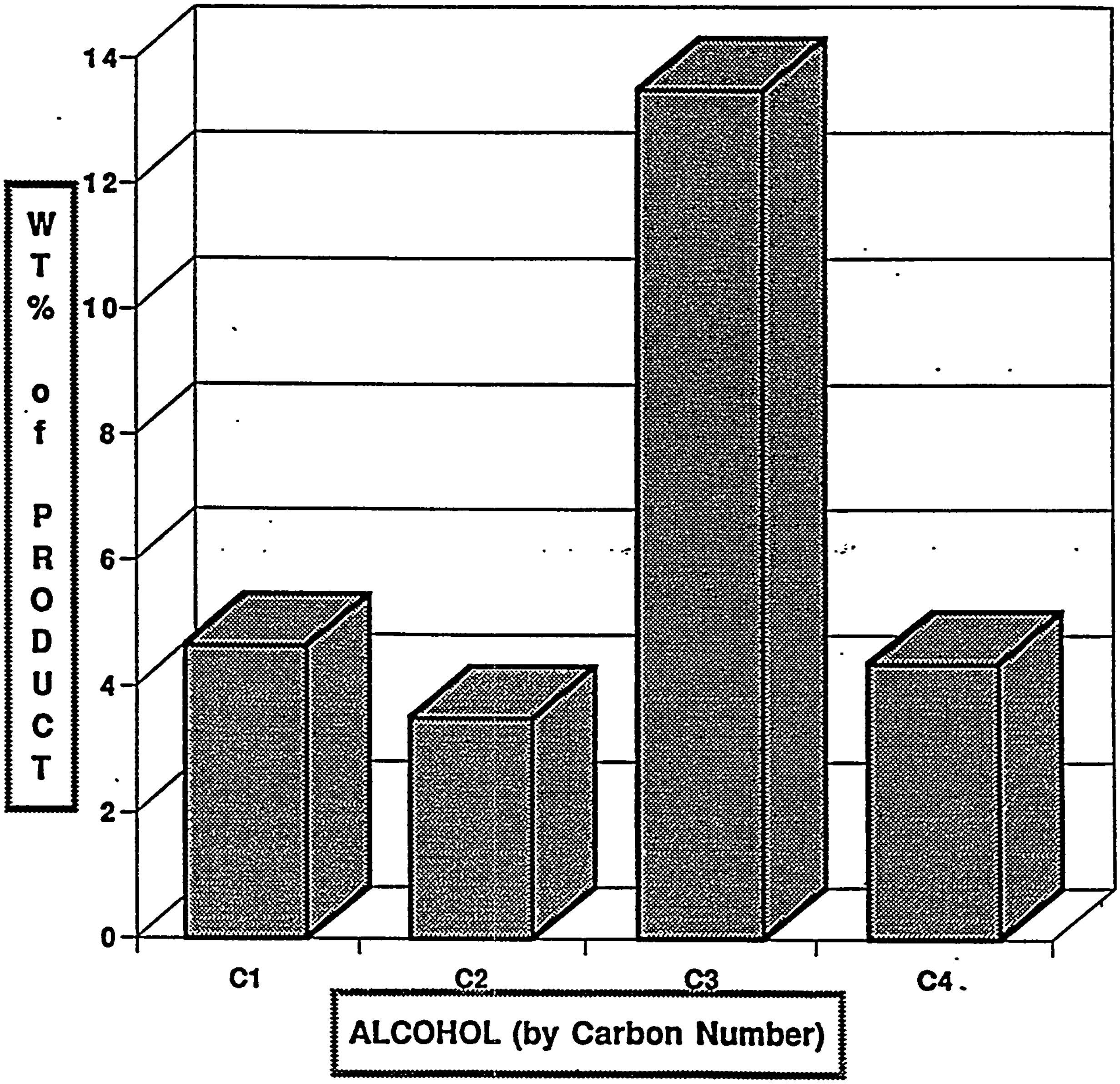


Figure 4.3-2. Product Distribution for 10DAN47 (Zn, Cr, Mn Spinel with Excess Zn plus Potassium)

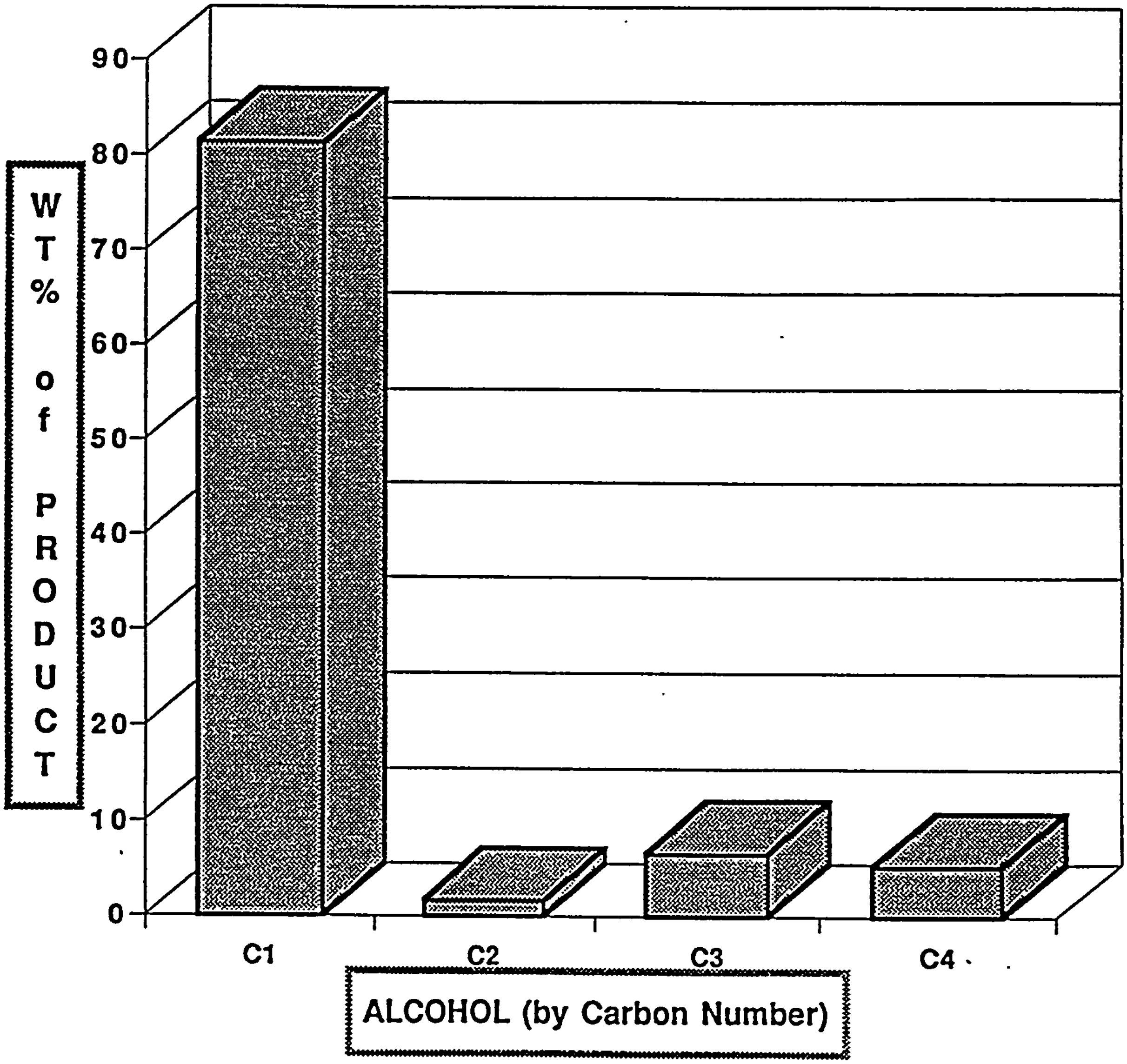


Figure 4.3-3. Product Distribution for 10DAN52 (Zn, Cr, Mn Spinel with Excess Zn plus Cerium)

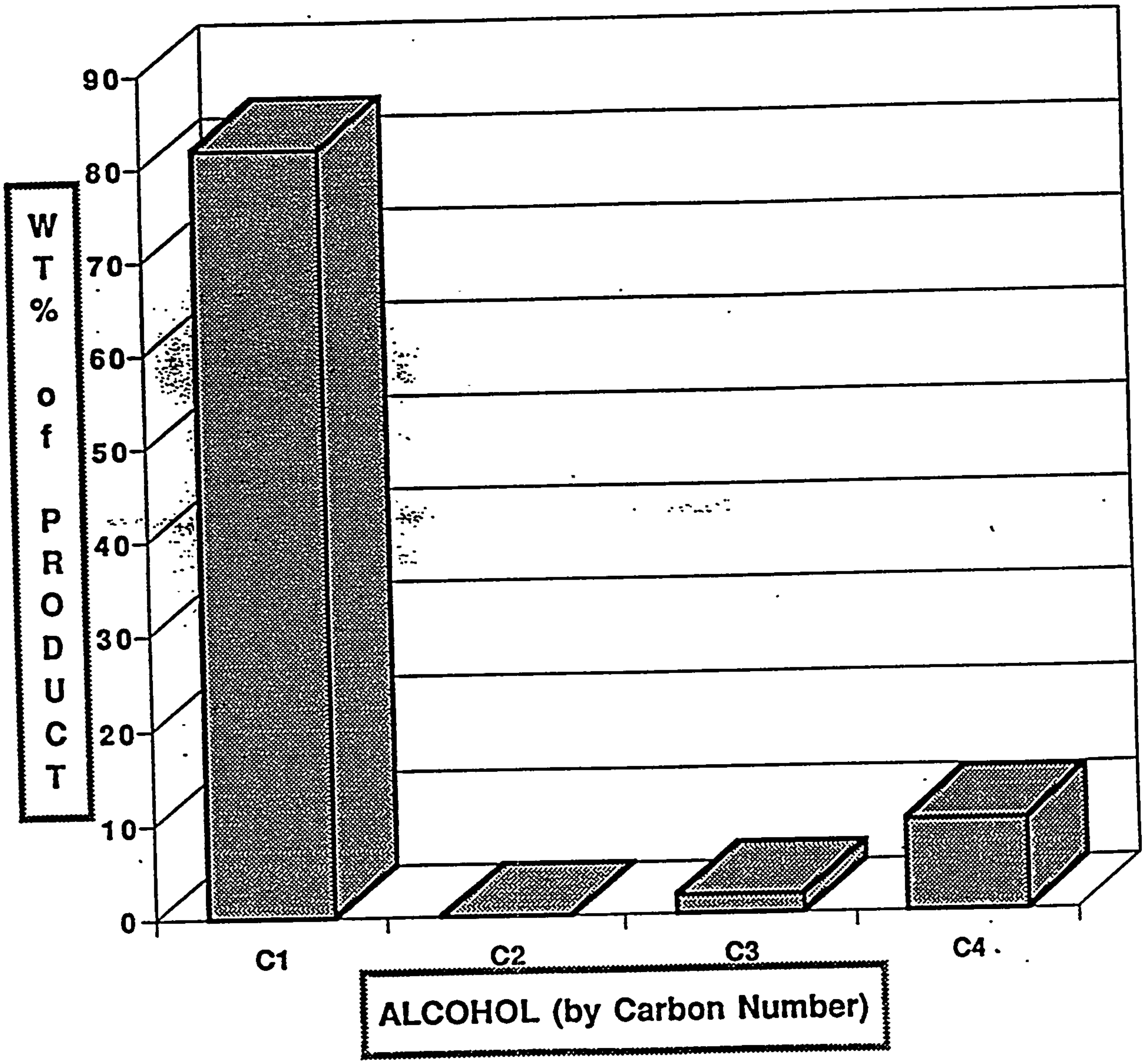
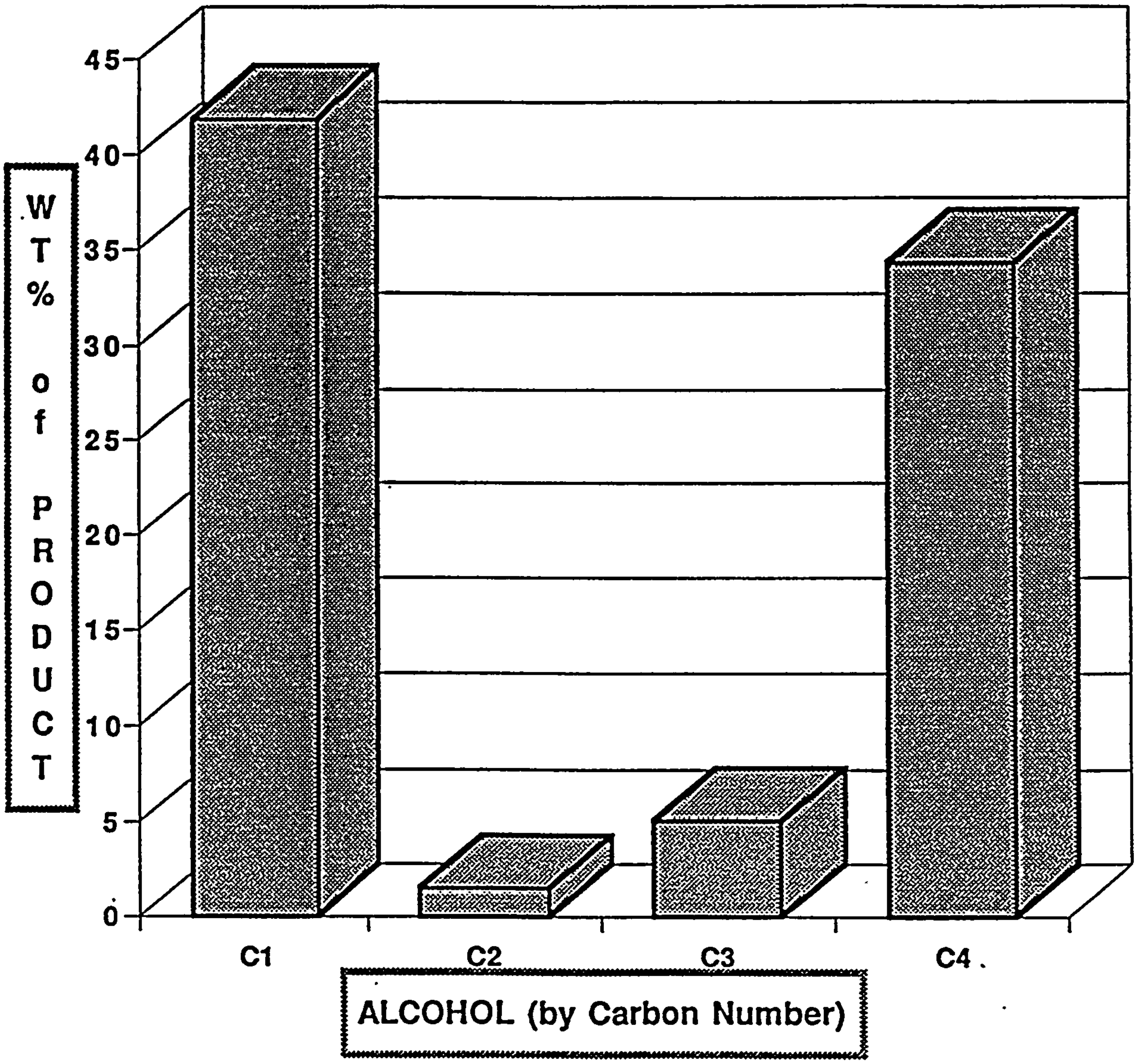


Figure 4.3-4. Product Distribution for 10DAN54 (Zn, Cr, Mn Spinel with Excess Zn plus Palladium)



4.4 "Potassium-Free" Isobutanol Catalysts

Since ICP analyses of our nominally potassium-free catalysts showed the presence of up to 2.5 wt% potassium,we prepared and tested four catalysts made via a "potassium-free" preparation method. The preparation procedure used ammonium hydroxide instead of potassium carbonate in the precipitation step. It is quite possible that the potassium inadvertently carried over from the preparation was acting as a promoter in the resulting catalysts. The new catalysts are based on two specific formulations from the previous designed set (10DAN54 and 10DAN 55) which contain only palladium. Both "potassium-free" formulations were prepared with palladium only and also with an additional K/Ce promoter package, making a total of four new catalysts (see Table 4.4-1). The results appear in Table 4.4-2 and show that the two formulations made via the "potassium-free" method, and containing no added K/Ce promoters, are significantly less selective for isobutanol. The results confirm our belief that the original formulations, thought to be "potassium-free", do indeed require added potassium to promote HAS.

Table 4.4-1. "Potassium-Free" Catalyst Compositions

Catalyst	Pd (g/5g cat)	K (g/5g cat)	Ce (g/5g cat)
Support Composition: Zn 3.0 / Mn 0.5 / Cr 0.5 / O 4.5			
10DAN94	0.8394	0	0
10DAN95	0.8385	0.379	2.0281
10DAN54	0.835	0	0
Support Composition: Zn 1.0 / Cr 1.0 / O 2.5			
10DAN96	0.5792	0	0
10DAN97	0.5791	0.2634	1.3971
10DAN55	0.5777	0	0

Table 4.4-2. Tests of "Potassium-Free" Catalysts

Run #	Catalyst	Temp (°C)	ROH Sel (mol%)	ROH Act (g/kg-hr)	i-BuOH Act (g/kg-hr)	C3-C4 / Total ROH*	i-BuOH / Total ROH*
	10DAN54	400	73.4	81	30	0.461	0.344
	10DAN55	400	na	88	19	0.366	0.216
1	10DAN94	400	49.1	112.4	9.3	0.09	0.083
2	10DAN95	400	40.6	97.1	16.6	0.214	0.171
3	10DAN96	400	20.7	52.2	6.3	0.177	0.121
4	10DAN97	400	56.5	127.1	38.2	0.342	0.302

*By weight

Conditions: 1000 psig, $H_2/CO = 1$, GHSV 12000

We later made further attempts to prepare an alkali-free mixed-metal oxide material to use for further catalyst tests. ICP-OES analyses of the mixed metal oxides prepared by ammonium hydroxide precipitation are shown in Table 4.4-3. It is clear that the NH_4OH base coprecipitations did not yield the desired materials (Table 4.4-3, no.1-5). Both the Zn/(Cr+Mn) and Mn/Cr molar ratios were always lower than the expected values. Examination of the coprecipitation and washing procedure showed that a significant amount of zinc remained in the mother liquor and decreasing levels of zinc were washed out in subsequent washes (Table 4.4-4). We speculate that water-soluble diammine or tetraammine complexes are being formed.

We tried using ammonium carbonate as the precipitating base. The precipitations were carried out at a pH significantly lower than that used in the case of the ammonium hydroxide (pH 8.0 vs. 11.0). The amount of free ammonia would be drastically reduced and it was hoped that the formation of soluble ammine complexes would be minimized. The results (Table 4.4-3, no. 6-9) showed that the precipitations using ammonium carbonate were also complicated by soluble complex formation. Surprisingly there were significant amounts of Cr and Zn present in the mother liquor. Atomic absorption showed that potassium was still present at ppm levels in the precipitate, probably due to low levels of alkali impurities in the ammonium carbonate and metal nitrates.

We explored different procedures to wash out the potassium contamination resulting from the KOH/K_2CO_3 precipitation. We have been able to consistently lower the potassium levels down to ~100-300 ppm as measured by atomic absorption (Tables 4.4-3 and 4.4-4). This may be considered a low level but we previously have shown that the potassium will concentrate on the surface of the catalyst during the firing and reduction of the catalyst.

We have tried using a very dilute zinc nitrate solution in the final wash with the hope that ion exchange would aid in the potassium removal. The ICP-OES study (Table 4.4-4, no. 6) showed that this was not successful. The final potassium level was not significantly lower than in the normal washing procedure. The zinc content of the final extrudate was much higher than the targeted value. Apparently we did not get simple ion exchange during the washing.

Since catalyst test results clearly indicate that potassium at specific levels is beneficial for overall performance, no further effort was directed toward removing it from the catalyst preparation procedures.

Table 4.4-3. Analytical results (ICP-OES) for precipitated metal oxides, wt% and molar ratios

11DAN69
1 - Zn3MnCr.5-NH4OH

	Precip	Expected
Cr	11.0	
Mn	14.0	
K	0.0	
Zn	26.0	
Zn/(Cr+Mn)	1.04	2.00
Mn/Cr	1.27	2.00

11DAN73
2 - Zn3Mn1.5Cr-NH4OH

	Precip	Expected
Cr	15.0	
Mn	15.0	
K	0.0	
Zn	15.0	
Zn/(Cr+Mn)	0.50	1.20
Mn/Cr	1.00	1.50

11DAN65
3 - ZnMn1.5Cr - NH4OH

	Precip	Expected
Cr	17.0	
Mn	17.0	
K	0.0	
Zn	14.0	
Zn/(Cr+Mn)	0.41	0.40
Mn/Cr	1.00	1.50

11DAN59
4 - Zn3MnCr-NH4OH

	Precip	Expected
Cr	17.0	
Mn	16.0	
K	0.0	
Zn	19.0	
Zn/(Cr+Mn)	0.58	1.50
Mn/Cr	0.94	1.00

11DAN62
5 - ZnMnCr.5 - NH4OH

	Precip	Expected
Cr	14.0	
Mn	17.0	
K	0.0	
Zn	15.0	
Zn/(Cr+Mn)	0.48	0.67
Mn/Cr	1.21	2.00

10DAN126
6 - Zn2MnCr-(NH4)2CO3

	Precip	Expected
Cr	16.0	
Mn	14.0	
K	0.0	
Zn	3.0	
Zn/(Cr+Mn)	0.10	1.00
Mn/Cr	0.88	1.00

10DAN114
7 - ZnMn1.5Cr.5-(NH4)2CO3

	Precip	Expected
Cr	11.0	
Mn	19.0	
K	0.0	
Zn	13.0	
Zn/(Cr+Mn)	0.43	0.50
Mn/Cr	1.73	3.00

10DAN119
8 - ZnMnCr-(NH4)2CO3

	Precip	Expected
Cr	19.0	
Mn	17.0	
K	0.0	
Zn	13.0	
Zn/(Cr+Mn)	0.36	0.50
Mn/Cr	0.89	1.00

10DAN123
9 - Zn3Mn1.5Cr.5-(NH4)2CO3

	Precip	Expected
Cr	12.0	
Mn	16.0	
K	0.0	
Zn	12.0	
Zn/(Cr+Mn)	0.43	1.50
Mn/Cr	1.33	3.00

11DAN92
10 - ZnMnCr.5-KOH/K2CO3

	Precip	Expected
Cr	2.0	
Mn	4.4	
K	375ppm	
Zn	4.8	
Zn/(Cr+Mn)	0.75	0.67
Mn/Cr	2.20	2.00

Table 4.4-4. Analytical results (ICP-OES) for metal oxide precipitation studies, including solids and washes.

1 - Zn3MnCr - NH4OH (ppm)			11DAN85			
	Precip/orig	Precip/wash1	Precip/wash2	Mother Liq	Wash 1	Wash 2
Cr	110.0	250.0	80.0			
Mn	110.0	240.0	70.0			
K	<100	<100	<100	140.0	<100	<100
Zn	390.0	770.0	240.0	1700.0	720.0	70.0
Zn/(Cr+Mn)	1.77	1.57	1.60			
Mn/Cr	1.00	0.96	0.88			

2 - Zn3MnCr - NH4OH		11DAN86					
	Precip/orig	Precip/wash1	Precip/wash2	Mother Liq	Wash 1	Wash 2	Wash 3
Cr	11.3	11.9	11.7	1ppm	<1ppm	<1ppm	<1ppm
Mn	12.2	12.8	12.6	1ppm	<1ppm	<1ppm	<1ppm
K	<100ppm	<100ppm	<100ppm	<100ppm	<100ppm	<100ppm	<100ppm
Zn	36.6	36.8	36.0	0.2	800ppm	100ppm	<1ppm
Zn/(Cr+Mn)	1.56	1.49	1.48				
Mn/Cr	1.08	1.08	1.08				

3 - ZnMnCr - (NH4)2CO3		11DAN98						
	Precip/orig	Precip/wash1	Precip/wash2	wet cake	Mother Liq	Wash 1	Wash 2	Wash 3
Cr	3.2	2.9	4.7	3.8	87 ppm	1.3 ppm	<ppm	<1
Mn	6.9	6.5	10.0	8.4	<ppm	<ppm	<ppm	<1
K	8.5 ppm	20 ppm ±10	25 ppm	16ppm	4 ppm	<ppm	<ppm	<1
Zn	3.7	3.4	5.2	4.4	540 ppm	<ppm	<ppm	<1
Zn/(Cr+Mn)	0.37	0.36	0.35	0.36				
Mn/Cr	2.16	2.24	2.13	2.20				

4 - ZnMnCr - KOH/K2CO3		11DAN89						
	Precip/orig	Precip/wash1	Precip/wash2	Precip/wash3	Mother Liq	Wash 1	Wash 2	Wash 3
Cr	1.9	2.3	3.4	2.6	7.8ppm	1.7ppm	1ppm	<1ppm
Mn	2.0	2.5	3.7	2.8	<1ppm	<1ppm	<1ppm	<1ppm
K	2.8	0.5	0.1	<500ppm	3.1	0.5	550ppm	<200ppm
Zn	2.3	2.9	4.2	3.2	<1ppm	<1ppm	<1ppm	1ppm
Zn/(Cr+Mn)	0.60	0.60	0.59	0.60				
Mn/Cr	1.09	1.10	1.10	1.09				

5 - ZnMn1.5Cr.5 - KOH/K2CO3			11DAN96		
	Precip/orig	Precip/wash1	Precip/wash2	Precip/wash3	Mother Liq
Cr	0.8	1.0	1.3	1.7	0 ppm
Mn	2.7	3.0	3.8	4.9	0 ppm
K	1.4	0.3	440 ppm	102 ppm	1.5
Zn	1.9	2.3	2.8	3.5	0.2
Zn/(Cr+Mn)	0.54	0.58	0.55	0.53	
Mn/Cr	3.29	3.00	2.92	2.88	

6 - Zn3Mn.5Cr.5-KOH/K2CO3-Zn(NO3)2 wash		11DAN112
	dry extrudate	
Cr	4.7	
Mn	3.4	
K	200ppm	
Zn	46.0	
Zn/(Cr+Mn)	4.62	
Mn/Cr	0.68	

4.5 Precipitation Agent and pH Effects

We have determined that precipitating pH markedly affects the reducibility of the ZnMnCr oxides. Temperature programmed reduction experiments show that the nature of the metal oxides change when the mixed metal oxides are prepared at the different pH's. Table 4.5-1 summarizes the TPR data that was done at two different temperature ramping rates.

Table 4.5-1. TPR Results of $Zn_{1.25}Cr_{0.47}Mn_{0.16}$ Oxides

Sample Variables and TPR Data

Sample Ref. No.	pH	Sample Weight (g)	Heating Rate (°C/min)	Peak max (°C)	Peak max (°C)	Peak Area (mV-sec)	Peak Area (mV-sec)
3DAN79	7.5	0.107	25	491	565(sh)	21771	-
3DAN79 *	7.5	0.099	10	416	499	14482	2761
3DAN79 *	7.5	0.107	10	400	466(sh)	16227	-
3DAN69	9.5	0.099	25	447	-	10163	-
3DAN69	9.5	0.104	25	453	-	11262	-
3DAN69 *	9.5	0.101	10	357	402	9600	-
3DAN75	11.0	0.104	25	481	-	11612	-
3DAN75	11.0	0.101	25	490	-	10943	-
3DAN75 *	11.0	0.096	10	381	418	7396	-

Heated to 100°C for 15 min under vacuum
5% H2 in Argon; Initial Temperature = 30°C, Final Temperature = 800°C
* = Mixed with quartz chips; other samples run without quartz chips.

Figures 4.5-1, 4.5-2 and 4.5-3 show the TPR traces done at 10°C/min on ~0.1 gram of crushed catalyst mixed with 0.5 g of quartz chips. As the precipitating pH changes from 7.5 to 11, the peak maxima for the TPR curves shift to different temperatures. In all three cases, there appear to be two metal oxide species that are being reduced. The results appear to be very dependent upon the heating rate! We have found that the peak maxima shift by ~100°C when going from 25°C/min to 10°C/min. TPR runs done at the higher rates show only one fairly symmetrical peak or one that is slightly asymmetric. At the lower heating rate the TPR scans show two distinct peaks. This has chemical consequences in determining that there are one or two species being reduced. We have not determined what causes these changes in the TPR results.

Figure 4.5-1. TPR of 3DAN79, pH 7.5

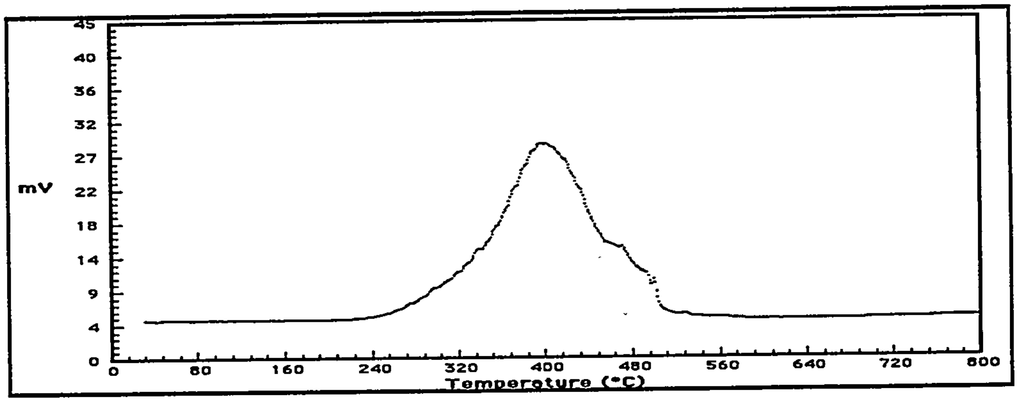


Figure 4.5-2. TPR of 3DAN69, pH 9.5

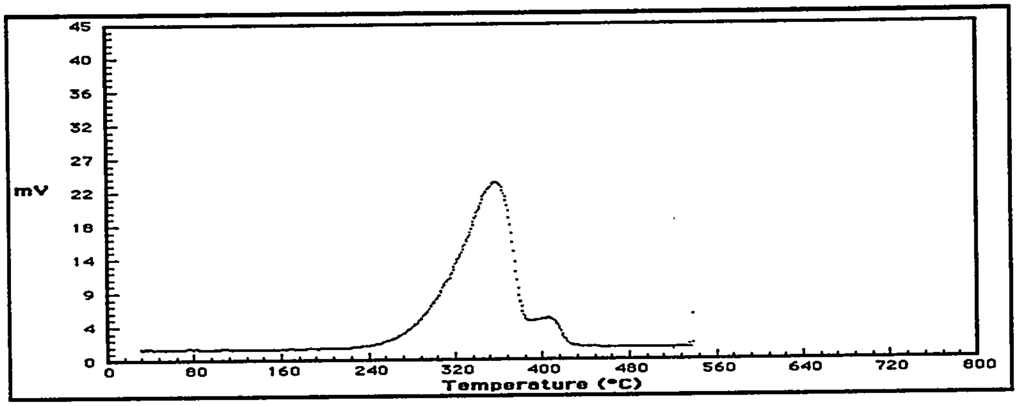
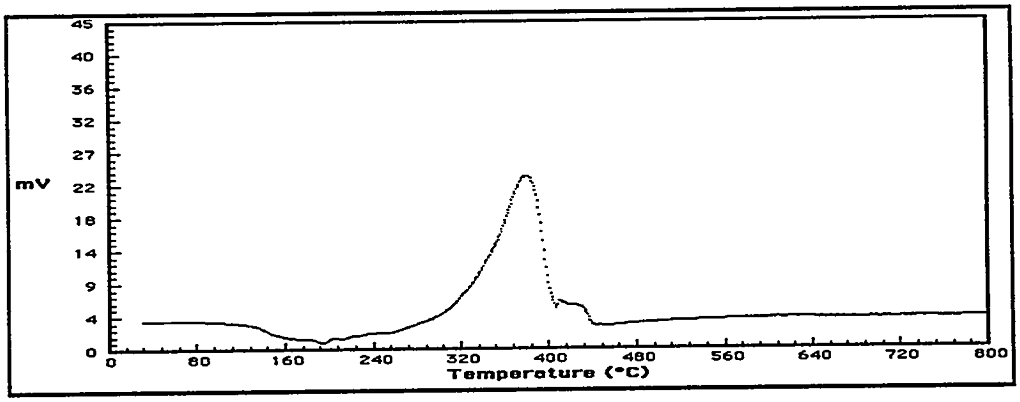


Figure 4.5-3. TPR of 3DAN75, pH 11.0



We have also determined that the precipitation agent influences the surface composition of the mixed-metal oxides. Sample 3DAN134 was precipitated using potassium carbonate, whereas sample 10DAN87 was prepared using ammonium hydroxide. The surface composition of the unfired mixed metal oxides was probed using SEM-EDS. The results are summarized along with the bulk ICP-OES analysis in Table 4.5-2. We found that the surface compositions were quite different from the bulk compositions. This in itself was not surprising since there have been many cases of surface enrichment in mixed-metal oxide and mixed-metal catalysts. Usually this preferential enrichment occurs during calcination or the reaction with the reactants during the catalytic reaction. Thus, finding that the surface composition is so different from the bulk composition in the uncalcined material was unexpected.

Table 4.5-2. Elemental Analysis of $Zn_3(Cr_{0.5}Mn_{0.5})$ Oxide

SAMPLE No.	WEIGHT PERCENT					Zn	Mn	ZnO
	K	Zn	Cr	Mn	O	Mn+Cr	Cr	Zn(MnCr)2O4
SEM-EDS Results								
3DAN134	15.42	41.05	8.88	8.96	23.36			
moles	0.39	0.63	0.17	0.16	1.46	1.88	0.96	2.76
10DAN87	1.03	41.2	15.13	24.03	18.19			
moles	0.03	0.63	0.29	0.44	1.14	0.87	1.50	0.73
ICP-OES Results								
3DAN134	2.5	35	4.9	4.7				
moles	0.06	0.54	0.09	0.09		2.98	0.91	4.96
10DAN87	0.003	33	7.9	8.9				
moles	0.00	0.50	0.15	0.16		1.61	1.07	2.22

We were quite surprised to find that the surface compositions were different depending upon whether ammonium hydroxide or potassium carbonate was used as the base during the precipitation. This preferential surface enrichment depending upon the precipitating agent could be quite important since it is the surface that participates in the catalytic conversion. This shows that the pH as well as the identity of the base strongly affects the surface composition of coprecipitated metal oxides, which has important ramifications in the catalytic activity of these and other metal oxide catalysts.

Further studies were conducted to learn how the physical and chemical properties of the catalysts are affected by precipitation pH. The surface compositions of materials precipitated with K_2CO_3 at three different pH's and fired at 300°C were probed with ESCA. The ESCA results along with the bulk analysis of unfired materials are listed in Table 4.5-3. The surface compositions of the three samples were all similar, with Zn/(Mn+Cr), Mn/Cr, and ZnO/[Zn(Mn,Cr)$_2$O$_4$] ratios being relatively close to one another. The major difference in the calcined materials was in the levels of impurities detected. Sample 3DAN79 had significant levels of potassium and chloride on the surface, whereas the other two samples showed no potassium and lower levels of chloride. We are not sure what the source of the chloride is, but it is not inconceivable that the metal nitrates and/or potassium carbonate used would have small chloride impurities. Another possible source of the chloride is from the ESCA vacuum chamber. Samples containing volatile chlorides were examined in the ESCA right before our samples were examined. It is possible that the samples picked up chloride while the ESCA experiments were being done.

The surface concentrations of the major metal cations differed from the bulk concentrations in these samples. The measured bulk Zn/(Mn+Cr) and Mn/Cr molar ratios were 2.2 and 0.18 respectively. The surface Zn/(Mn+Cr) and Mn/Cr molar ratios were approximately 1.2 and 0.20 respectively. Therefore the surface is deficient in Zn versus the bulk composition. One can speculate why the surface has less Zn than the bulk. As one possibility, the zinc may have migrated into the bulk to form compounds with the Mn and Cr during the 300°C firing. A second possibility is that the precipitation gave an inhomogeneous mixture of Zn-Mn-Cr with the outer shell being richer in Mn and Cr than the inner core. Our studies with the reduced metal oxides may render this observation irrelevant, as discussed below.

The ZnO/[Zn(Mn,Cr)$_2$O$_4$] ratio indicates how much ZnO would be formed if the Zn(Mn,Cr)$_2$O$_4$ spinel phase was preferentially formed. Here we assume that all the Mn and Cr were converted into the spinel phase and occupy the octahedral sites. The Zn occupies the tetrahedral sites and any excess Zn is converted into ZnO. This is a highly questionable assumption in this case. If the Mn and Cr are in oxidation states that favor other phases being formed or if the materials have not been fired at a high enough temperature or for a long enough time to allow spinel formation, then this assumption would be incorrect. Nevertheless the ZnO/[Zn(Mn,Cr)$_2$O$_4$] ratio allows one to attempt to correlate activity/selectivity with the ZnO, spinel phase, and their interface. The ratio based upon the bulk measurements was ~3.4. The ratio at the surface was ~1.4. This indicates that the ZnO/spinel interface is higher at the surface than in the bulk. A one-to-one ratio would roughly maximize the ZnO/spinel interface assuming all other things being equal. A negative ZnO/[Zn(Mn,Cr)$_2$O$_4$] ratio indicates that there is a deficiency in the Zn concentration to convert all the Mn and Cr into the Zn(Mn,Cr)$_2$O$_4$ spinel.

Table 4.5-3 also shows how the surface composition changed in the TPR experiments after reduction with 5% hydrogen in argon. There were some interesting changes in the surface concentrations of some of the components. The most dramatic changes occurred in the potassium, zinc, chromium, and chloride surface concentrations. In all cases the K, Cr, and Cl levels increased significantly, while the Zn levels decreased. The Zn/(Mn+Cr), Mn/Cr, and ZnO/[Zn(Mn,Cr)$_2$O$_4$] molar ratios reflected the change. This suggests that KCl or a potassium oxychloride of chromium might have migrated to the surface during the reduction. Again we are not sure of what mechanisms were responsible for the surface enrichment. Since the increase in the surface potassium matched up with the increase in the surface chloride and not with the increase in the surface chromium, the migration of KCl to the surface is more consistent with our data. The increase in the surface chromium was probably due to the migration of the chromium oxide or oxyhydroxide species.

Table 4.5-4 reports the binding energies of the different elements from the XPS experiments. Although the absolute assignment of oxidation states and phase identification without standards is wrought with hazards, we have been able to make qualitative assessments that have shed some light on the catalytic materials. The relative concentrations of the different "oxidation states" of Cr in the calcined solids are independent of, or only slightly dependent on, the pH of precipitating. The Cr^{6+}/Cr^{3+} ratios were 2/1, 3.5/1, and 2.7/1 for pH of 7.5, 9.5 and 11.0 respectively. We were unable to make the assignment of the oxidation states for Mn due to the inherent difficulty with Mn_xO_z's, but the relative atom%'s of the 645 and 642 eV peaks were fairly constant, the 642 eV peak ranging from 80.5 to 82.7 atom %. On the basis of these measurements and given a 10-20% error in the curve deconvolution and integration, it is hard to discern whether the pH affects the oxidation state of the metals in the calcined materials.

What is clear from the XPS is that only partial reduction of Cr and Mn oxides has occurred. In the case of Cr, peaks at 578.2, 576.5, and 575.3 eV were present after reduction versus the 579 and 576.5 eV peaks (possibly Cr^{+6} and Cr^{+3} as CrO_3 and Cr_2O_3) in the calcined materials. The XPS showed that Cr_2O_3 was difficult to reduce, with it making up ~2/3 of the Cr species on the surface. We are not certain what species are responsible for the 578.2 and 575.3 eV peaks. We speculate that the 578.2 eV peak could be a reduced chromate species such as K_3CrO_4. Surprisingly we did not see a peak at 577.2 eV, which has been reported for $ZnCr_2O_4$. The case of Mn is even less clear. The peak at 645.1 eV does not correspond to any Mn species and is possibly an artifact of the deconvolution software. The shift of the major Mn peak to lower binding energies indicated that the Mn is indeed being reduced. Due to the large spread of binding energies reported for Mn species and the close overlap of values for the different Mn oxides, we were not even able to identify oxidation states for the two major species of Mn.

These ESCA/XPS studies of the calcined and reduced metal oxides have shed some light on the surface chemistry, but they also bring up some questions regarding the TPR results previously reported. We had shown that the order of ease of reducibility for the samples was 3DAN69>3DAN75>3DAN79, with 3DAN69 requiring the lowest temperature for reduction and 3DAN79 requiring the highest temperature. The ESCA/XPS indicate that the pre- and post-reduction surface concentrations of the different oxidation states were fairly independent of the precipitating pH. So what is causing the differences seen in the TPR experiments? We speculate that the differences seen in the TPR experiments were due to physical differences in the materials, rather than to chemical differences. We have shown previously that surface area, porosity and pore size distribution are strongly dependent upon the precipitating pH. Therefore sample 3DAN79 should be harder to reduce than the other samples due to the lower surface area and porosity. According to our models the other two samples, 3DAN69 and 3DAN75, should have similar surface areas and slightly different porosities. Another physical property that may strongly affect the TPR is the relative particle size. Based upon the surface areas, one would expect 3DAN79 to have the larger sized particles whereas the other samples having higher surface areas would have smaller sized particles. It is known that as supported metals become more highly dispersed, they become easier to reduce. Extrapolating, one would assume that smaller sized metal oxide particles would also be easier to reduce than larger ones. Thus we conclude that the differences in the reducibility of the samples are due to the differences in particle size of the metal oxides.

Table 4.5-3. Bulk and Surface Composition of Calcined and Reduced ZnCrMn Oxide as a Function of pH

BULK COMPOSITION - ICP - OES RESULTS

	WEIGHT PERCENT							MOLAR RATIOS		
	K	Zn	Mn	Cr	O	Cl	C	Zn	Mn	ZnO
								Mn+Cr	Cr	Zn(MnCr)2O4
EXPECTED (moles)	0	1.25	0.16	0.47	-	-	-	1.98	0.34	2.97
3DAN69 pH=9.5										
UNCALCINED	1	36	2.1	11	-	-	-			
moles	0.03	0.55	0.04	0.21				2.20	0.18	3.41
3DAN75 pH=11										
UNCALCINED	5.7	32	1.8	9.8	-	-	-			
moles	0.15	0.49	0.03	0.19				2.21	0.17	3.43

SURFACE COMPOSITION - ESCA RESULTS

	ATOM PERCENT							MOLAR RATIOS		
	K	Zn	Mn	Cr	O	Cl	C	Zn	Mn	ZnO
								Mn+Cr	Cr	Zn(MnCr)2O4
3DAN79 pH=7.5										
CALCINED	5.90	12.10	1.70	8.50	49.80	6.30	15.70	1.19	0.20	1.37
REDUCED	10.40	5.70	1.50	15.80	42.40	12.30	12.00	0.33	0.09	-0.34
3DAN69 pH=9.5										
CALCINED	0.00	13.30	1.60	9.00	48.60	4.10	23.50	1.25	0.18	1.51
REDUCED	5.10	8.70	2.00	18.40	46.90	8.70	10.20	0.43	0.11	-0.15
3DAN75 pH=11										
CALCINED	0.00	12.90	2.10	8.80	59.74	3.77	19.91	1.18	0.24	1.37
REDUCED	2.50	10.10	1.70	18.90	50.50	6.40	10.00	0.49	0.09	-0.02

Table 4.5-4. XPS Results of Calcined and Reduced ZnCrMn Oxide as a Function of pH

	Zn		Cr				Mn				C(1s)			O(1s)		
	B.E.	FWHM	B.E.	Atom %	Delta E	FWHM	B.E.	Atom %	Delta E	FWHM	B.E.	Atom %	FWHM	B.E.	Atom %	FWHM
3DAN79 pH=7.5																
CALCINED	1021.8	2.2	579.0	33.0	9.1		645.1	18.0	11.2	2.9	288.4	9.7	1.8	532.8	7.1	1.8
			576.4	67.0	9.6	2.6	641.9	82.0	11.4	3.0	286.5	13.2	1.9	531.5	34.8	1.8
											284.8	77.1	1.7	529.9	58.0	1.7
REDUCED	1021.8	2.4	578.1	16.4	9.7	2.5	645.1	16.4	11.2		288.0	9.6	1.8	532.7	6.6	1.5
			576.3	66.0	9.7	2.1	640.9	83.6	11.4		286.5	17.3	1.9	531.3	23.7	1.6
			575.2	17.6	9.5	1.2					284.8	63.5	1.6	529.9	69.7	1.6
											282.9	9.6	1.8			
3DAN69 pH=9.5																
CALCINED	1021.8	2.2	579.0	22.4	9.1	2.8	645.1	19.5	11.2	3.2	288.5	13.5	1.9	532.8	8.2	1.8
			576.5	77.6	9.6	2.6	642.0	80.5	11.4	3.1	286.4	15.5	1.9	531.5	36.2	1.7
											284.7	71.1	1.8	529.9	55.6	1.7
REDUCED	1021.6	2.3	578.2	16.5	9.7	2.5	645.0	16.7	11.2	3.5	288.2	14.0	1.8	532.5	6.1	1.5
			576.5	62.3	9.7	2.0	641.2	83.3	11.4	3.4	286.5	15.1	1.8	531.3	20.0	1.5
			575.3	21.2	9.5	1.3					284.8	65.1	1.7	529.9	73.9	1.4
											282.9	5.8	1.8			
3DAN75 pH=11.0																
CALCINED	1021.8	2.1	579.1	27.1	9.1	3.1	645.0	17.3	11.2	2.9	288.3	17.2	1.9	532.8	8.0	1.8
			576.5	72.9	9.6	2.6	642.2	82.7	11.4	2.9	286.5	20.1	1.9	531.5	30.0	1.6
											284.8	62.7	1.8	530.0	62.0	1.7
REDUCED	1021.5	2.2	578.3	17.8	9.7	2.5	645.1	16.5	11.2	3.3	288.3	16.7	1.8	532.8	6.7	1.5
			576.5	65.2	9.7	2.0	641.2	83.5	11.4	3.3	286.6	16.6	1.8	531.2	21.7	1.5
			575.4	17.0	9.5	1.2					284.7	63.3	1.8	529.9	71.7	1.4
											282.8	3.4	1.8			

4.6 Potassium Traverse

As discussed above, we discovered potassium as an impurity in the mixed metal oxides. The potassium was probably incorporated into the solid during the coprecipitation using K_2CO_3. To further clear up the effects of K, Pd, and Ce on the activity and selectivity of these catalysts, $Zn_3Mn_{.5}Cr_{.5}O_{4.5}$ and $Zn_1Cr_1O_{2.5}$ were prepared using ammonium hydroxide in the coprecipitation step. A set of four Pd-based catalysts having various levels of K and Ce was prepared from this alkali-free material. The first two catalysts were repeats of the best two catalysts from the fractional factorial design, based on rate and selectivity to total alcohols.

Tables 4.6-1 and 4.6-2 contain the catalytic results for the potassium traverse. The base case was the Pd-$Zn_3(Cr_{0.5}Mn_{0.5})O_x$ with [Pd] = 6 wt%. From Figures 4.6-1 – 4.6-2, the K level is found to be critical in determining the performance of the catalysts. The hydrocarbon selectivity remains relatively unaffected with the exception of methane. The methane selectivity decreases significantly as the potassium is increased (Figure 4.6-1). The influence of potassium levels on alcohol selectivity is quite different (Figure 4.6-2). As the K levels increase from 0 to 7 wt%, the selectivity for methanol decreases, goes through a minimum at ~3.5 wt%, and then increases at higher loadings. The isobutanol selectivity increases at low loadings, goes through a maximum at ~3.5 wt%, and then decreases. n-Propanol selectivity increases steadily as K loadings increase. Figure 4.6-3 shows how the total HC and ROH selectivity and the ROH_{total} rate vary with potassium levels. The total alcohol selectivity increases and total HC selectivity decreases as potassium levels increase. Unfortunately the ROH_{total} rate hits a minimum at about the same potassium levels as when isobutanol selectivity is at its maximum. Interestingly, the selectivities for methane and C_4 hydrocarbons roughly follow those of methanol and isobutanol.

These results show that the formulations made via the "potassium-free" method, and containing no added K/Ce promoters, are significantly less selective for isobutanol. This confirms our belief that the original formulations, thought to be "potassium-free", do indeed require added potassium to promote higher alcohol synthesis.

Table 4.6-1. Molar Selectivity as a Function of K and Ce (CO_2-free basis)

CATALYST#	10DAN54	10DAN94	10DAN129	10DAN131	10DAN132	10DAN130	10DAN95
TEST#	PR174	AVERAGE	AVERAGE	AVERAGE	AVERAGE	AVERAGE	AVERAGE
K Levels =>	?	0.00	3.00	7.00	0.00	0.00	3.00
Ce Levels =>	?	0.00	0.00	0.00	6.00	13.00	13.00
SPECIES							
CH4	6.21	36.20	16.92	15.71	45.74	37.10	36.21
C2H6	7.09	7.35	7.51	8.69	10.36	7.17	8.86
C3H8	2.92	3.90	6.79	7.36	5.68	5.91	5.19
C4H10	6.26	5.26	11.87	6.57	6.62	11.51	5.34
CH3OH	22.05	40.11	18.43	31.88	26.43	26.48	29.56
C2H5OH	1.55	0.00	0.00	0.62	0.00	0.00	0.00
n-C3H7OH	4.20	0.63	7.67	14.69	0.00	2.35	2.97
i-C3H7OH	1.79	0.00	0.90	2.38	0.00	0.00	0.00
n-C4H9OH	0.00	0.00	0.88	1.60	0.00	0.00	0.00
i-C4H9OH	37.47	6.55	29.03	8.88	5.18	9.48	11.88
sec-C4H9OH	6.32	0.00	0.00	0.00	0.00	0.00	0.00
2Me-C4H9OH	4.15	0.00	0.00	1.61	0.00	0.00	0.00
TOTAL HC	22.48	47.29	46.56	48.75	68.40	61.69	55.59
TOTAL ROH	77.52	52.71	43.09	38.34	31.60	38.31	44.41
ROH RATE	76.00	107.62	85.62	99.44	90.15	55.60	97.22

Table 4.6-2. Catalyst Runs of K and Ce Traverses with Pd - $Zn_{3.0}Mn_{0.5}Cr_{0.5}O$

Catalyst ref	**Test ref**	**ROH Sel (C Mol %)**	**Total ROH Activity (g/kg-hr)**	**MeOH Activity (g/kg-hr)**	**i-BuOH Activity (g/kg-hr)**	**C_3+C_4 / Total ROH (wt basis)**
10DAN54	pr174	77.5	76.0	32.1	31.5	0.49
10DAN94	PR005	43.8	103.7	92.6	9.9	0.11
	PR019	27.7	106.8	97.4	8.4	0.14
	PR025	27.6	112.4	102.3	9.3	0.09
10DAN129	PR402	43.6	85.4	39.7	36.2	0.55
	PR424	49.1	88.7	39.2	35.6	0.57
	PR422	47.0	82.8	37.9	34.5	0.55
				0.0	0.0	
10DAN131	PR425	44.3	105.2	65.3	10.8	0.37
	PR421	40.8	94.1	64.1	9.2	0.34
	PR401	61.2	99.0	67.1	11.4	0.34
				0.0	0.0	
10DAN132	PR453	23.3	103.6	93.1	10.5	0.10
	PR449	21.5	88.0	79.4	8.6	0.10
	PR433	21.1	92.3	82.6	9.7	0.11
				0.0	0.0	
10DAN130	PR454	26.9	62.2	50.1	9.0	0.19
	PR432	25.0	58.4	45.0	10.6	0.23
	PR450	24.8	52.8	42.9	7.8	0.19
				0.0	0.0	
10DAN95	PR044	37.5	99.8	74.9	19.2	0.25
	PR020	29.4	94.7	74.3	16.3	0.22
	PR024	29.1	97.1	76.4	16.6	0.21

Conditions: 400°C, 1100 psi, $H_2/CO = 1$, GHSV 12000

Figure 4.6-1. Hydrocarbon Selectivity as a Function of K Loading (CO_2-free basis)

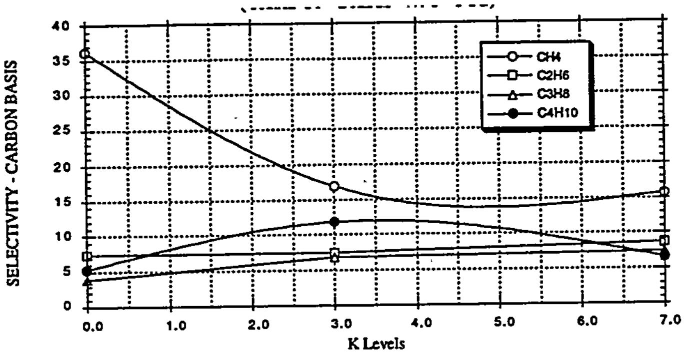


Figure 4.6-2. Alcohol Selectivity as a Function of K Loading (CO_2-free basis)

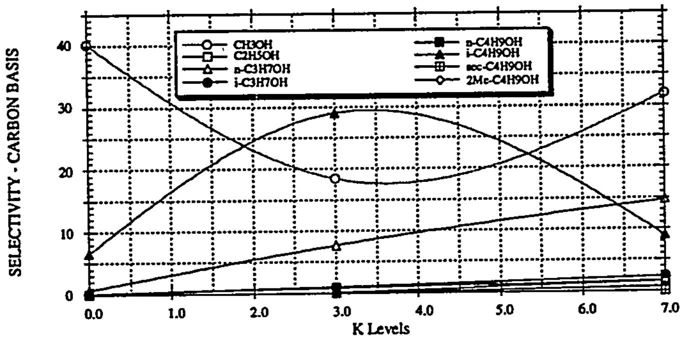
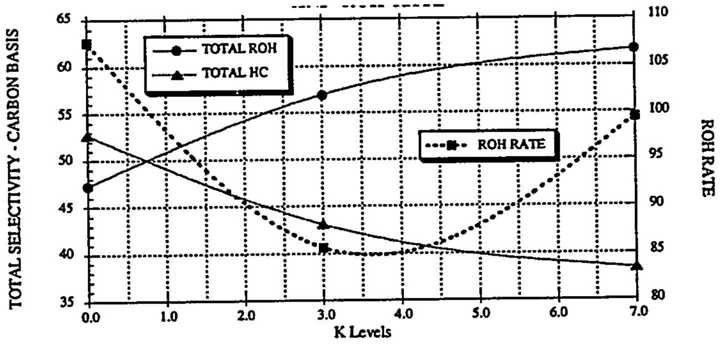


Figure 4.6-3. Total Hydrocarbon and Alcohol Selectivity and Alcohol Rate



To expand on the original set of potassium loadings (0 -7%), further tests were conducted with two additional levels of K, 3.5 and 15 wt%. The test results are presented in Table 4.6-3 and Figures 4.6-4 – 4.6-6. The base case was the Pd-$Zn_3(Cr_{0.5}Mn_{0.5})O_x$ with [Pd] = 6 wt%. The K level was clearly critical in determining the performance of the catalysts. Potassium levels influenced the alcohol selectivity quite strongly. The selectivity for methanol decreased, went through a minimum at ~2.0 – 2.5 wt%, and then increased at higher loadings. The isobutanol selectivity increased at low loadings, reached a maximum at ~2.0 – 2.5 wt%, and then dropped off quickly at higher potassium loadings. n-Propanol selectivity increased steadily as K loadings increased. The hydrocarbon selectivity remained relatively unaffected with the exception of methane. The methane selectivity decreased significantly as the potassium was increased (Figure 4.6-5). Figure 4.6-6 shows how the total HC and ROH selectivity and the ROH_{total} rate varied with potassium levels. The total alcohol selectivity increased and total HC selectivity decreased as potassium levels increased. Unfortunately the ROH_{total} rate was at a minimum at the potassium levels for which isobutanol selectivity was at its maximum. Interestingly, the selectivities for methane and C_4 hydrocarbons roughly followed that of methanol and isobutanol. We do not know whether the C_4 hydrocarbon fraction consists of only n-butane or whether it contains unsaturated C_4 such as isobutene. GC-MS analysis may be of use here but has not been done.

Table 4.6-3. Catalytic Selectivity, Carbon Percent Basis Excluding Carbon Dioxide (Rates are in g/kg cat-hr)

		1	2	3		1	2	3		1	2	3	
	CATALYST #	10DAN94	10DAN94	10DAN94	10DAN94	10DAN129	10DAN129	10DAN129	10DAN129	10DAN134	10DAN134	10DAN134	10DAN134
	TEST #	PR005	PR019	PR025	AVERAGE	PR402	PR422	PR424	AVERAGE	PR471	PR487	PR491	AVERAGE
	K Levels =>	0.00	0.00	0.00	0.00	3.00	3.00	3.00	3.00	3.50	3.50	3.50	3.50
	Ce Levels =>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Species												
1	CH4	38.29	34.88	35.42	36.20	24.31	13.86	12.59	16.92	19.62	16.79	18.00	18.13
2	C2H6	7.16	7.60	7.30	7.35	7.56	7.27	7.69	7.51	7.56	12.09	12.71	10.79
3	C3H8	4.69	3.57	3.43	3.90	6.00	7.22	7.16	6.79	5.38	9.74	10.40	8.51
4	C4H10	6.04	5.03	4.71	5.26	8.15	14.02	13.45	11.87	5.72	9.06	9.25	8.01
5	CH3OH	36.33	41.99	42.01	40.11	17.89	18.85	18.57	18.43	26.88	23.75	22.59	24.41
6	C2H5OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	n-C3H7OH	0.74	0.66	0.50	0.63	6.87	8.24	7.90	7.67	7.92	7.52	7.06	7.50
8	i-C3H7OH	0.00	0.00	0.00	0.00	0.00	0.00	2.70	0.90	0.00	0.00	0.00	0.00
9	n-C4H9OH	0.00	0.00	0.00	0.00	0.98	0.86	0.80	0.88	2.17	1.59	1.60	1.79
10	i-C4H9OH	6.74	6.27	6.62	6.55	28.24	29.68	29.16	29.03	22.72	18.24	17.25	19.40
11	sec-C4H9OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	2Me-C4H9OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.03	1.23	1.15	1.47
	TOTAL HC	56.18	51.08	50.86	52.71	46.02	42.37	40.89	43.09	38.28	47.67	50.35	45.43
	TOTAL ROH	43.82	48.92	49.14	47.29	53.98	57.63	59.11	56.91	61.72	52.33	49.65	54.57
	ROH RATE	103.68	106.76	112.41	107.62	85.39	82.81	88.67	85.62	112.76	101.78	102.39	105.64

		1	2	3		1	2	3	
	CATALYST #	10DAN131	10DAN131	10DAN131	10DAN131	10DAN133	10DAN133	10DAN133	10DAN133
	TEST #	PR401	PR421	PR425	AVERAGE	PR472	PR486	PR490	AVERAGE
	K Levels =>	7.00	7.00	7.00	7.00	15.00	15.00	15.00	15.00
	Ce Levels =>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Species								
1	CH4	6.89	19.83	20.42	15.71	9.55	12.35	12.84	11.58
2	C2H6	4.06	11.33	10.67	8.69	5.86	7.99	7.99	7.28
3	C3H8	4.07	9.39	8.60	7.36	8.90	10.49	11.09	10.16
4	C4H10	5.53	7.55	6.65	6.57	13.65	13.85	14.43	13.98
5	CH3OH	42.37	27.91	25.36	31.88	27.52	20.93	19.46	22.64
6	C2H5OH	0.00	0.00	1.85	0.62	0.00	0.00	0.00	0.00
7	n-C3H7OH	16.09	14.50	13.48	14.69	17.96	16.16	15.91	16.68
8	i-C3H7OH	4.67	0.00	2.46	2.38	5.83	6.71	7.21	6.59
9	n-C4H9OH	1.48	1.48	1.84	1.60	0.00	2.59	2.73	1.77
10	i-C4H9OH	12.49	6.92	7.25	8.88	10.72	8.93	8.34	9.33
11	sec-C4H9OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	2Me-C4H9OH	2.34	1.10	1.40	1.61	0.00	0.00	0.00	0.00
	TOTAL HC	20.55	48.10	46.35	38.34	37.97	44.68	46.35	43.00
	TOTAL ROH	79.45	51.90	53.65	61.66	62.03	55.32	53.65	57.00
	ROH RATE	99.03	94.07	105.23	99.44	42.84	43.28	43.32	43.15

Figure 4.6-4. Alcohol Selectivity as a Function of K Loading — $Zn_3Mn_{.5}Cr_{.5}O_x$ (Carbon Basis w/o CO_2)

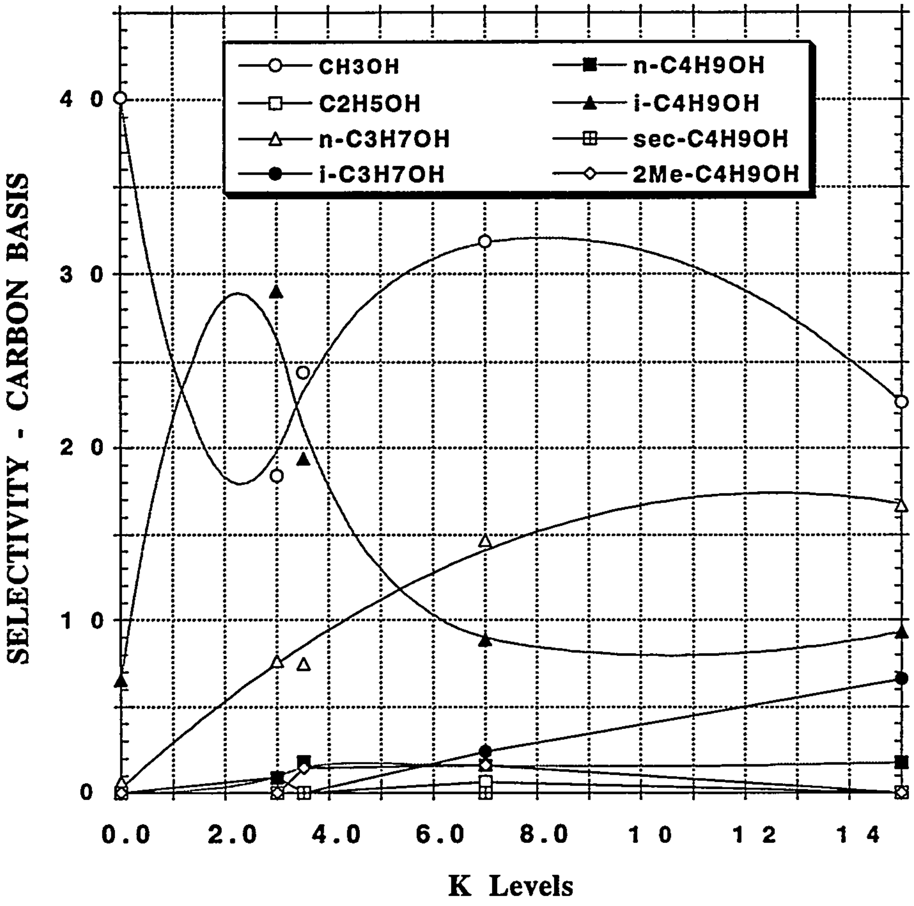


Figure 4.6-5. Hydrocarbon Selectivity as a Function of K Loading (Carbon Basis w/o CO_2)

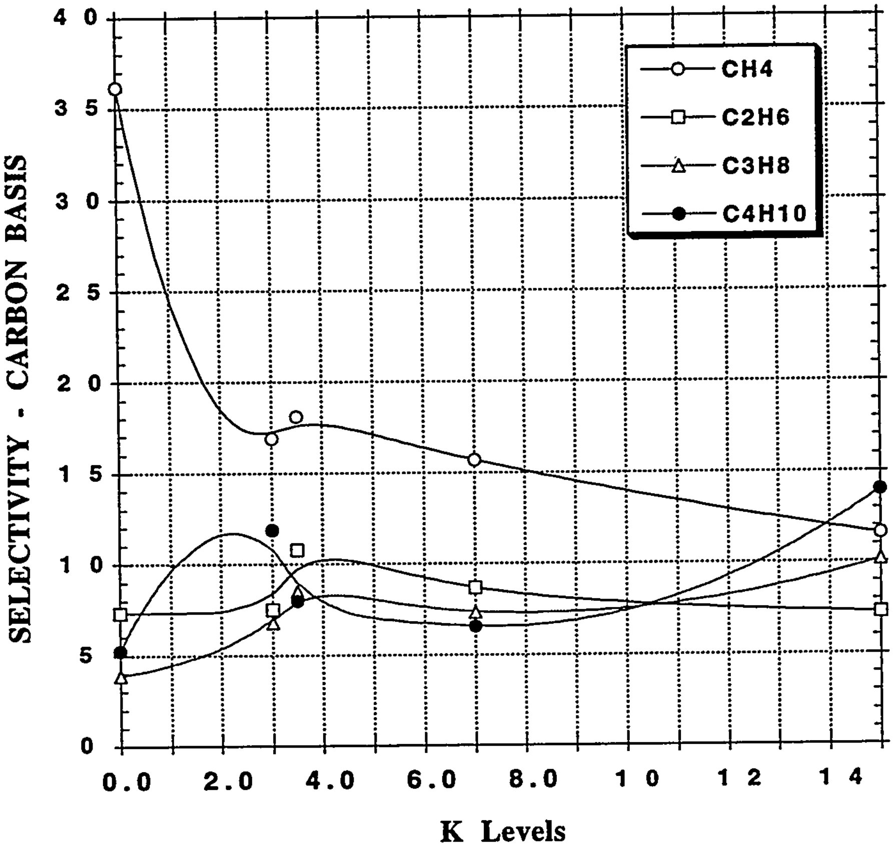
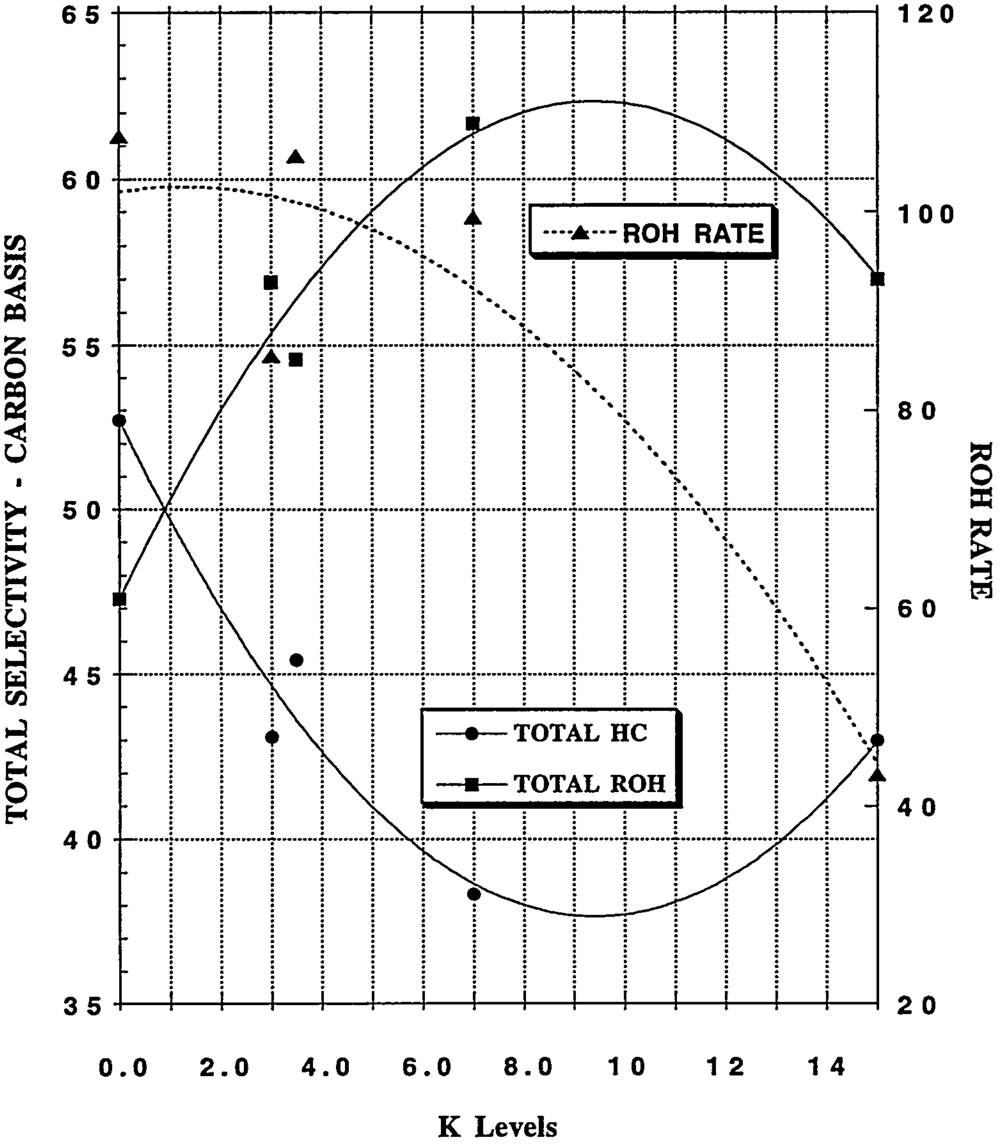


Figure 4.6-6. Alcohol Rate and Total Hydrocarbon and Alcohol Selectivity



4.7 Cerium Traverse

To further gain further information on the effects of Ce on the activity and selectivity of these catalysts, a set of four Pd-based catalysts having various levels of K and Ce was prepared from alkali-free support material, as described in the preceding section. Table 4.6-1 also contains the catalytic results for the Ce traverse. Again the base case was the Pd-$Zn_3(Cr_{0.5}Mn_{0.5})O_x$ with [Pd] = 6 wt%. From Figures 4.7-1 – 4.7-3, it is clear that the Ce effect is quite different from that seen for the potassium. The selectivities to the various hydrocarbons remain relatively unaffected (Figure 4.7-1) and are approximately at the same values as in the case with potassium, with the exception of methane. This suggests that the selectivity to higher hydrocarbons is unaffected by the K and Ce promoters, and is more dependent on the Pd or metal oxide composition. The methane selectivity is strongly affected by K, but not by Ce. The influence of cerium levels on alcohol selectivity is only significant in the case of methanol (Figure 4.7-2). As the Ce levels increase from 0 to 13 wt%, the selectivity for methanol decreases and then appears to level off at ~25%. The isobutanol selectivity is fairly flat along the Ce transverse at around 7%. n-Propanol is the only other alcohol formed in any significant amounts, but only after the Ce levels reach approximately 8 wt%. Figure 4.7-3 shows how the total HC and ROH selectivity and the ROH_{total} rate vary with cerium levels. The total alcohol selectivity decreases and total HC selectivity increases as cerium levels increase. The ROH_{total} rate decreases steadily across the Ce traverse. Again we see that the selectivity for the C_4 hydrocarbons follows that of isobutanol, but there is no such correlation with the methane and methanol.

Additional tests with Ce promoter were not done since the total rate for alcohol synthesis decreased as Ce levels increased. The total hydrocarbon selectivity increased and total alcohol selectivity decreased as cerium increased. Although methanol selectivity decreased 15% with the addition of Ce, the selectivity to higher alcohols did not improve significantly.

Figure 4.7-1. Hydrocarbon Selectivity as a Function of Ce Loading (CO_2-free basis)

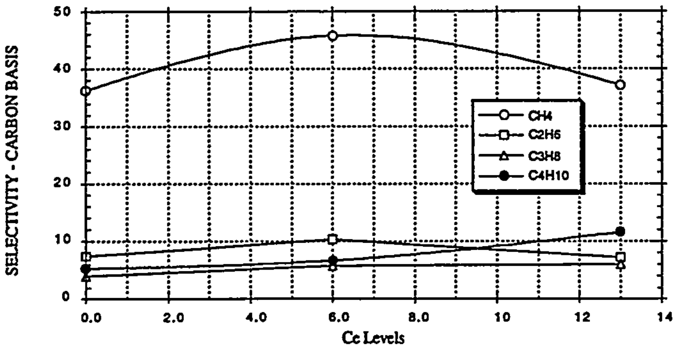


Figure 4.7-2. Alcohol Selectivity as a Function of Ce Loading (CO_2-free basis)

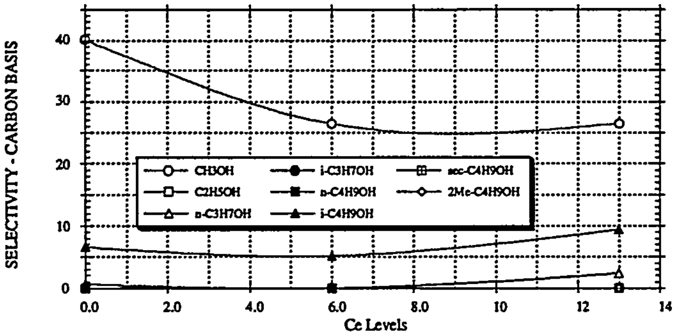
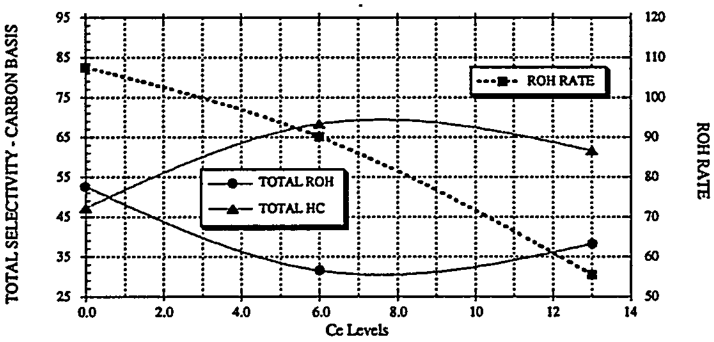


Figure 4.7-3. Total Hydrocarbon and Alcohol Selectivity and Alcohol Rate



4.8 Effects of Process Variables on Catalyst Performance

4.8.1 Tests with Catalyst 11-DAN-115

A set of statistically designed experiments (#3) was constructed to examine the effects process variables, including:

- Space velocity
- Pressure
- Temperature
- Syngas Ratio

Examination of the literature on the effects of these variables on higher alcohol synthesis (HAS) raises the following points of interest:

Space velocity. Methanol formation is fast with respect to HAS, as HAS often appears to result from consecutive reactions of methanol. Methanol formation is so fast under reaction conditions that it is essentially controlled by chemical equilibrium. Linear alcohols approach a pseudo-steady state, but branched species do not. This is a consequence of the linear alcohols being intermediate products, while the branched alcohols are terminal ones. Thus, long residence times favor HAS.

Pressure. The thermodynamic equilibrium for methanol formation dictates that methanol concentration grows quadratically with total pressure, while the concentration of higher alcohols exhibits a weaker dependence, resulting from kinetic considerations. Thus, pressure is not a large handle for boosting HAS vs. methanol. However, hydrocarbon production is minimized at higher pressures, so total alcohol selectivities should rise.

Temperature. HAS increases with increasing temperature, due to the kinetics of HAS, which increases with temperature, whereas the methanol formation equilibrium is disfavored by thermodynamics. Among the higher alcohols, the concentrations of branched products increase with temperature, whereas those of the linear products go through distinct maxima. This is consistent with the terminal nature of the branched alcohols and the intermediate nature of the linear, primary alcohols. In the case of copper-based catalysts, a practical higher temperature limit results from catalyst deactivation due to sintering.

Syngas Ratio. The optimum syngas ratio (H_2/CO) for methanol formation is 2:1 and higher. In contrast, for HAS the ratio is sub-stoichiometric. Thus lowering the syngas ratio will enhance HAS.

Based on a combination of *a priori* kinetic and thermodynamic arguments, the most favorable region for higher alcohol synthesis should lie where pressure and temperature are at the high design points and space velocity and syngas ratio are at the low design points.

Important points to consider here, to act as a guide in selecting suitable variable ranges, include the following:

- Space velocity cannot fall much below 100 cc/min (GHSV=6,000) or the catalyst will simply not produce enough product per unit time.

- Compression costs become increasingly significant as the total pressure rises much above 1000 psi.

- Operation of the catalyst in a slurry-phase reactor may encounter problems at these high temperatures for lack of a suitable stable solvent.

- The syngas ratio selected should fall within reasonable, attainable limits, ranging from hydrogen-rich to the mix obtained from a Shell gasifier (H_2/CO=1:2).

The catalyst employed (11-DAN-115) was the most promising of our isobutanol catalysts at that time, made using ammonium hydroxide as the precipitating agent and with a known amount of added potassium (2.0 wt%). The design limits are as follows:

	Temp (°C)	Pressure (psi)	H_2/CO ratio	GHSV
High	430	1300	2:1	18000
Mid-point	400	1000	1:1	12000
Low	370	700	1:2	6000

The design starts as an 8 point / 4 variable fractional factorial design, with mid-points (center points) interspersed throughout to check for anomalies during the course of the experiments (e.g., catalyst activation/deactivation).

The runs are listed below, in terms of high, mid or low levels

Run Code	H_2/CO	Pressure	Temperature	GHSV
CP	Mid	Mid	Mid	Mid
1	High	High	High	High
2	High	High	Low	Low
3	High	Low	High	Low
4	High	Low	Low	High
5	Low	High	High	Low
6	Low	High	Low	High
7	Low	Low	High	High
8	Low	Low	Low	Low
CP	Mid	Mid	Mid	Mid

The design runs were intended to be executed as shown in Table 4.8-1 and can be divided into three separate groups for analysis.

Design Group 1

Three center point conditions (CP-1, 2 & 3) and two design points (#1 and #8) were run first, as shown in Table 4.8-2. This "mini-design" allows us to see if the variable ranges selected are in the region where the catalyst can actually run effectively. Examination of the catalyst under all "high" conditions (point #1) and all "low" conditions (point #8), as well as tracking the center points as the runs proceed gives us this information "up front".

Examination of the incomplete data set allowed us to confirm that the catalyst could run under the extreme conditions of the process design, hence the design limits were reasonable.

Examination of trends in the center point data shows the following:

- The catalyst is not very selective for total alcohols: an initial selectivity of 42-45% declines to 9-19% with time.
- The catalyst tends to make more methanol vs. isobutanol with age (initial MeOH/i-BuOH ratio = 4, but later becomes 6-10).
- Isobutanol rates are initially high (as high as 53 g/kg-hr), but decline to 14-17 g/kg-hr (see Figure 4.8-1). The difference between the two reactors (R1 and R2) is significant, but not severe.
- The alcohol product distribution is also somewhat unexpected (see Figure 4.8-2). The higher alcohol production is centered around the C3 fraction (both n-propanol and isopropanol), reminiscent of the bare support, and unlike that observed for the "best" catalyst, 10-DAN54, from the catalyst formulation design, which exhibited a large C4 (isobutanol) productivity and only a small amount of n-propanol (see Figure 4.8-3). These observations suggest a maldistribution of promoters over the catalyst surface.

These results indicate that the catalyst preparation procedure is probably at fault. Recall that after our initial formulation design we discovered a catalyst that was 85% selective to alcohols. This catalyst was made via a potassium carbonate precipitation procedure. Preparation of a nominally identical catalyst using the ammonium hydroxide precipitation method yielded a catalyst with a selectivity of 60% to total alcohols. The catalyst used in this design was a remake of the ammonium hydroxide precipitated material. It is clear that the potassium carbonate precipitation method is superior if the goal is to obtain selective catalysts.

Design Group 2

These design points (#2-4, see Table 4.8-1) superficially show some interesting results, as shown in Table 4.8-3. However it should be noted that the isobutanol rate and ratio of MeOH/i-BuOH for design point #2 are in error. Closer examination of the chromatographic traces for this design point shows that the major C4 alcohol here is, in fact, n-butanol, not isobutanol.

HAS activities are low for design points #3 and #4 (isobutanol activities of 8-13 g/kg-hr) and total alcohol selectivities are poor (10-18%). The reactors eventually plugged under design point #4 conditions, and the catalyst was replaced with a fresh charge (of nominally the same composition) from the same preparation batch.

Design Group 3

The second catalyst charge was started up at center point conditions and aged rapidly (see Figure 4.8-4). There was a marked difference between the two reactors, but both showed the same trends in performance. The alcohol product distribution for this new charge, shown in Figure 4.8-5, closely resembles that for 10-DAN-54 and is distinctly different from that shown by the earlier charge. This result indicates sample to sample variability within the same batch. Catalyst selectivities are still low (16-60%).

Design points #5, #6 and #7 were then run and the catalyst was finally returned to center point conditions (see Table 4.8-4).

Design points #5 and #7 are of particular interest: here the catalyst produces isobutanol at a respectable rate (20-30 g/kg-hr) and with a methanol to isobutanol mole ratio of less than 1, meaning that under these conditions more isobutanol than methanol is being produced on a mole basis.

Design points #5 and #7 have high temperature (430°C) and low syngas ratio (H_2/CO = 1:2) as common process parameters, suggesting that these may be the key process variables that promote isobutanol formation.

Returning to center point conditions, we see that the catalyst has recovered a great deal of the activity loss experienced on start up (see especially R2 in Figure 4.8-4). This is an unusual result and suggests that catalyst start-up and pretreatment conditions may be critical to active, stable performance.

Table 4.8-1. Run order for process designed set.

RUN#	DESIGN POINT	H2/CO RATIO	PRESSURE (PSIG)	TEMP. (C)	SPACE VELOCITY (GHSV)
1	Center Point	1:1	1000	400	12000
2	#8	1:2	700	370	6000
3	Center Point	1:1	1000	400	12000
4	#1	2:1	1300	430	18000
5	Center Point	1:1	1000	400	12000
6	#2	2:1	1300	370	6000
7	#3	2:1	700	430	6000
8	#4	2:1	700	370	18000
9	#5	1:2	1300	430	6000
10	#6	1:2	1300	370	18000
11	#7	1:2	700	430	18000
12	Center Point	1:1	1000	400	12000

Table 4.8-2. Results of process parameter design — group 1. Selectivities and ratios are on a molar basis, and rates are g/kg catalyst-hr.

Design Pt.	Total ROH Selectivity		i-BuOH Rate		Ratio MeOH/i-BuOH	
	REACTOR 1	REACTOR 2	REACTOR 1	REACTOR 2	REACTOR 1	REACTOR 2
CP-1	44.9	42.5	26.9	53.9	4.1	4.2
CP-1	37.5	34.7	22.8	43.4	4.8	5.0
CP-1		25.5		34.5		6.1
8	45.5	37.0	8.0	10.8	4.5	5.8
8	45.0	36.6	9.6	10.6	5.1	6.5
8	44.3	35.8	9.8	11.7	5.1	7.0
8	43.0	35.4	9.8	12.0	5.2	7.6
8	41.3	34.5	10.0	12.4	5.2	7.8
8	39.9	33.7	10.1	12.7	5.1	8.3
8	38.5		10.1		5.1	
CP-2	24.4	31.2	19.0	29.6	5.9	11.1
CP-2		18.2		25.3		9.2
CP-2		17.0		25.6		10.5
1	10.2	12.9	32.3	59.2	3.1	4.9
1	20.9	15.3	53.6	54.4	2.8	5.2
1	19.5	14.2	51.5	41.6	2.9	7.2
1	19.5	14.0	51.4	41.4	3.0	7.3
1	18.2	13.2	51.4	41.2	3.0	6.8
1	22.5	12.7	50.2	41.7	3.1	7.0
1	21.5	12.1	49.7	42.2	3.1	7.1
1	20.4	11.4	49.6	40.4	3.1	7.2
1	19.2	11.5	46.5	51.1	3.1	5.5
1	18.7		46.6		3.1	
CP-3	22.9	15.9	14.7	29.1	4.7	6.5
CP-3	20.3	9.6	14.6	19.3	6.1	10.5
CP-3	19.2	8.8	13.7	17.5	6.1	10.8

Table 4.8-3. Results of process parameter design — group 2. Selectivities and ratios are on a molar basis, and rates are g/kg catalyst-hr.

Design Pt.	Total ROH Selectivity		i-BuOH Rate		Ratio MeOH/i-BuOH	
	REACTOR 1	REACTOR 2	REACTOR 1	REACTOR 2	REACTOR 1	REACTOR 2
3	18.7	10.2	10.6	13.6	3.6	4.4
3	18.9	11.2	10.2	13.1	2.3	3.2
3	16.2	10.1	9.3	12.2	1.7	2.0
3	15.0	9.6	9.0	11.9	1.5	1.6
3	15.3	9.2	8.9	11.5	1.4	1.5
3	16.3	9.1	9.1	11.3	1.4	1.7
3	17.2	8.9	9.1	11.1	1.4	1.7
3	17.2	7.2	9.0	6.9	1.4	2.8
3	17.1	8.6	8.9	10.7	1.4	1.8
3		8.7		11.0		1.8
2	12.1	10.9	27.7	88.6	2.6	2.2
2	19.4	13.6	84.0	125.2	1.9	2.0
2	23.2	13.8	130.3	124.2	2.0	1.8
4	13.3	7.2	72.7	11.7	16.8	0.0
4	9.6	8.1	10.3	10.1	16.6	26.0
4	9.5	8.6	9.3	10.0	30.0	51.8
4	10.4	9.2	8.8	9.5	39.7	58.2
4	12.1	9.5	8.8	9.3	48.4	65.8
4	11.9	9.8	8.8	9.4	47.1	72.8
4	12.8	9.9	8.5	9.2	51.1	79.8
4	12.9	10.0	8.3	9.2	46.4	82.0
4	12.7		8.2		49.7	

Table 4.8-4. Results of process parameter design — group 3. Selectivities and ratios are on a molar basis, and rates are g/kg catalyst-hr.

Design Pt.	Total ROH Selectivity		i-BuOH Rate		Ratio MeOH/i-BuOH	
CP-4	49.5	46.1	43.9	58.1	3.2	3.9
CP-4	42.5	42.7	38.4	56.9	3.7	4.2
CP-4	40.0	39.5	34.8	55.4	3.9	4.4
CP-4	37.1	37.3	32.0	54.4	4.1	4.7
CP-4	34.7	34.8	30.1	51.8	4.4	4.8
CP-4	32.5	33.2	27.7	49.1	4.6	4.6
CP-4	29.9		24.7		5.1	
CP-4	29.8		22.0		5.3	
6	48.9	59.2	37.0	38.3	5.5	14.6
6	50.3	59.3	29.3	30.5	17.6	18.9
6	50.0	60.4	25.7	30.8	22.0	18.4
6	49.5		23.7		22.6	
5	26.0	22.2	14.3	20.4	1.4	4.7
5	20.2	26.4	15.4	32.4	1.0	0.9
5	19.7	25.9	14.7	37.1	1.1	0.8
5		24.3		37.6		0.9
5		22.9		37.7		0.9
5		21.8		38.5		0.9
5		20.6		37.4		1.0
5		19.6		37.2		1.0
7	37.3	32.2	30.6	57.8	0.8	0.9
7	29.6	25.9	29.3	36.0	0.7	0.9
7	28.1	24.9	28.3	34.0	0.7	1.0
7		23.9		32.4		1.0
CP-5	21.4	20.5	28.9	50.2	2.9	3.0
CP-5	21.3	22.9	29.5	58.6	2.9	3.2
CP-5	22.1	22.6	33.1	58.2	2.6	3.5
CP-5	17.2	21.9	22.0	57.5	4.0	3.6
CP-5	17.4	21.0	20.5	57.4	4.1	3.7
CP-5	17.4	19.1	19.2	57.4	4.2	3.1
CP-5	17.4	18.8	18.8	56.4	4.4	3.3
CP-5	17.4	18.4	18.9	57.9	4.5	3.2
CP-5	18.7	17.8	23.1	50.9	5.5	3.6
CP-5		16.5		51.3		3.8

Figure 4.8-1. Catalyst performance at center point conditions, followed with time.

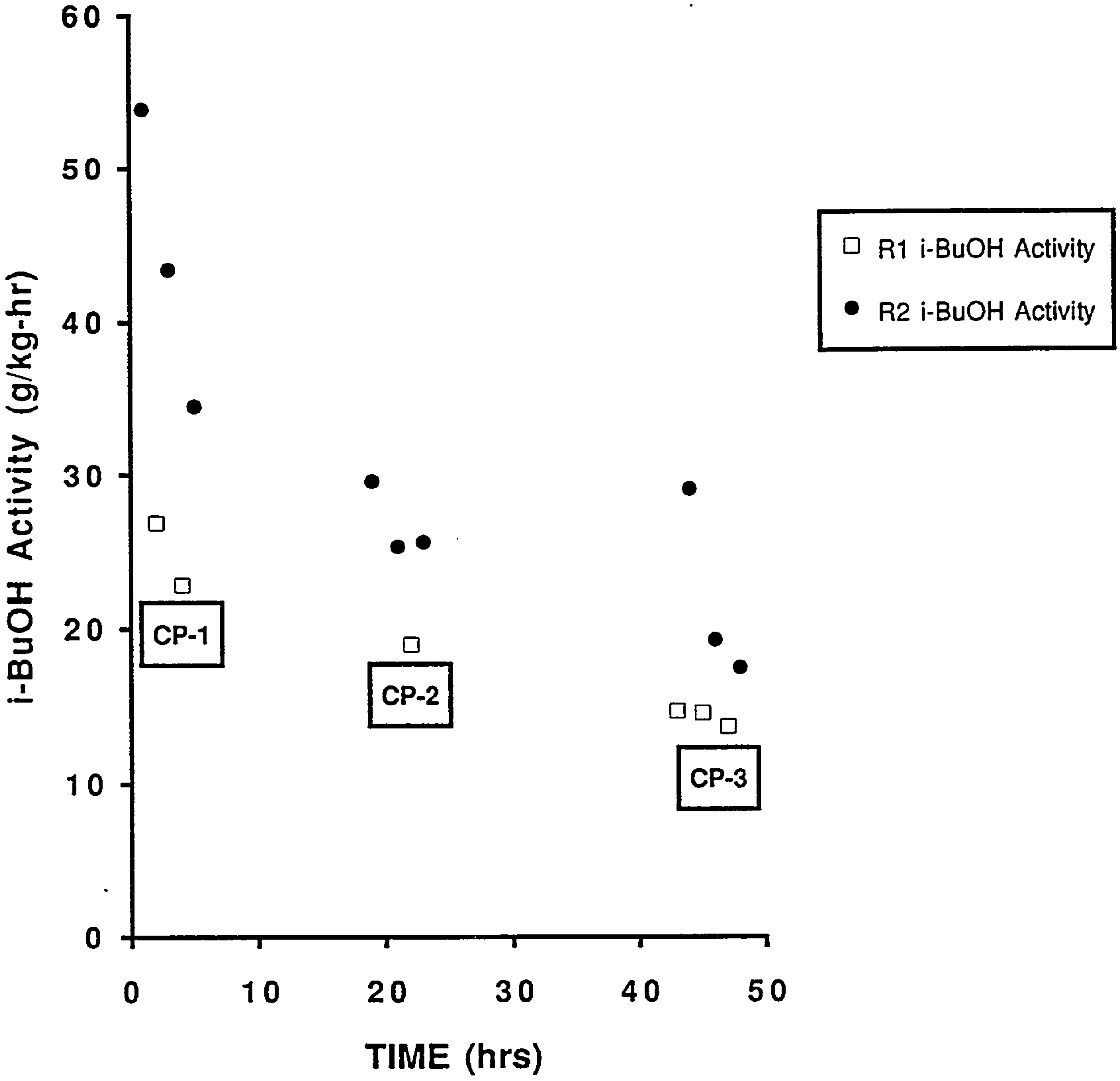


Figure 4.8-2. Typical alcohol distribution from process design experiments (10DAN135, charge 1).

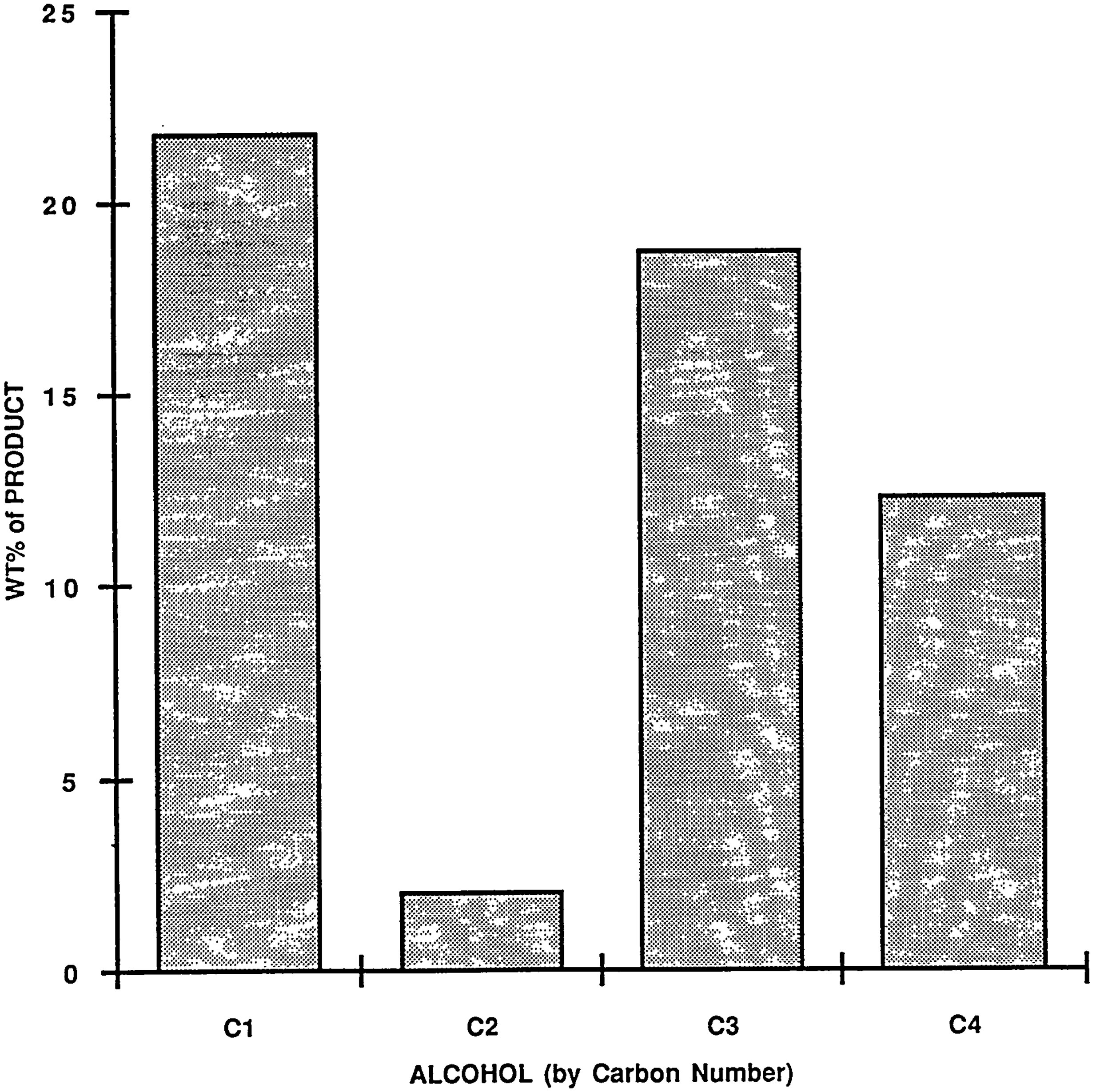


Figure 4.8-3. Typical alcohol distribution from catalyst formulation design (10DAN54).

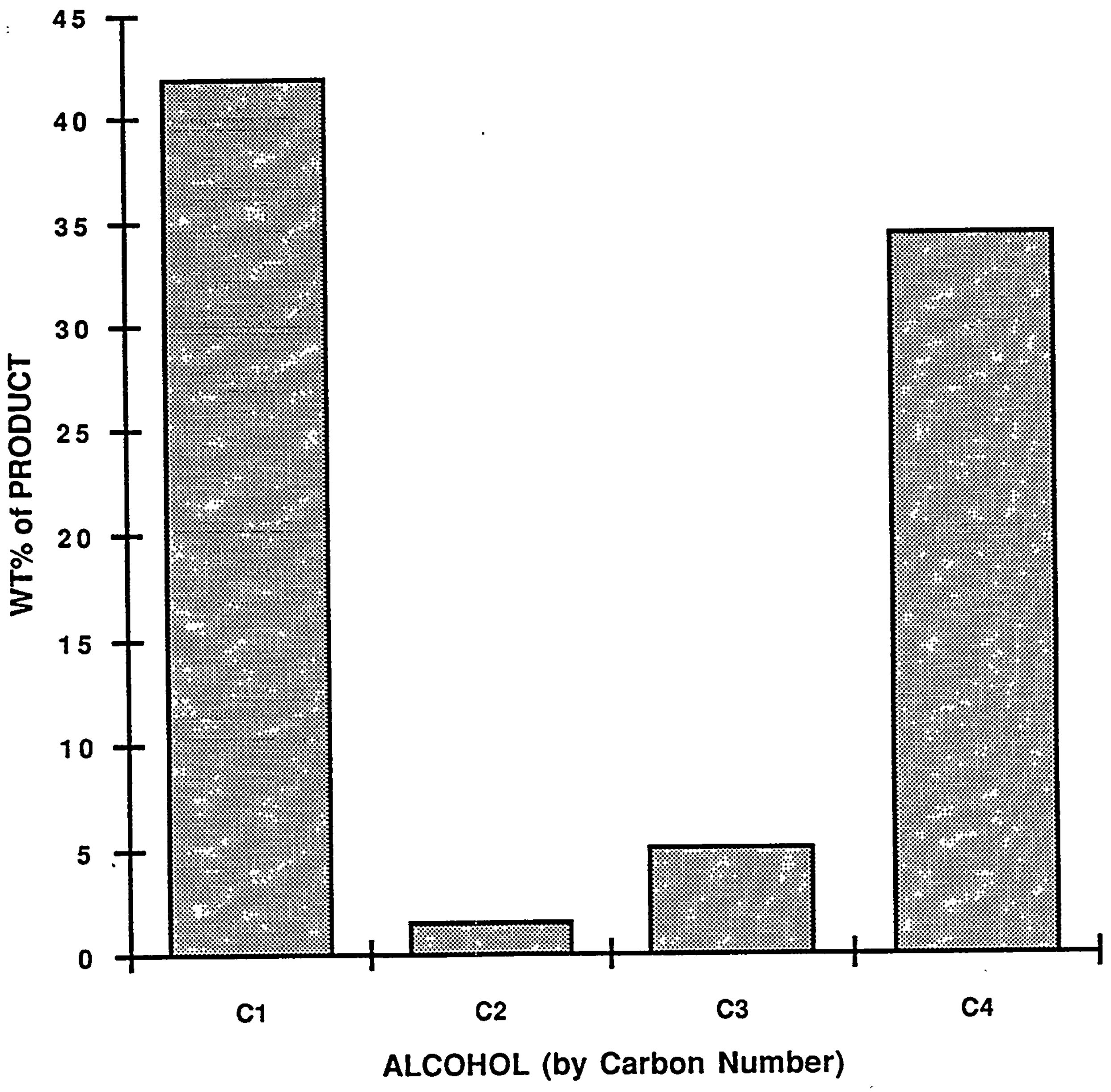


Figure 4.8-4. Process design center points after replacing catalyst with a fresh charge.

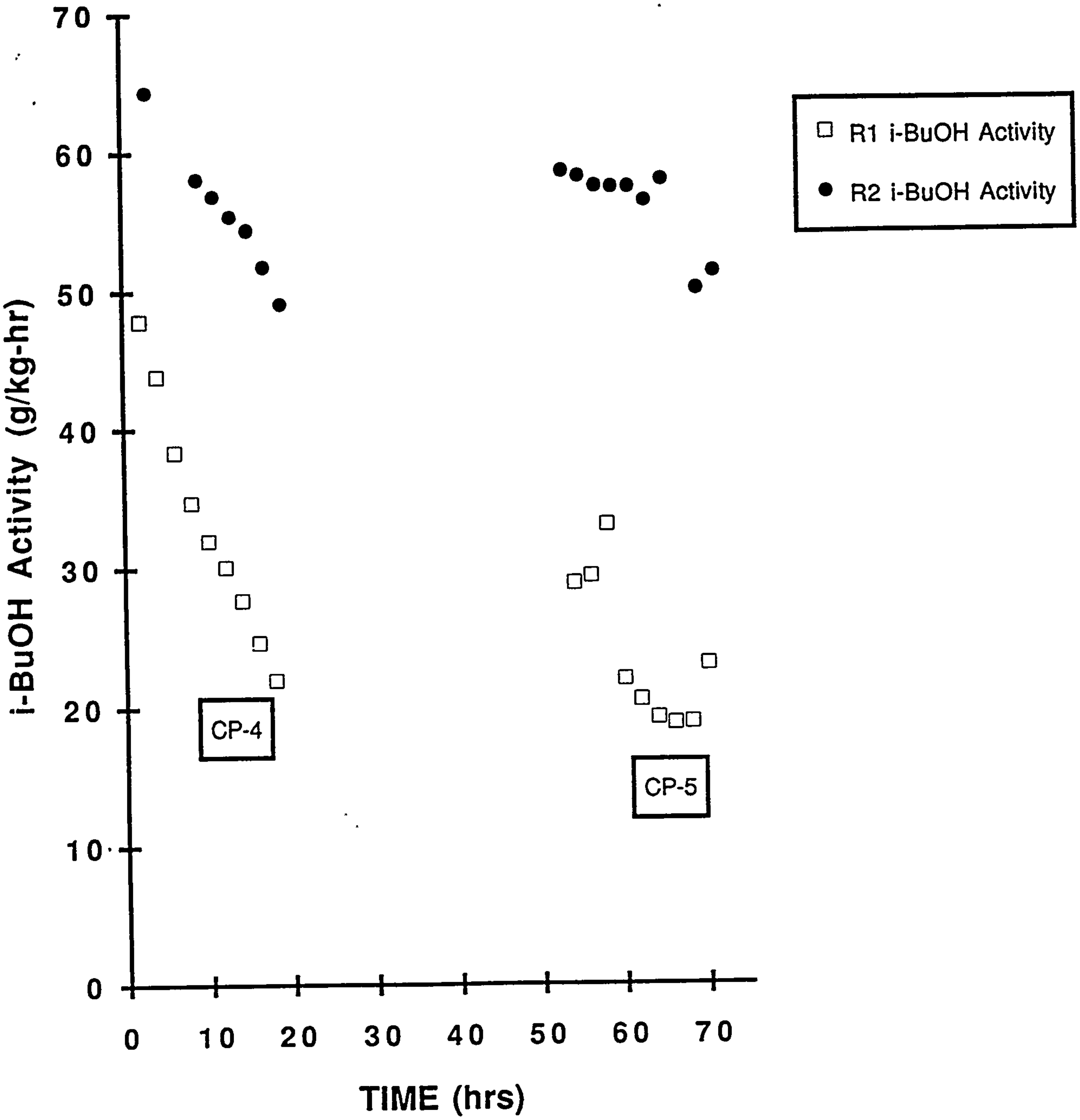
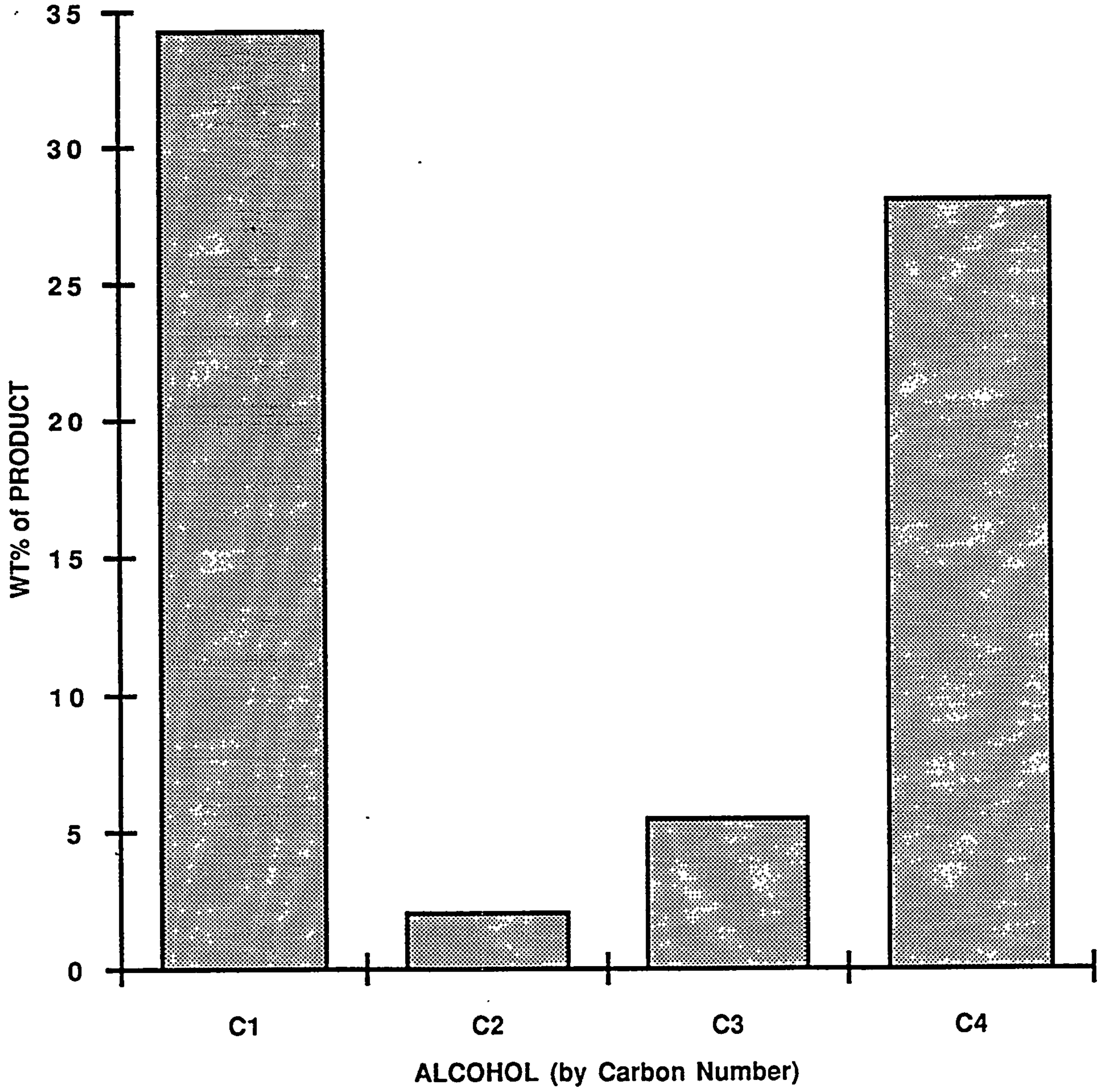


Figure 4.8-5 Alcohol distribution for second charge of catalyst.



These attempts to run a designed set of experiments with catalyst 11-DAN-115 to determine the effect of process parameters (temperature, pressure, space velocity and syngas ratio) on catalyst performance were unsuccessful. The catalyst employed, a cousin of 10-DAN-54 (our "best" isobutanol catalyst) prepared via ammonium hydroxide precipitation, was not very selective to total alcohols and showed marked differences from sample to sample. Overall performance also decayed with time. These trends were not observed to the same extent with the same formulation prepared by potassium carbonate precipitation (e.g., 10-DAN-54), indicating that we will have to revisit the catalyst preparation procedure in order to obtain selective and stable materials.

Nonetheless, the design provided useful information: two design points showed that the catalyst can achieve the production of methanol and isobutanol in a 1:1 mole ratio, with an isobutanol activity of > 30 g/kg-hr.

Use of ammonium hydroxide or ammonium carbonate as the precipitating base does not give the desired compositions for the mixed metal oxides, most likely due to the formation of water-soluble ammine complexes.

4.8.2 Tests with 10-DAN-54

We devoted a significant effort to testing a promising isoalcohol catalyst, 10-DAN-54 (a K/Pd promoted Zn/Cr/Mn spinel oxide) under various process conditions. Two separate charges of 10-DAN-54 were tested and produced reasonably consistent numbers under standard test conditions (400°C, 1000 psi, 12000 GHSV and syngas ratio = 1:1). This catalyst produces 200-252 g/kg-hr of total alcohols (total alcohol selectivities of 57-68%) with an isobutanol rate of 94-130 g/kg-hr and a MeOH/i-BuOH product mole ratio of 3. For the second charge, both space velocity (GHSV) and temperature were varied.

<u>Space Velocity:</u> At lower space velocities, productivities fall, but higher alcohols are favored, resulting in a higher proportion of higher alcohols vs. methanol (MeOH/i-BuOH product mole ratio falls from 3.2 to 1.7 on going from 12000 to 3000 GHSV).

Methanol formation is fast with respect to higher alcohol synthesis (HAS), as HAS results from consecutive reactions from methanol. Methanol formation is so fast under reaction conditions that it is essentially controlled by chemical equilibrium. Thus, long residence times favor HAS.

The isobutanol rate is still a respectable 48 g/kg-hr at GHSV = 3000.

<u>Temperature:</u> The rate of HAS increases with increasing temperature because of the more favorable kinetics, whereas the methanol equilibrium is disfavored by thermodynamics. Thus higher temperatures favor isobutanol over methanol. The concern here is that the

syngas that no longer reacts to form methanol can now form hydrocarbons rather than higher alcohols, so a trade-off may exist in manipulating this variable to promote HAS.

At temperatures of 380°C and 400°C, the MeOH/i-BuOH product mole ratio stays constant at 3.6-3.8; in contrast, at 420°C, this ratio becomes 1.0 showing that HAS is favored at the higher temperature. However, selectivity to total alcohols falls from 48-57% down to 34%; hydrocarbon formation is also favored by higher temperatures and this effect appears to outweigh the benefit of increased isobutanol formation vs. methanol.

Catalyst Aging: The catalyst was returned to start-up conditions after 102 hours and showed little deactivation:

	20 hrs on stream	122 hrs on stream
Total ROH activity (g/kg-hr)	200	204
Isobutanol activity (g/kg-hr)	94	89
MeOH/i-BuOH product mole ratio	3.2	3.8
ROH Selectivity	68	48

The catalyst appears to keep a constant alcohol productivity with time, but hydrocarbon production increases, resulting in an overall loss in selectivity.

Conversion: Using temperature and space velocity traverses, we have looked at the effects of conversion on catalyst performance for the 10-DAN-54 catalyst. The data are shown graphically in Figures 4.8-6 – 4.8-11 and the details are given in Tables 4.8-5 – 4.8-8. Increasing conversion (whether by increasing temperature or decreasing space velocity) results in a loss in selectivity to total alcohols and a concurrent increase in hydrocarbon formation, especially methane. It appears that operating the catalyst in the 15-20% conversion range is required to preserve a reasonable selectivity to total alcohols.

Pressure: Results of a pressure traverse with the 10-DAN-54 catalyst show that alcohol activity increases with increasing pressure (see below), with an increase of 11.5 g/kg-hr of isobutanol for every 100 psi increase in the 700 and 1320 psi range. However, the methanol/i-butanol mole ratio increases from 3 to 5 over the same interval, showing that increasing pressure favors methanol formation over higher alcohol synthesis. Overall selectivity to alcohols remains essentially unchanged.

	700 psi	1000 psi	1320 psi
Total ROH activity (g/kg-hr)	106	204	292
Isobutanol activity (g/kg-hr)	49	89	120
MeOH/i-BuOH product mole ratio	3.1	3.8	4.8
ROH Selectivity (%)	40	48	39

Pressure is thus a good handle for raising the overall reaction rate, but at the price of losing some selectivity to higher alcohols.

Syngas Ratio: The catalyst 10-DAN-54 was tested with syngas feeds varying from (a) 2:1 H_2/CO, (b) our standard 1:1 and (c) 1:2. The results are summarized below:

	$H_2/CO = 2$	$H_2/CO = 1$	$H_2/CO = 0.5$
Total ROH activity (g/kg-hr)	328	213	663
ROH Selectivity (%)	11.6	10.6	29
Isobutanol activity (g/kg-hr)	23	25	213
MeOH/i-BuOH product mole ratio	3.8	2.2	0.38

Methanol formation is favored at high syngas ratio, as expected. The results for the low syngas ratio ($H_2/CO = 0.5$) were encouraging, but the catalyst quickly plugged. Repeated attempts to run the catalyst at a syngas ratio of 0.5 resulted in reactor plugging each time. Examination of the catalyst revealed a wax deposit on the surface, which was analyzed by mass spectrometry. The wax consists of a clean hydrocarbon mixture, with a range (C_{24}-C_{48}) of high molecular weight, linear products. The distribution is egg-shaped, peaking at C_{28} and tailing away at higher molecular weights. Carbon deposition also occurs at the reactor *inlet* (prior to the catalyst) and this is responsible for reactor plugging. This last observation made us suspect that the reactor tube itself is catalyzing syngas conversion at the low syngas ratios. Tests with empty tubes confirmed this.

Detailed analysis of the data obtained from the syngas ratio traverse on our Pd-promoted spinel oxide catalysts 10-DAN-54 revealed an unusual alcohol product distribution, with maxima in alcohol productivity in the C_1 and C_3 ranges; the expected maxima usually occur in the C_1 and C_4 ranges. The selectivity to total alcohols was also low (10-30%). These anomalies suggested that some change had occurred in the surface composition of the catalyst.

Analysis of the carbon deposited in the reactor inlet revealed the presence of significant quantities of iron and nickel, probably carried into the reaction system by carburization of the reactor tube and consequent metal dusting. The metals provide sites for Fischer-Tropsch (F-T) chemistry to occur, as was observed—recall the isolation of a C_{24}-C_{48} molecular weight linear hydrocarbon wax on the catalyst after discharge from the reactor.

To ensure that carbonyls were not being introduced to the reactor from the feed gas, an activated carbon bed (to remove iron and nickel carbonyls) was inserted upstream of the catalyst bed. A molecular sieve bed to remove any entrained water from the feed cylinders was also added.

Figure 4.8-6. Plot of Selectivity to Alcohols vs. Conversion with Changing Space Velocity, for Catalyst 10-DAN-54. See Table 4.8-5 for Conditions.

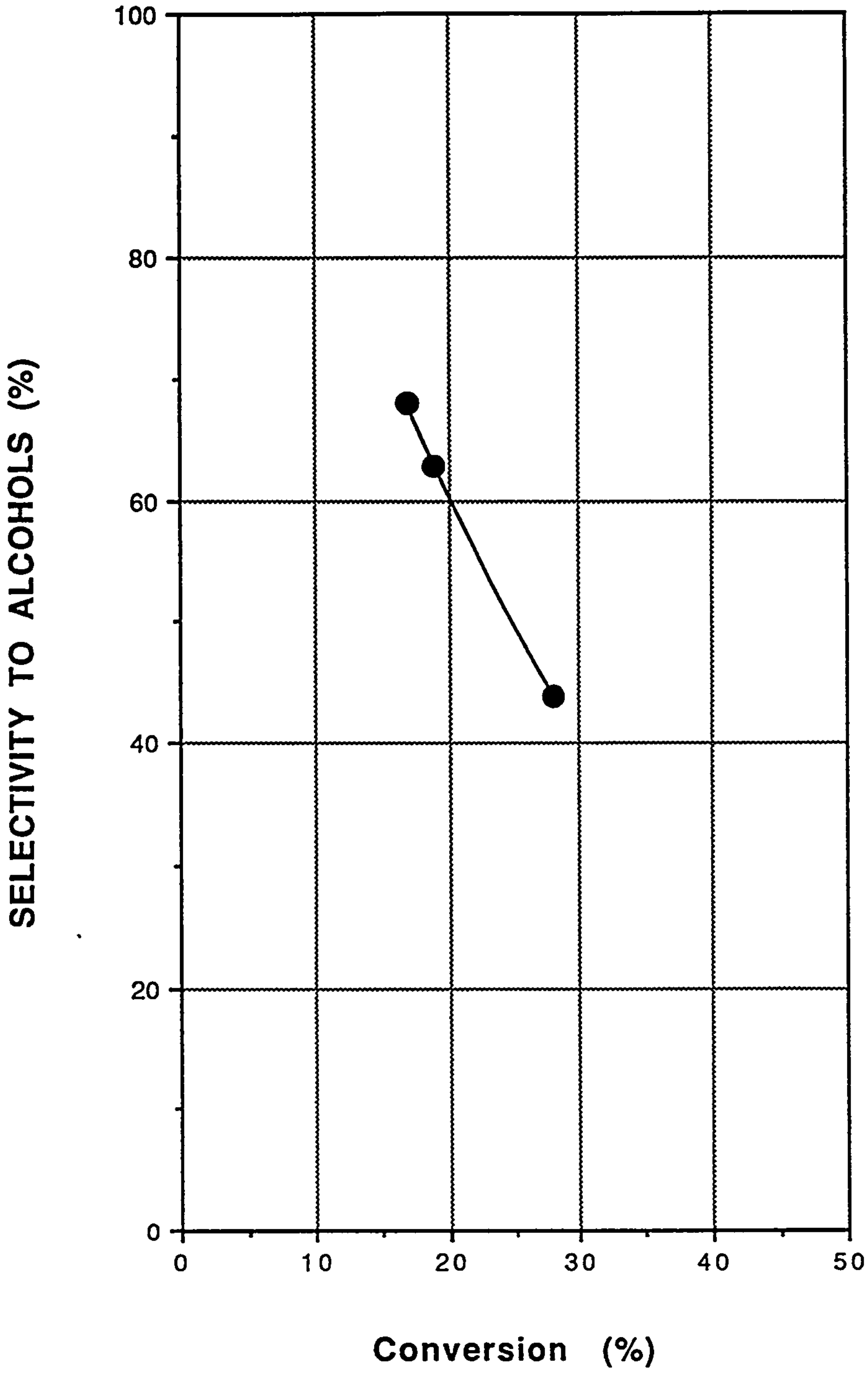


Figure 4.8-7. Plot of Product Composition vs. Conversion with Changing Space Velocity, for Catalyst 10-DAN-54. See Table 4.8-5 for Conditions.

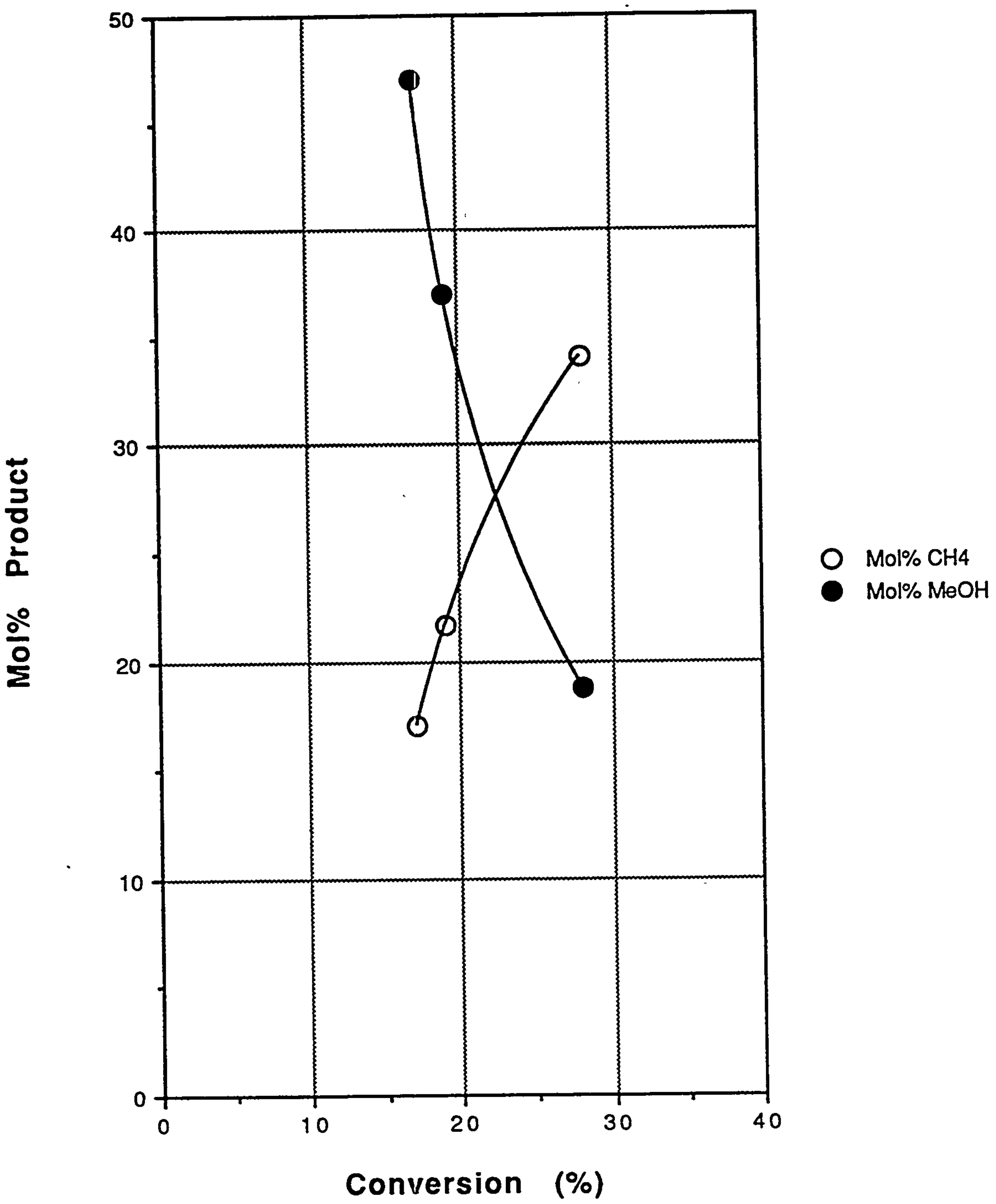


Figure 4.8-8. Plot of Methanol vs. Methane Yields with Changing Space Velocity, for Catalyst 10-DAN-54. See Table 4.8-5 for Conditions.

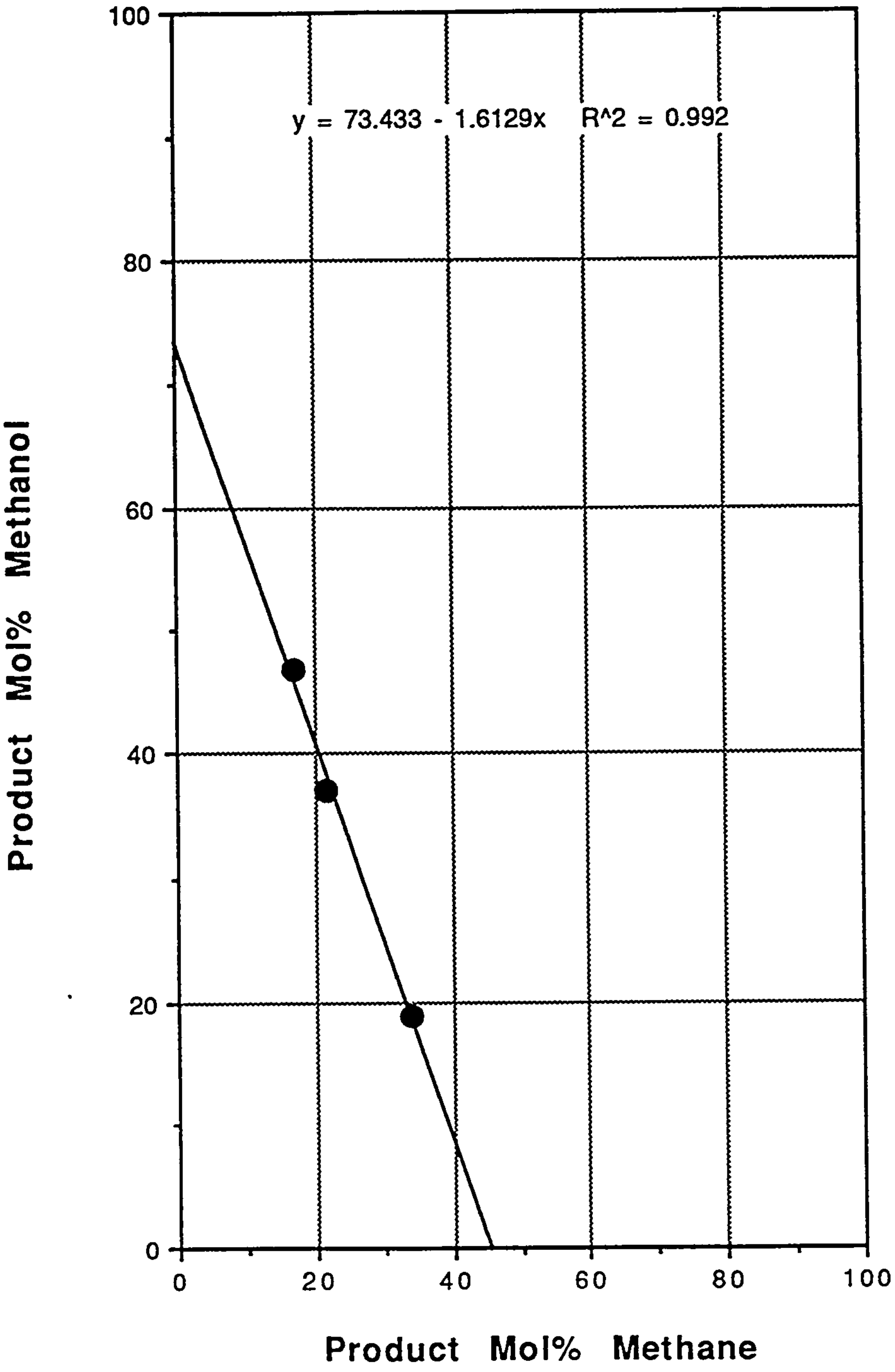


Figure 4.8-9. Plot of Selectivity to Alcohols vs. Conversion with Changing Temperature, for Catalyst 10-DAN-54. See Table 4.8-7 for Conditions.

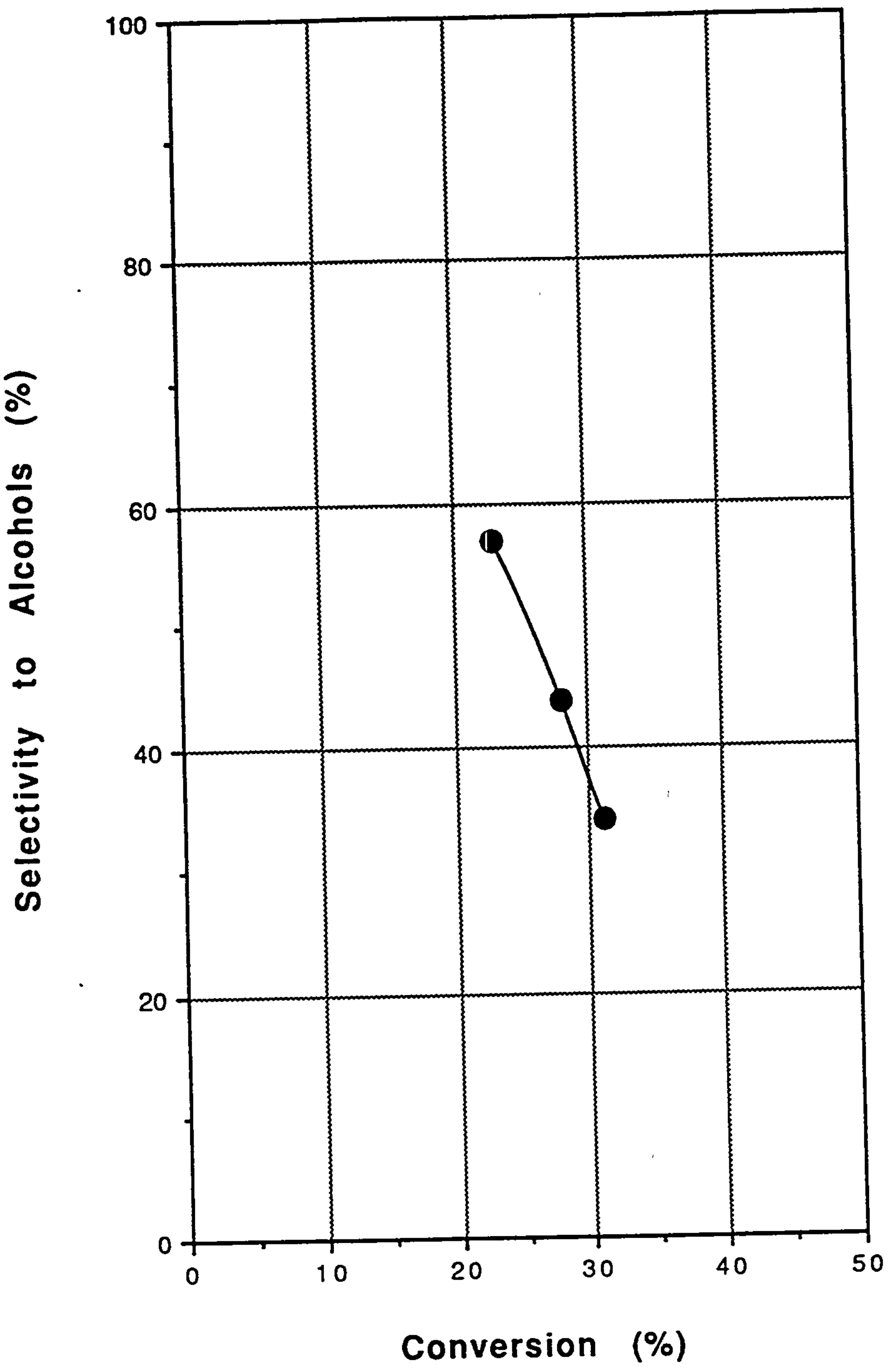


Figure 4.8-10. Plot of Product Composition vs. Conversion with Changing Temperature, for Catalyst 10-DAN-54. See Table 4.8-7 for Conditions.

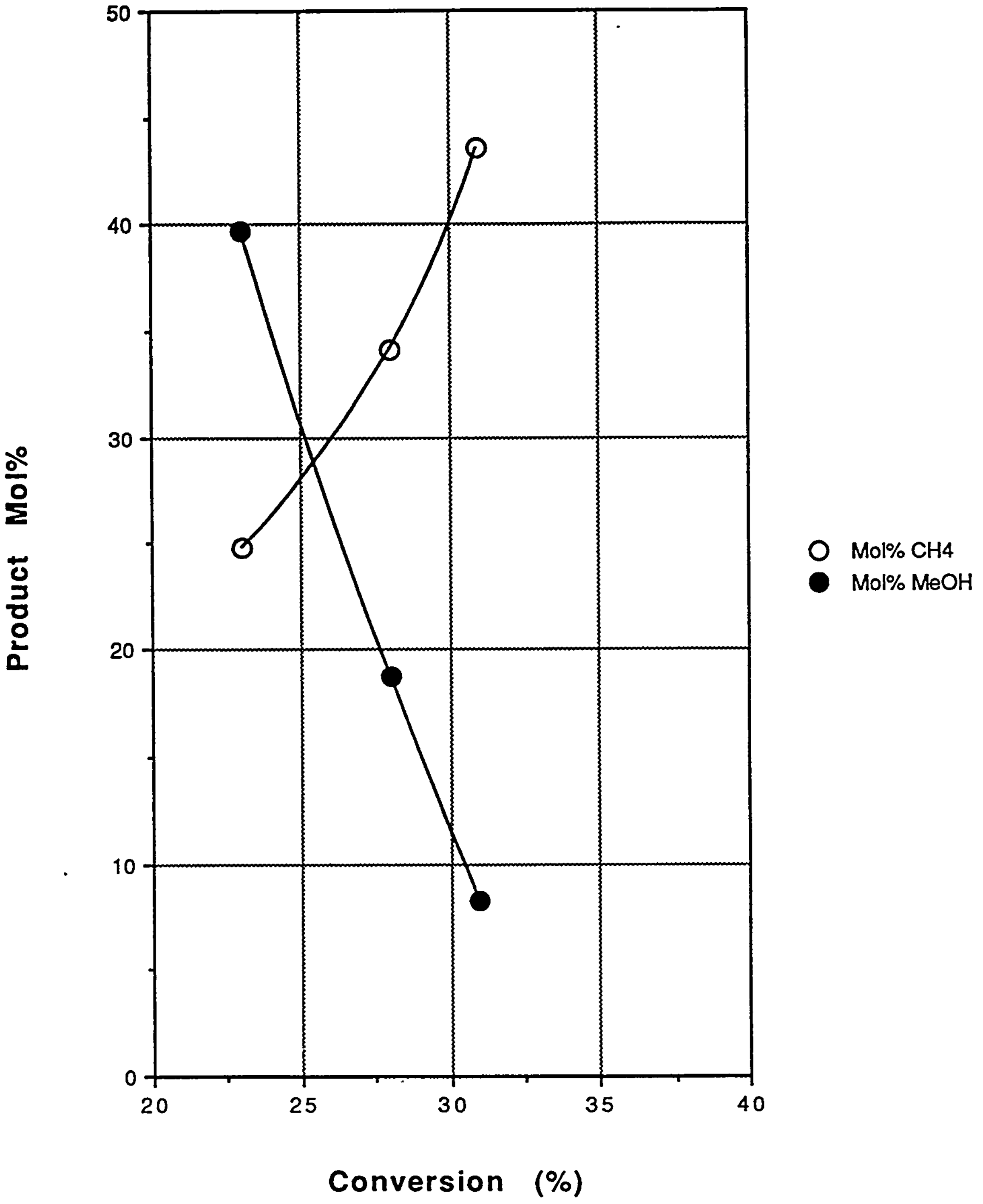


Figure 4.8-11. Plot of Methanol vs. Methane Yields with Changing Temperature, for Catalyst 10-DAN-54. See Table 4.8-7 for Conditions.

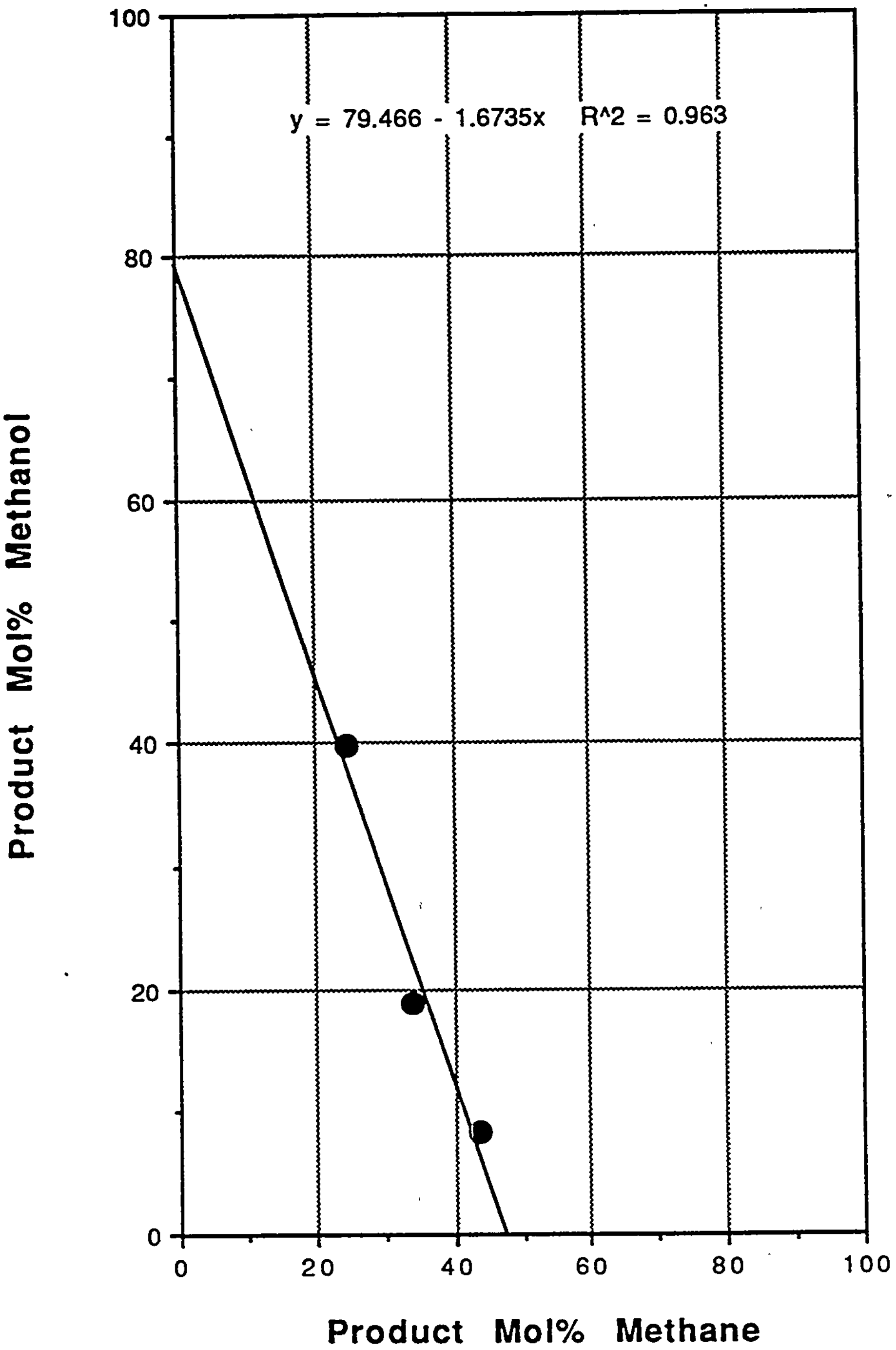


Table 4.8-5. Effect of Changing Space Velocity on Performance of Catalyst 10-DAN-54.

	GHSV = 12000	GHSV = 6000	GHSV = 3000
Total alcohol rate (g/kg-hr)	200	144	78
Total alcohol selectivity (%)	68	63	44
Isobutanol rate (g/kg-hr)	94.3	89	48
MeOH/i-BuOH mole ratio	3.2	2.3	1.7
Total hydrocarbon rate (g/kg-hr)	60	57	69
% Conversion	17	19	28

Conditions: 1000 psi, 400°C, $H_2/CO = 1.0$

Table 4.8-6. Effect of Conversion on Product Composition for Catalyst 10-DAN-54, with Changing Space Velocity. See Table 4.8-5 for Conditions.

	17% Conversion	19% Conversion	28% Conversion
Mol% CH_4	17.03	21.71	34.12
Mol% C_2H_6	9.36	11.24	14.8
Mol% C_3H_8	3.67	4.86	9.21
Mol% C_4H_{10}	3.04	3.45	4.73
Mol% MeOH	47	36.99	18.79
Mol% EtOH	0	0.32	0.72
Mol% i-PrOH	0	0	1.67
Mol% n-PrOH	2.29	2.24	2.34
Mol% Total PrOH	2.29	2.24	4.01
Mol% secBuOH	2.36	2.26	2.26
Mol% i-BuOH	14.72	15.89	11.08
Mol% n-BuOH	0	0	0
Mol% Total BuOH	17.08	18.15	13.33

Table 4.8-7. Effect of Changing Temperature on Performance of Catalyst 10-DAN-54.

	T = 380°C	T = 400°C	T = 420°C
Total alcohol rate (g/kg-hr)	92	78	81
Total alcohol selectivity (%)	57	44	34
Isobutanol rate (g/kg-hr)	45	48	54
MeOH/i-BuOH mole ratio	3.6	1.7	1
Total hydrocarbon rate (g/kg-hr)	43	69	114
% Conversion	23	28	31

Conditions: 1000 psi, GHSV = 3000, $H_2/CO = 1.0$

Table 4.8-8. Effect of Conversion on Product Composition for Catalyst 10-DAN-54, with Changing Temperature. See Table 4.8-7 for Conditions.

	23% Conversion	28% Conversion	31% Conversion
Mol% CH_4	24.8	34.12	43.61
Mol% C_2H_6	10.52	14.8	16.35
Mol% C_3H_8	5.67	9.21	10.99
Mol% C_4H_{10}	3.04	3.45	4.73
Mol% MeOH	39.77	18.79	8.26
Mol% EtOH	0.43	0.72	0.79
Mol% i-PrOH	1.11	1.67	1.32
Mol% n-PrOH	2.06	2.34	2.26
Mol% Total PrOH	3.17	4.01	3.58
Mol% secBuOH	1.44	2.26	2.39
Mol% i-BuOH	11.04	11.08	8.23
Mol% n-BuOH	0	0	0
Mol% Total BuOH	12.47	13.34	10.62

4.8.3 Tests with 10-DAN-55

Using copper-lined reactor tubes, we were able to test catalysts at a 1:2 syngas ratio at 400°C without catalysis being dominated by the tube walls. We conducted some scoping studies with 10-DAN-55, a K/Pd promoted Zn/Cr spinel oxide catalyst with promise for higher alcohol synthesis. The intent of these tests was to see what effect higher pressures and higher temperatures had on catalyst performance at a syngas ratio of 1:2 and a GHSV of 6000. Pressure was first increased to 1500 psi (from 1000), then temperature was raised to 420°C, then 450°C. The results are shown below.

	400°C 1000 psi	400°C 1500 psi	420°C 1500 psi	450°C 1500 psi
Sel. Total Alcohols (%)	83	85	79	44
Total Alcohol Rate (g/kg-hr)	47	86	85	90
Isobutanol Rate (g/kg-hr)	26	41	52	53
MeOH/i-BuOH mole ratio	2.2	3.1	1.4	1.4
Hydrocarbon rate (g/kg-hr)	6	10	16	80
Estimated conversion (%)	14	16	15	13

Increasing pressure from 1000 to 1500 psi nearly doubled the rate to total alcohols with no loss in selectivity, but the methanol to isobutanol mole ratio increased from 2.2 to 3.1. These trends were observed for 10-DAN-52 and 10-DAN-54 in our earlier pressure traverse at a 1:1 syngas ratio.

Increasing temperature to 420°C showed an increase in isobutanol rate and in a decrease in the methanol to isobutanol mole ratio with little loss in selectivity. At 420°C and 1500 psi, the catalyst had a selectivity to total alcohols of 79% and produced 52 g/kg-hr of isobutanol with a methanol to isobutanol mole ratio of 1.42.

However, increasing temperature above 420°C resulted in a marked increase in hydrocarbon formation and the production of isobutyraldehyde and olefins (confirmed by GC/MS). Here the copper tube may have been partially dehydrogenating the products.

4.9 Effects of Co-Feeding Products and Intermediates with Syngas

The addition of various products or intermediates to the feed can provide useful information concerning the path of a reaction and also can help in considering possible process alternatives. The following studies were conducted with catalyst 10-DAN-55 (Pd on $ZnCr_2O_4$), and should be representative of results with other members of this catalyst family.

4.9.1 Effect of Methanol Feed

The effect of methanol addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) has been examined. Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas ratio of 1:2. The results are summarized below.

		Methanol Feed		
	no MeOH	MeOH (32 g/kg-hr)	MeOH (160 g/kg-hr)	MeOH (3200 g/kg-hr)
Sel. Total Alcohols (%)	75	78	78	96
Total Alcohol Rate (g/kg-hr)	79	83	89	1246
Methanol rate (g/kg-hr)	39	40	43	1183
Isobutanol Rate (g/kg-hr)	36	39	42	62
MeOH/i-BuOH mole ratio	4.3	4.1	4.1	32.3
Hydrocarbon rate (g/kg-hr)	16	14	15	23
Estimated conversion (%)	13	11	11	-

Methanol addition had no significant effect on catalyst performance. At the temperature of operation (400°C), the methanol synthesis equilibrium lies heavily in favor of the reactants (CO and H_2). The methanol feed simply reverts to CO and H_2 over the catalyst rather than continuing on to higher alcohols.

Thus, for this catalyst system, methanol feed/recycle will have no obvious advantages for boosting HAS for this catalyst system. The methanol to ethanol step is generally accepted as being rate determining in HAS, so the effect of ethanol addition was examined next.

4.9.2 Effect of Ethanol Feed

The effect of ethanol addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) was examined (16-DMM-58). Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas ratio = 1:2. (Synthesis gas ratio refers to the mole ratio of H_2 to CO.) The results are summarized below:

		Ethanol Feed		
	no EtOH	29 g/kg-hr	70 g/kg-hr	127 g/kg-hr
Ref	PR 220	PR 265	PR 290	PR 321
Time on Stream, hrs	72	118	142	161
Sel. Total Alcohols (%)	84	77	72	68
Total Alcohol Rate (g/kg-hr)	115	115	135	147
Methanol Rate (g/kg-hr)	48	41	42	38
Ethanol Rate (g/kg-hr)	0	0	0	6
n-Propanol rate (g/kg-hr)	0	-	19	28
Isopropanol rat (g/kg-hr)e	0	2	5	8
Isobutanol Rate (g/kg-hr)	57	60	69	68
MeOH/i-BuOH mole ratio	3.3	2.7	2.4	2.2
Hydrocarbon rate (g/kg-hr)	14	22	34	45

The isobutanol rate increased by a modest 19% over the range studied. Significant quantities of n-propanol and isopropanol were observed as more ethanol is added. The methanol/i-butanol ratio fell from 3.3 to 2.2. Feeding a large excess of ethanol (~500 g/kg-hr) resulted in a doubling in the isobutanol rate, but with concurrent formation of large amounts of ethane.

4.9.3 Effect of n-Propanol Feed

The effect of n-propanol addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) was examined (16-DMM-62). Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas ratio = 1:2. The results are summarized below:

		n-Propanol Feed		
	no n-PrOH	25 g/kg-hr	110 g/kg-hr	236 g/kg-hr
Ref	PR 499	PR 517	PR 541	PR 583
Time on Stream, hrs	570	588	612	654
Sel. Total Alcohols (%)	67	70	72	72
Total Alcohol Rate (g/kg-hr)	97	131	143	192
Methanol Rate (g/kg-hr)	54	50	44	44
Ethanol Rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	3	6	3	9
Isopropanol rate (g/kg-hr)	0	0	0	1
Isobutanol Rate (g/kg-hr)	38	75	93	138
MeOH/i-BuOH mole ratio	5.8	2.7	1.9	1.3
Hydrocarbon rate (g/kg-hr)	27	35	37	52

Addition of small amounts of n-propanol to the syngas feed appeared to qualitatively improve the performance; the isobutanol rate doubled on the first incremental addition (isobutanol rate rises from 38 g/kg-hr to 75 g/kg-hr) and the methanol/i-butanol ratio fell from 5.8 to 2.7.

Further addition of up to 236 g/kg-hr of isopropanol resulted in an additional increase in the isobutanol rate to 138 g/kg-hr (MeOH/i-BuOH ratio = 1.3). The hydrocarbon rate also increased and propane was the major hydrocarbon product. The overall rate was increased by a factor of 4 over the range studied. n-Propanol addition was more effective than ethanol addition in boosting the isobutanol rate.

The isopropanol rate was not significantly affected by the addition of n-propanol. The methanol rate fell with n-propanol addition and no ethanol was seen, suggesting that there is no back reaction to lighter alcohols from n-propanol.

4.9.4 Effect of Isopropanol Feed

The effect of i-propanol addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) was examined (16-DMM-61). Test conditions were 1000 psi 400°C, GHSV=12000 and syngas ratio = 1:2. The results are summarized below:

		Isopropanol Feed		
	no i-PrOH	29 g/kg-hr	106 g/kg-hr	225 g/kg-hr
Ref	PR 398	PR 418	PR 439	PR 487
Time on Stream, hrs	403	423	444	492
Sel. Total Alcohols (%)	72	67	61	58
Total Alcohol Rate (g/kg-hr)	107	119	120	146
Methanol Rate (g/kg-hr)	54	51	43	39
Ethanol Rate (g/kg-hr)	0	0	0	0
n-Propanol Rate (g/kg-hr)	5	7	11	16
Isopropanol Rate (g/kg-hr)	0	0	4	17
Isobutanol Rate (g/kg-hr)	48	61	61	75
MeOH/i-BuOH mole ratio	4.5	3.3	2.8	2.1
Hydrocarbon rate (g/kg-hr)	25	36	49	69

Addition of small amounts of isopropanol to the syngas feed appeared to qualitatively improve the performance; the isobutanol rate increased by 27% on the first incremental addition (isobutanol rate rose from 48 g/kg-hr to 61 g/kg-hr) and the methanol/i-butanol ratio fell from 4.5 to 3.3.

Further addition of up to 225 g/kg-hr of isopropanol resulted in isopropanol breakthrough and an additional increase in the isobutanol rate to 75 g/kg-hr (MeOH/i-BuOH ratio = 2.1). The hydrocarbon rate also increased and propane was the major hydrocarbon product.

Interestingly, the n-propanol rate also increased modestly, perhaps suggesting some pathway exists for conversion of isopropanol to n-propanol. The methanol rate fell with isopropanol addition and no ethanol was seen, suggesting that there is no back reaction to lighter alcohols from isopropanol.

4.9.5 Effect of Carbon Dioxide Feed

The effect of carbon dioxide addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) was examined (16-DMM-64). Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas ratio = 1:1. The results are summarized below:

		Carbon Dioxide Feed (%)		
	No CO2	3%	6%	No CO2
Ref	PR 064	PR 093	PR 160	PR 233
Time on Stream, hrs	64	93	160	233
Sel. Total Alcohols (%)	83	89	89	84
Total Alcohol Rate (g/kg-hr)	192	137	107	165
Methanol Rate (g/kg-hr)	108	102	90	103
Ethanol Rate (g/kg-hr)	1	2	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	18	12	6	12
Isobutanol Rate (g/kg-hr)	64	21	11	51
MeOH/i-BuOH mole ratio	7	19	33	8
Hydrocarbon rate (g/kg-hr)	23	9	6	18

Addition of carbon dioxide to the syngas feed adversely affected the performance of a spinel oxide catalyst 10-DAN-55 (Pd on $ZnCr_2O_4$); the total alcohol rate fell by 44% and the isobutanol rate by 83% on addition of 6% carbon dioxide. In concert, the methanol rate decreased by a modest 17%, such that the methanol/i-butanol ratio rose from 7 to 33.

It should be remembered that the water gas shift (WGS) equilibrium must be taken into account when viewing these results, as these materials are excellent WGS catalysts. The equilibrium

$$CO + H_2O = CO_2 + H_2$$

lies to the right under the reaction conditions employed here (Keq = 8), so the effect of carbon dioxide on catalyst performance cannot be disentangled from that of water: the introduction of carbon dioxide to the system will automatically result in an increase in the water content of the gas mixture.

The inhibition of higher alcohol synthesis by carbon dioxide has been observed in other HAS catalyst systems. This observation is explained by assuming that water rather than carbon dioxide inhibits HAS by competing for adsorption with the intermediate C_1 species on the catalyst surface, preventing the homologation reactions from proceeding.

Methanol formation is thus not as sensitive to the water/carbon dioxide equilibrium and, in addition, the mechanism proposed for methanol synthesis involves carbon dioxide as an intermediate. The extra water produced via the WGS equilibrium may help to drive the alcohol equilibrium back to the left, viz.:

$$n\,CO + 2n\,H_2 = C_nH_{2n+1}OH + (n-1)\,H_2O$$

An advantage of carbon dioxide addition is that the rate of hydrocarbon formation is suppressed to an even greater extent such that the selectivity to total alcohols shows a modest increase from 83% to 89%. The extra water produced via the WGS equilibrium may also help to drive the hydrocarbon equilibrium back to the left, viz.:

$$n\,CO + (2n+1)\,H_2 = C_nH_{2n+2} + n\,H_2O$$

or perhaps water helps to titrate acid sites on the catalysts responsible for hydrocarbon formation.

The catalyst recovered slowly after stopping the addition of carbon dioxide: normally changes in process parameters and alcohol feeds result in a new steady state within 4-8 hours, but on turning off the carbon dioxide feed, the catalyst was still returning to pre-carbon dioxide feed performance after 48 hrs. This suggests some surface intermediate is being slowly lost, perhaps carbonate.

4.9.6 Effect of Water Feed

The effect of water addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) was examined (16-DMM-65). Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas ratio = 1:1. The results are summarized below:

		Water Feed		
	None	150 g/kg-hr	334 g/kg-hr	490 g/kg-hr
Ref	PR 233	PR 303	PR 328	PR 332
Time on Stream, hrs	233	303	328	332
Sel. Total Alcohols (%)	84	78	86	89
Total Alcohol Rate (g/kg-hr)	165	166	107	92
Methanol Rate (g/kg-hr)	103	125	92	85
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	12	6	3	0
Isobutanol Rate (g/kg-hr)	51	35	12	7
MeOH/i-BuOH mole ratio	8	14	32	48
Hydrocarbon rate (g/kg-hr)	18	24	9	6

Addition of water to the syngas feed adversely affected the performance of the catalyst; the total alcohol rate fell by 44% and the isobutanol rate by 86% on addition of up to 490 g/kg-hr of water. In concert, the methanol rate decreased by only 17%, resulting in an increase in the methanol/i-butanol ratio from 8 to 48.

These results are essentially identical to those obtained through carbon dioxide addition. It should be remembered that the water gas shift (WGS) equilibrium must be taken into account when viewing these results, as these materials are excellent WGS catalysts. The introduction of water to the system will automatically result in an increase in the carbon dioxide content of the gas mixture.

ESCA analysis of the spent catalyst, after water addition, indicated the formation of a carbonate layer on the catalyst surface, supporting this hypothesis.

The WGS activity is potentially beneficial, as it is less expensive to remove carbon dioxide from the recycle stream by extraction than water via distillation.

4.9.7 Aging of Catalyst During Feeding Experiments

A single sample of catalyst 10-DAN-55 was used for the above experiments, and it showed some effects of aging with time on stream (see below). We believe that this is due to loss of palladium surface area with time (total time elapsed = 279 hrs, or about 12 days continuously on stream). Palladium is the major component in the formulation that promotes HAS and we believe that sintering of the metal is responsible for the loss in selectivity. SEM photographs and surface analysis confirm this hypothesis.

Ref.	PR 220	PR 398	PR 499
Time on Stream, hrs	72	403	570
Sel. Total Alcohols (%)	84	72	67
Total Alcohol Rate (g/kg-hr)	115	107	97
Methanol Rate (g/kg-hr)	48	54	54
Ethanol Rate (g/kg-hr)	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0
n-Propanol rate (g/kg-hr)	0	5	3
Isobutanol Rate (g/kg-hr)	57	48	38
MeOH/i-BuOH mole ratio	3.3	4.5	5.8
Hydrocarbon rate (g/kg-hr)	14	25	27

4.10 Preparation of an Improved Catalyst (16-DMM-68)

We set out to prepare an improved version of 10-DAN-54, our previous "best" catalyst for higher alcohol synthesis. This new catalyst, 16-DMM-68, has extra added potassium which should increase its selectivity to total alcohols and allow operation at higher conversions. The catalyst is a Zn/Cr/Mn spinel oxide promoted with Pd and K. (The composition is 2.25 wt% K, 5.9 wt% Pd on the ZnCrMn spinel oxide containing excess ZnO.) The procedure involved the preparation the base spinel oxide via controlled pH precipitation, followed by incipient wetness impregnation of the spinel with solutions of potassium and palladium as the nitrates. This material (16-DMM-68) has acceptable elemental analysis for the expected composition and possesses the desired high surface area of >80 m^2/g. Catalyst 16-DMM-68 was characterized and then tested under standard conditions (400°C, 1000 psi, GHSV = 12000, syngas ratio (H_2/CO) = 1) in order to compare its performance with 10-DAN-54.

4.10.1 Comparison with 10-DAN-54

The results of tests with 16-DMM-68 are summarized below and are compared to 10-DAN-54 under identical conditions (400°C, 1000 psi, GHSV = 12000, H_2/CO = 1):

	16-DMM-68	10-DAN-54
Ref. No.	PR-020	PR-620
Sel. Total Alcohols (%)	84	68
Total Alcohol Rate (g/kg-hr)	233	200
Methanol Rate (g/kg-hr)	119	75
Ethanol Rate (g/kg-hr)	0	0
Isopropanol rate (g/kg-hr)	0	0
n-Propanol rate (g/kg-hr)	12	11
Isobutanol Rate (g/kg-hr)	102	94
MeOH/i-BuOH mole ratio	4.7	3.2
Hydrocarbon rate (g/kg-hr)	26	60

16-DMM-68 was slightly more active and significantly more selective for alcohols than 10-DAN-54, probably due to the extra alkali added. 16-DMM-68 also produced more methanol and, as a consequence, the methanol to isobutanol mole ratio rose from 3.2 (in the case of 10-DAN-54) to 4.7 for 16-DMM-68.

4.10.2 Testing at Higher Temperatures and Pressures

We tested 16-DMM-68 at elevated temperatures (>400°C) and pressures (>1000 psi). GHSV was held constant at 12000 and the syngas ratio was also held constant at 1:1. The results are summarized below:

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1180 psi	T = 440°C P = 1500 psi
Ref. No.	PR-020	PR-113	PR-170	PR-125
Sel. Total Alcohols (%)	84	86	54	64
Total Alcohol Rate (g/kg-hr)	233	407	159	304
Methanol Rate (g/kg-hr)	119	248	35	99
Ethanol Rate (g/kg-hr)	0	7	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	12	21	15	27
Isobutanol Rate (g/kg-hr)	102	130	109	179
MeOH/i-BuOH mole ratio	4.7	7.6	1.3	2.2
Hydrocarbon rate (g/kg-hr)	26	37	94	112
Conversion (%)	14	24	23	28

The data showed that the catalyst was most effective for higher alcohol synthesis (HAS) at elevated temperatures and pressures. Note that the *combination* of high temperature and high pressure is required for optimal for HAS. This is because the sum of the individual effects promotes HAS over both hydrocarbon formation (favored at higher temperatures) and methanol formation (favored at higher pressures).

This catalyst (with extra added alkali as compared with 10-DAN-54) can also operate effectively at syngas conversions up to 28%. (See PR-125 in the table above.) 10-DAN-54 was limited to conversions of < 20%; otherwise hydrocarbon formation became a serious inefficiency.

4.10.3 Modifications of the 10-DMM-68 Composition

A series of catalysts was synthesized using our catalyst 10-DMM-68 as the center point. The support used was the standard Zn/Cr/Mn spinel oxide. The K and Pd levels employed are shown below:

	K Level (wt%)	Pd Level (wt%)
High	3.5	9.0
Mid point (16-DMM-68)	2.25	6.0
Low	1.0	3.0

Four new catalysts were prepared using the high/high, high/low, low/high and low/low combinations of K and Pd. Each catalyst was tested at 4 different process conditions, in the order shown below:

1. 400°C, 1000 psi
2. 400°C, 1500 psi
3. 440°C, 1500 psi
4. 440°C, 1000 psi

Stainless steel tubes were used as reactors for convenience, as it was thought that problems caused by reactor tube walls catalyzing syngas conversion were a cause for concern only at low syngas ratios ($H_2/CO < 1$). This proved to be a false assumption as the data subsequently showed.

The results from this "mini-design" are displayed in Tables 4.10-1 – 4.10-5. Data analysis was performed using Data Desk® software using the following protocol:

Input variables:

K level
Pd level
temperature
pressure

Output variables:

Selectivity to total alcohols
Total alcohol rate
Methanol rate
Ethanol rate
Isopropanol rate
n-Propanol rate
Isobutanol rate
Methanol/isobutanol mole ratio
Total hydrocarbons rate
Conversion

A correlation table between input and output variables was developed which showed little interaction between the input and output variables. The strongest correlation was between hydrocarbon rate and temperature. High temperature operation (at 440°C) results in drastic loss in selectivities to total alcohols (down to 18-30%), and this obscures the effect of the catalyst formulation variables. We had previously observed problems with the tube walls catalyzing syngas conversion at 400°C using a syngas ratio (H_2/CO) = 0.5, but it appears that at higher temperatures (e.g., 440°C), the tube walls can also catalyze syngas conversion with a more hydrogen-rich syngas mix. Comparison with tests in a copper-lined tube with 1:1 syngas confirm this hypothesis (see Table 4.10-6)

The design did suggest that higher Pd loadings would be beneficial for isobutanol synthesis. However, in copper-lined reactors, a test of a high Pd catalyst (9 wt%) did not give superior isobutanol activity as compared with the standard 6 wt% formulation. (See Tables 4.10-6 and 4.10-7).

The 6 wt% Pd formulation and a 9 wt% Pd formulation were tested with 1:2 syngas in copper-lined tubes; see Tables 4.10-8 and 4.10-9). The 6 wt% Pd catalyst, at 440°C and 1500 psi, produced 71 g/kg-hr of isobutanol with a methanol/isobutanol product mole ratio < 1. Under the same conditions, the 9 wt% Pd catalyst was again inferior, producing 52 g/kg-hr of isobutanol with a methanol/isobutanol product mole ratio = 1.7. Of particular interest here is that the 6 wt% Pd catalyst produced more higher alcohols than methanol on a molar basis at good rates using a syngas mix that could be derived from a Shell gasifier.

Table 4.10-1. Catalyst Tests with K/Pd Center Point Catalyst.

2.25 wt% K / 6.0 wt% Pd

Tested in a stainless steel tube

16DMM107

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR268	PR276	PR292	PR300
Sel. Total Alcohols (%)	74	77	45	46
Total Alcohol Rate (g/kg-hr)	192	319	290	192
Methanol Rate (g/kg-hr)	59	147	49	23
Ethanol Rate (g/kg-hr)	3	4	0	10
Isopropanol rate (g/kg-hr)	9	7	29	20
n-Propanol rate (g/kg-hr)	35	48	77	57
Isobutanol Rate (g/kg-hr)	83	109	135	83
MeOH/i-BuOH mole ratio	2.8	5.4	1.4	1.0
Hydrocarbon rate (g/kg-hr)	44	57	250	162
Conversion (%)	20	23	28	22

Table 4.10-2. Catalyst Tests with Low K / Low Pd.

1.0 wt% K / 3.0 wt% Pd

Tested in a stainless steel tube

16DMM102

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR217	PR225	PR241	PR249
Sel. Total Alcohols (%)	55	59	29	27
Total Alcohol Rate (g/kg-hr)	129	243	182	91
Methanol Rate (g/kg-hr)	50	119	44	23
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	11	9	13	5
n-Propanol rate (g/kg-hr)	17	30	45	28
Isobutanol Rate (g/kg-hr)	50	86	79	35
MeOH/i-BuOH mole ratio	4.0	5.5	2.2	2.5
Hydrocarbon rate (g/kg-hr)	66	99	306	170
Conversion (%)	15	18	25	16

Table 4.10-3. Catalyst Tests at High K / Low Pd.

3.5 wt% K / 3.0 wt% Pd

Tested in a stainless steel tube

16DMM102

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR116	PR124	PR146	PR166
Sel. Total Alcohols (%)	78	69	30	27
Total Alcohol Rate (g/kg-hr)	163	352	277	166
Methanol Rate (g/kg-hr)	66	167	40	18
Ethanol Rate (g/kg-hr)	4	14	21	12
Isopropanol rate (g/kg-hr)	5	19	41	28
n-Propanol rate (g/kg-hr)	19	45	50	32
Isobutanol Rate (g/kg-hr)	66	95	119	76
MeOH/i-BuOH mole ratio	4.0	7.0	1.4	1.0
Hydrocarbon rate (g/kg-hr)	29	92	460	330
Conversion (%)	17	24	34	26

Table 4.10-4. Catalyst Tests at Low K / High Pd.

1.0 wt% K / 9.0 wt% Pd

Tested in a stainless steel tube

16DMM105

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR218	PR246	PR242	PR250
Sel. Total Alcohols (%)	60	60	31	31
Total Alcohol Rate (g/kg-hr)	191	347	339	191
Methanol Rate (g/kg-hr)	70	152	58	32
Ethanol Rate (g/kg-hr)	2	5	1	0
Isopropanol rate (g/kg-hr)	8	18	53	31
n-Propanol rate (g/kg-hr)	28	43	96	61
Isobutanol Rate (g/kg-hr)	83	129	130	66
MeOH/i-BuOH mole ratio	3.4	4.7	1.8	2.0
Hydrocarbon Rate (g/kg-hr)	82	142	529	306
Conversion (%)	21	26	37	27

Table 4.10-5. Catalyst Tests at High K / High Pd.

3.5 wt% K / 9.0 wt% Pd

Tested in a stainless steel tube

16DMM101

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR115	PR125	PR145	PR165
Sel. Total Alcohols (%)	82	78	23	18
Total Alcohol Rate (g/kg-hr)	115	264	197	101
Methanol Rate (g/kg-hr)	54	126	28	16
Ethanol Rate (g/kg-hr)	0	7	6	8
Isopropanol rate (g/kg-hr)	2	18	29	6
n-Propanol rate (g/kg-hr)	15	37	47	23
Isobutanol Rate (g/kg-hr)	43	67	84	48
MeOH/i-BuOH mole ratio	5.2	7.5	1.3	1.3
Hydrocarbon rate (g/kg-hr)	15	46	487	331
Conversion (%)	11	18	31	24

Table 4.10-6. Catalyst Tests with K / Pd Center Point Catalyst.

2.25 wt% K / 6.0 wt% Pd

Tested in a copper lined tube

16DMM78

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR020	PR113	PR125	PR170
Sel. Total Alcohols (%)	84	86	64	54
Total Alcohol Rate (g/kg-hr)	233	407	304	159
Methanol Rate (g/kg-hr)	119	248	99	35
Ethanol Rate (g/kg-hr)	0	7	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	12	21	27	15
Isobutanol Rate (g/kg-hr)	102	130	179	109
MeOH/i-BuOH mole ratio	4.7	7.6	2.2	1.3
Hydrocarbon rate (g/kg-hr)	26	37	94	112
Conversion (%)	14	24	28	28

Table 4.10-7. Catalyst Tests at Low K / High Pd.

1.0 wt% K / 9.0 wt% Pd

16DMM108

Tested in a copper lined tube

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	PR321	-	PR329	-
Sel. Total Alcohols (%)	69	-	52	-
Total Alcohol Rate (g/kg-hr)	164	-	237	-
Methanol Rate (g/kg-hr)	63	-	65	-
Ethanol Rate (g/kg-hr)	0	-	15	-
Isopropanol rate (g/kg-hr)	0	-	7	-
n-Propanol rate (g/kg-hr)	10	-	28	-
Isobutanol Rate (g/kg-hr)	91	-	122	-
MeOH/i-BuOH mole ratio	2.8	-	2.1	-
Hydrocarbon Rate (g/kg-hr)	48	-	145	-
Conversion (%)	15	-	22	-

Table 4.10-8. Catalyst Tests with K / Pd Center Point Catalyst.

2.25 wt% K / 6.0 wt% Pd

Tested in a copper lined tube with 1:2 syngas

16DMM110

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	-	-	PR344	-
Sel. Total Alcohols (%)	-	-	63	-
Total Alcohol Rate (g/kg-hr)	-	-	96	-
Methanol Rate (g/kg-hr)	-	-	14	-
Ethanol Rate (g/kg-hr)	-	-	0	-
Isopropanol rate (g/kg-hr)	-	-	3	-
n-Propanol rate (g/kg-hr)	-	-	8	-
Isobutanol Rate (g/kg-hr)	-	-	71	-
MeOH/i-BuOH mole ratio	-	-	0.8	-
Hydrocarbon rate (g/kg-hr)	-	-	41	-
Conversion (%)	-	-	26	-

Table 4.10-9. Catalyst Tests at Low K / High Pd.

1.0 wt% K / 9.0 wt% Pd

Tested in a copper lined tube with 1:2 syngas

16DMM108

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	-	-	PR345	-
Sel. Total Alcohols (%)	-	-	47	-
Total Alcohol Rate (g/kg-hr)	-	-	92	-
Methanol Rate (g/kg-hr)	-	-	22	-
Ethanol Rate (g/kg-hr)	-	-	5	-
Isopropanol rate (g/kg-hr)	-	-	0	-
n-Propanol rate (g/kg-hr)	-	-	13	-
Isobutanol Rate (g/kg-hr)	-	-	52	-
MeOH/i-BuOH mole ratio	-	-	1.7	-
Hydrocarbon Rate (g/kg-hr)	-	-	69	-
Conversion (%)	-	-	20	-

4.11 Studies of Zn-Cr Spinel Supports

The catalyst that we investigated in many of our studies because of its good performance (16-DMM-68) is a formulation that contains 2.25 wt% K, 5.9 wt% Pd on a ZnCrMn spinel oxide that contains excess ZnO prepared via controlled pH precipitation. The significant features of this composition may be summarized as follows:

- the substitution of Mn for Cr
- the presence of excess ZnO
- the controlled pH precipitation of the spinel/ZnO
- the addition of alkali in the form of potassium
- the addition of Pd

In order to more critically study the effects of some of these features on catalyst performance, we prepared a comparative Zn/Cr spinel oxide support that contained excess ZnO and looked at the catalytic performance of:

(1) the bare Zn/Cr support,
(2) a potassium traverse on the bare Zn/Cr support to determine the effect of alkali addition in the absence of Pd,
(3) a potassium traverse on the Zn/Cr support impregnated with 6 wt% Pd, determined to be the optimum level on the Zn/Cr/Mn support,
(4) a cesium traverse on the bare support,
(5) cesium and palladium promoters on the Zn/Cr support,
(6) cesium addition to the Zn/Cr/Mn spinel oxide,
(7) Cs and Pd addition to the Zn/Cr/Mn spinel oxide,
(8) potassium promotion of Zn/Cr and ZnO supports,
(9) presence and absence of excess ZnO in the Zn/Cr spinel, and
(10) similar catalysts based in commercial Zn/Cr support.

Each catalyst was examined at 4 different process conditions:

- 400°C, 1000 psi
- 400°C, 1500 psi
- 440°C, 1500 psi
- 440°C, 1000 psi

4.11.1 Zn/Cr Spinel With Excess Zn (Bare Support)

The bare support was an inefficient methanol catalyst, producing alcohols at a total rate of 164 g/kg-hr, with a specific methanol rate of 160 g/kg-hr at 1000 psi, 400°C, 12000 GHSV and a syngas ratio (H_2/CO) = 1; see Table 4.11-1. The isobutanol rate was barely detectable at 2 g/kg-hr. Selectivity to total alcohols was only 50%.

Increasing pressure resulted in an increase in overall selectivity to total alcohols (from 50% to 61%) and in total alcohol productivity (the rate almost doubled from 164 g/kg-hr to 292 g/kg-hr), mainly through an increase in the methanol rate. Increasing temperature and pressure resulted in a minor increase in the isobutanol rate to 7 g/kg-hr, but total alcohol selectivity fell to only 29%.

4.11.2 Addition of K to the Zn/Cr Spinel with Excess Zn

Alkali addition (in the form of potassium at 1, 3, 5 and 7 wt%) resulted in an increase in selectivity to total alcohols vs. the bare support and a dramatic increase in higher alcohol synthesis. The data appear in Tables 4.11-2 – 4.11-5. For the 7 wt% K formulation, isobutanol could be made at rates > 100 g/kg-hr at 440°C and 1500 psi with selectivity to total alcohols of 85% and with a methanol/isobutanol mole ratio of 2.0. Under the same conditions, the bare support exhibited an isobutanol rate of 7 g/kg-hr, with selectivity to total alcohols of 29% and with a methanol/isobutanol mole ratio of 86 !

The lowest methanol/isobutanol mole ratio was obtained with the 5 wt% K formulation (1.6 at 440°C, 1500 psi and 0.94 at 440°C, 1000 psi).

The catalysts are compared at 440°C and 1500 psi in Figures 4.11-1 – 4.11-3.

4.11.3 Addition of K to 6 wt% Pd on Zn/Cr Spinel with Excess Zn

Pd additions resulted in further improvements in performance: isobutanol rates of > 130 g/kg-hr were observed at 440°C and 1500 psi for the 3, 5 and 7 wt% K catalysts, suggesting a broad optimum in the K loading. Selectivities increased with K loading. The data appear in Tables 4.11-6 – 4.11-9. The catalysts are compared at 440°C and 1500 psi in Figures 4.11-4 – 4.11-6. The lowest methanol/isobutanol mole ratio was obtained with the 5 wt% K formulation (1.2 at 440°C and 1500 psi).

The 5 wt% K, 5.9 wt% Pd catalyst produced > 100 g/kg-hr of isobutanol at 440°C and only 1000 psi, with 85% selectivities to total alcohols and with a methanol/isobutanol mole ratio of < 2.

The 7 wt% K, 5.9 wt% Pd catalyst at 440°C and 1000 psi produced isobutanol at 85 g/kg-hr, with a selectivity to total alcohols of 80% and a methanol/isobutanol mole ratio of 1.0.

4.11.4 Cesium Addition to a Zn/Cr Spinel With Excess Zn

A set of experiments was designed to determine whether cesium is a more effective promoter than potassium for higher alcohol synthesis and what level of cesium is preferred. We examined the effect of cesium addition to a Zn/Cr spinel oxide support that contained excess ZnO. Five catalysts containing 10, 7.5, 5, 3 and 1 wt% cesium were prepared and tested. The high-cesium catalysts (5, 7.5 and 10 wt%) were very efficient alcohol synthesis catalysts (>94% selective to total alcohols at 400°C, 1000 psi, GHSV = 12000, $H_2/CO = 1$), but were inactive (total alcohol rates < 130 g/kg-hr) — see Tables 4.11-10 – 4.11-12. These results were somewhat surprising, since the total number of atoms of Cs/m^2 of support at these wt% levels is in the same range as the optimum number of atoms for potassium addition (atomic wt K = 39, atomic wt Cs = 133). This implies that atomic size effects, not just acid site neutralization, are important. The highest isobutanol rate observed for these formulations was 87 g/kg-hr at 440°C, 1500 psi, GHSV = 12000, $H_2/CO = 1$ at the lowest cesium loading (5 wt%).

Follow-up tests at lower cesium loadings (1 and 3 wt%) yielded catalysts of very different performance — see Tables 4.11-13 and 4.11-14. The 1 wt% cesium formulation was relatively unselective at 400°C, 1000 psi, GHSV = 12000, $H_2/CO = 1$, with a total alcohol selectivity of only 58%, a clear indication of under-promotion. The isobutanol rate was also low, at only 31 g/kg-hr. The 3 wt% cesium gave a more selective (88% selectivity to total alcohols) and more active (isobutanol rate = 93 g/kg-hr) catalyst under the same conditions.

Operation of the 3 wt% cesium catalyst at higher temperatures and pressures gave impressive results: isobutanol rates > 170 g/kg-hr were observed at 440°C and 1500 psi with selectivity to total alcohols of 77% and with a methanol/isobutanol mole ratio of 1.4: this performance is as good as that of our best Pd/K catalyst.

4.11.5 Addition of Cs and Pd to the Zn/Cr Spinel with Excess Zn

We examined the effect of adding palladium in addition to cesium to a Zn/Cr spinel oxide support that contained excess Zn. Three catalysts containing 1, 3 and 5 wt% cesium and 5.9 wt% Pd were prepared and tested — see Tables 4.11-15 – 4.11-17.

The low-cesium catalyst (1% Cs, 5.9% Pd) was clearly under-promoted, with a 43% selectivity to total alcohols, a total alcohol rate = 120 g/kg-hr, an isobutanol rate of < 100 g/kg-hr and a methanol/isobutanol mole ratio = 2.8 at 440°C, 1500 psi, GHSV = 12000, $H_2/CO = 1$.

The 3 wt% Cs, 5.9 wt% Pd catalyst showed improved performance, with a 67% selectivity to total alcohols, a total alcohol rate of 238 g/kg-hr, an isobutanol rate of 161 g/kg-hr and a methanol/isobutanol mole ratio = 1.2 under the same conditions.

The high-Cs catalyst, 5 wt% Cs, 5.9 wt% Pd, showed similar performance to the 3 wt% Cs, 5.9 wt% Pd catalyst with a 81% selectivity to total alcohols, a total alcohol rate = 233 g/kg-hr, an isobutanol rate of 150 g/kg-hr and a methanol/isobutanol mole ratio = 1.2 under the same conditions.

Interestingly, the overall performance at 440°C and only 1000 psi was even better. Recall that the addition of Pd allows operation at lower pressures. Here the high Cs formulation appears to give the best overall performance: isobutanol rate > 150 g/kg-hr with a selectivity to total alcohols of 88% and a methanol/isobutanol mole ratio of 0.58: this represents our best overall performance to date.

4.11.6 Cs Addition to Zn/Cr/Mn Spinel with Excess Zn

This spinel was the support used in the synthesis of 10-DAN-54, our benchmark catalyst. Three catalysts were prepared and tested, containing 1, 3 and 5 wt% cesium on the support.

These catalysts showed a lower overall total alcohol rate than those using the spinel without Mn present — see Tables 4.11-18 – 4.11-20. The optimal Cs loading is also lower — 1 wt% rather than the 3-5 wt% required for the Zn/Cr spinel formulations. This is consistent with Mn substitution for Cr lowering the overall acidity of the spinel. The difference cannot be attributed to the two supports being of different surface areas (thus requiring a different Cs loading) as the surface areas are very close (for the Zn/Cr = 94 m^2/g, for the Zn/Cr/Mn = 85 m^2/g).

4.11.7 Cs and Pd Addition to a Zn/Cr/Mn Spinel with Excess Zn

Three catalysts containing 1, 3 and 5 wt% cesium and 5.9 wt% Pd were prepared and tested — see Tables 4.11-21 – 4.11-23. Once again catalyst activities are lower than for the corresponding formulations on the Zn/Cr spinel. The 5 wt% Cs/5.9 wt% Pd formulation was tested at temperatures above 440°C and the results are shown in Table 4.11-24.

Operation at temperatures above 440°C results in a further increase in the isobutanol rate, a further decrease in the methanol rate, but a marked increase in the hydrocarbon rate suggesting that these formulations may be slightly under promoted in alkali. Promoter optimization may be necessary for successful operation in this higher temperature regime.

4.11.8 Potassium Promotion of Zn/Cr/O and ZnO

We have prepared comparative catalysts based on Zn/Cr spinel oxide support that does not contains excess ZnO and on ZnO by itself, both prepared by controlled pH precipitation. We examined the effect of potassium promotion on (a) a Zn/Cr/O spinel and (b) on ZnO; these two individual components are used together to make our current best support, which is Zn/Cr/O with excess ZnO (1:2 ratio). A potassium traverse (1, 3, 5 wt% K) was conducted on each material and the results are displayed in Tables 4.11-25 – 4.11-32. Comparisons with results previously reported for the spinel with excess ZnO are shown below:

Comparison of (a) Zn/Cr/O, (b) ZnO and (c) Zn/Cr/O with excess ZnO
all promoted with Potassium[1]
440°C, 1500 psi, GHSV = 12000, H_2/CO = 1:1

	Zn/Cr 3 wt% K PR039	ZnO 1 wt% K PR141	Zn/Cr/O w. ex.ZnO 5 wt% K[2] PR195
Sel. Total Alcohols (%)	64	70	71
Total Alcohol Rate (g/kg-hr)	131	85	178
Methanol Rate (g/kg-hr)	39	42	47
Isobutanol Rate (g/kg-hr)	90	38	117
MeOH/i-BuOH mole ratio	1.8	4.5	1.6
Hydrocarbon rate (g/kg-hr)	47	23	14

[1] These results are for those potassium levels that showed the highest isobutanol rates.

[2] Results previously reported.

All the materials were prepared in the same way, by precipitation at constant pH = 10 from the corresponding nitrate salts by controlled addition of a potassium hydroxide / potassium carbonate solution. The surface area of the Zn/Cr/O spinel is around 80 m^2/g, while that of the ZnO is < 20 m^2/g, which explains why less potassium is needed for ZnO. The combination of the spinel and excess ZnO also has a high surface area (~ 80 m^2/g), suggesting that ZnO may be dispersed over the surface of the spinel and that this "high surface area" ZnO may require more potassium for optimal performance.

The combination of the two components is better than each of the individual parts: the Zn/Cr/O with excess ZnO is as selective and is more active for total alcohols (and more importantly, for isobutanol) than any of the individual components.

4.11.9 Presence and Absence of Excess ZnO

Spinel oxide catalysts promoted with cesium and both cesium and palladium have been prepared without the presence of excess ZnO and have been compared to those prepared with excess ZnO. The presence of the excess ZnO is purported to improve catalyst performance by creating defects in the regular spinel lattice; these defect sites are thought to be active alcohol synthesis sites. Our best catalysts contain excess ZnO.

We have looked at the effect of the presence or absence of excess zinc oxide on the performance of Zn/Cr spinel oxide catalysts (a) promoted with cesium and (b) promoted with both cesium and palladium. Three levels of cesium were examined (1, 3 and 5 wt%); see

Tables 4.11-33 – 4.11-35. The largest isobutanol rates are obtained at high temperatures and pressures (440°C and 1500 psi). Test results for representative catalysts on the two different supports are shown below:

Test conditions: 440°C, 1500 psi, GHSV=12000, $H_2/CO=1$

	Zn/Cr w ex.ZnO with 3 wt% Cs[1] PR490	Zn/Cr only with 3 wt% Cs PR290
Sel. Total Alcohols (%)	77	44
Total Alcohol Rate (g/kg-hr)	248	200
Methanol Rate (g/kg-hr)	58	48
Isobutanol Rate (g/kg-hr)	171	121
MeOH/i-BuOH mole ratio	1.4	1.6
Hydrocarbon rate (g/kg-hr)	18	179

[1] Results previously reported.

Three different Cs/Pd catalysts were examined (1, 3 and 5 wt% Cs with 5.9 wt% Pd) - see Tables 4.11-36 – 4.11-38. The addition of Pd allows the catalysts to operate at lower pressures with good isobutanol rates (> 100 g/kg-hr).

Test conditions: 440°C, 1000 psi, GHSV=12000, $H_2/CO=1$. Test results for representative catalysts on the two supports are shown below:

	Zn/Cr w ex.ZnO with 5 wt% Cs and 6 wt% Pd[1] PR598	Zn/Cr only with 5 wt% Cs and 6 wt% Pd PR498
Sel. Total Alcohols (%)	88	71
Total Alcohol Rate (g/kg-hr)	212	187
Methanol Rate (g/kg-hr)	23	16
Isobutanol Rate (g/kg-hr)	154	126
MeOH/i-BuOH mole ratio	0.58	0.5
Hydrocarbon rate (g/kg-hr)	19	57

[1] Results previously reported.

The presence of the excess zinc oxide results in a more active and selective catalyst to total alcohols and increased isobutanol rates, demonstrating the effectiveness of zinc oxide addition to the spinel support.

4.11.10 Comparison with Catalysts Based on Commercial Material

Our best catalysts are prepared by controlled pH precipitation of the spinel oxide support. Potassium-promoted catalysts made via this procedure were compared with potassium-promoted materials derived from a commercially available Zn/Cr spinel prepared via an alternative procedure to determine the benefit of the controlled pH precipitation method in catalyst preparation.

The commercial material used was a Zn/Cr/O spinel methanol synthesis catalyst (Engelhard Zn-0312). Incremental potassium addition (1, 3 and 5 wt%) results in an increase in total alcohol selectivity, while isobutanol rates are maximized at 1 wt% potassium; see Tables 4.11-39 – 4.11-42. We have already prepared and tested Zn/Cr/O and Zn/Cr/O with excess ZnO catalysts in house using a controlled pH precipitation technique. The catalytic performance of all these materials is compared in the table below:

Comparison of (A) Commercial Zn/Cr/O, (B) In house Zn/Cr/O and
(C) In house Zn/Cr/O with excess ZnO
all promoted with Potassium[1]
440°C, 1500 psi, GHSV = 12000, H_2/CO = 1:1

	A 1 wt% K PR042	B 3 wt% K PR039	C 5 wt% K PR195
Sel. Total Alcohols (%)	53	64	71
Total Alcohol Rate (g/kg-hr)	167	134	178
Methanol Rate (g/kg-hr)	49	39	47
Isobutanol Rate (g/kg-hr)	103	90	117
MeOH/i-BuOH mole ratio	1.9	1.8	1.6
Hydrocarbon rate (g/kg-hr)	101	47	14

[1] These results are for those potassium levels that showed the highest isobutanol rates.

The selectivity to total alcohols on the commercial spinel can be increased to 70% by increasing the potassium loading to 3 wt%, but the isobutanol rate drops sharply to 67 g/kg-hr. Thus, overall, the commercial catalyst promoted with potassium is less active for isobutanol synthesis, and less selective to total alcohols when compared with our spinel formulation promoted with potassium and containing excess ZnO.

Figure 4.11-1. Selectivity to total alcohols vs. K loading on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

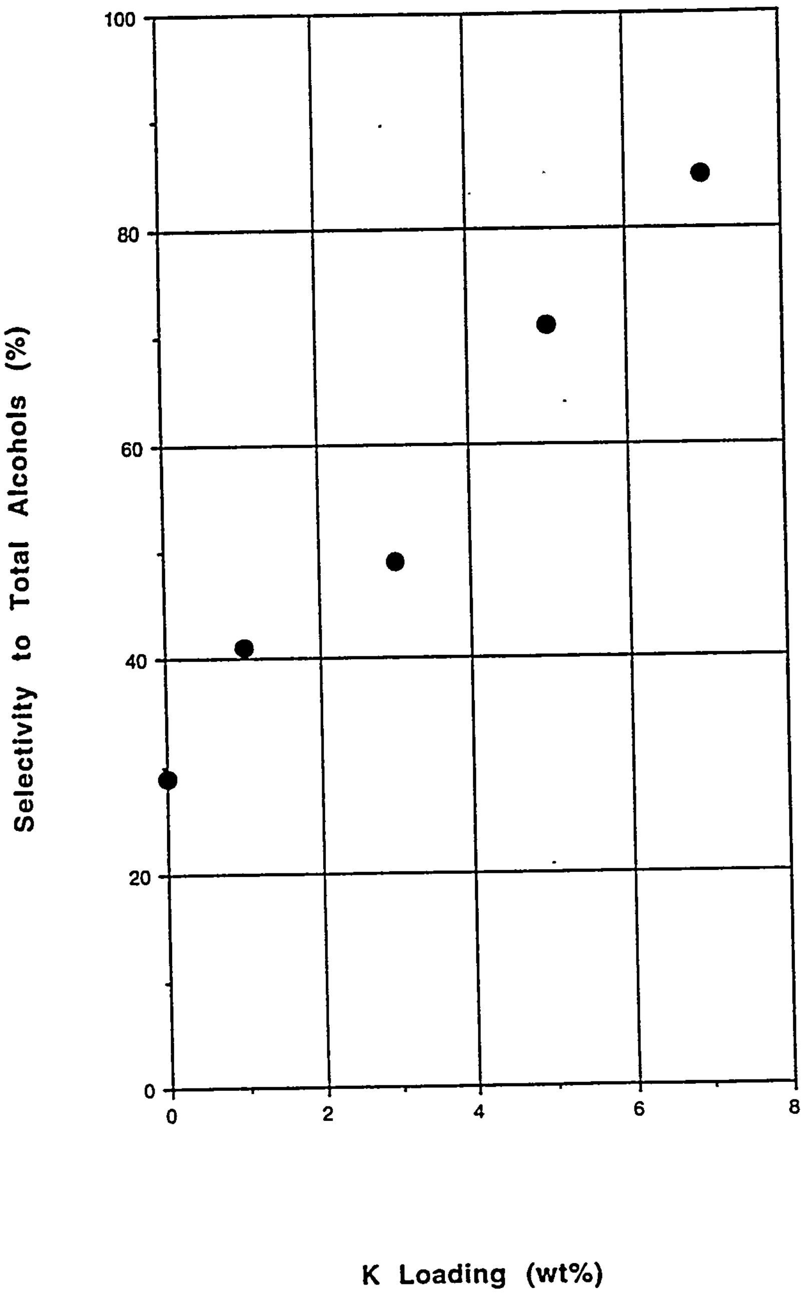


Figure 4.11-2. Rate to total alcohols vs. K loading on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

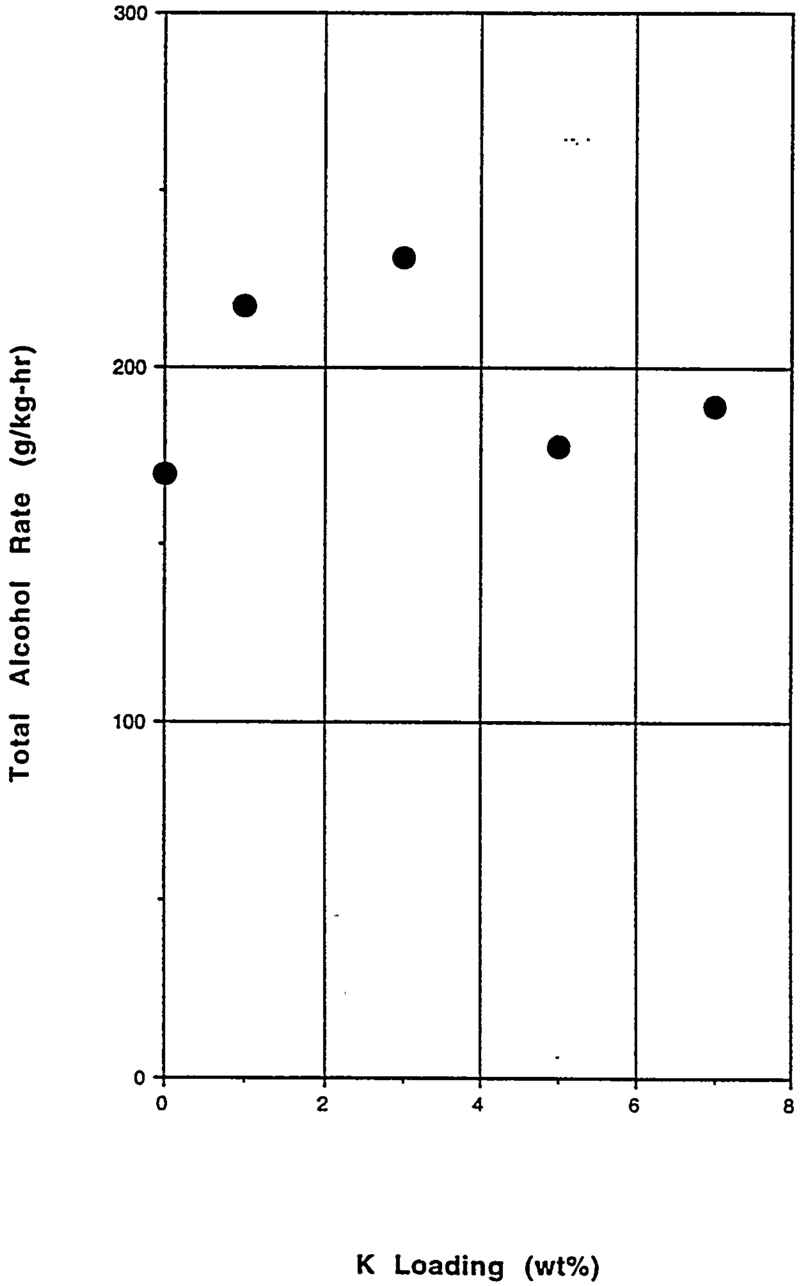


Figure 4.11-3. Rates to methanol and isobutanol vs. K loading on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

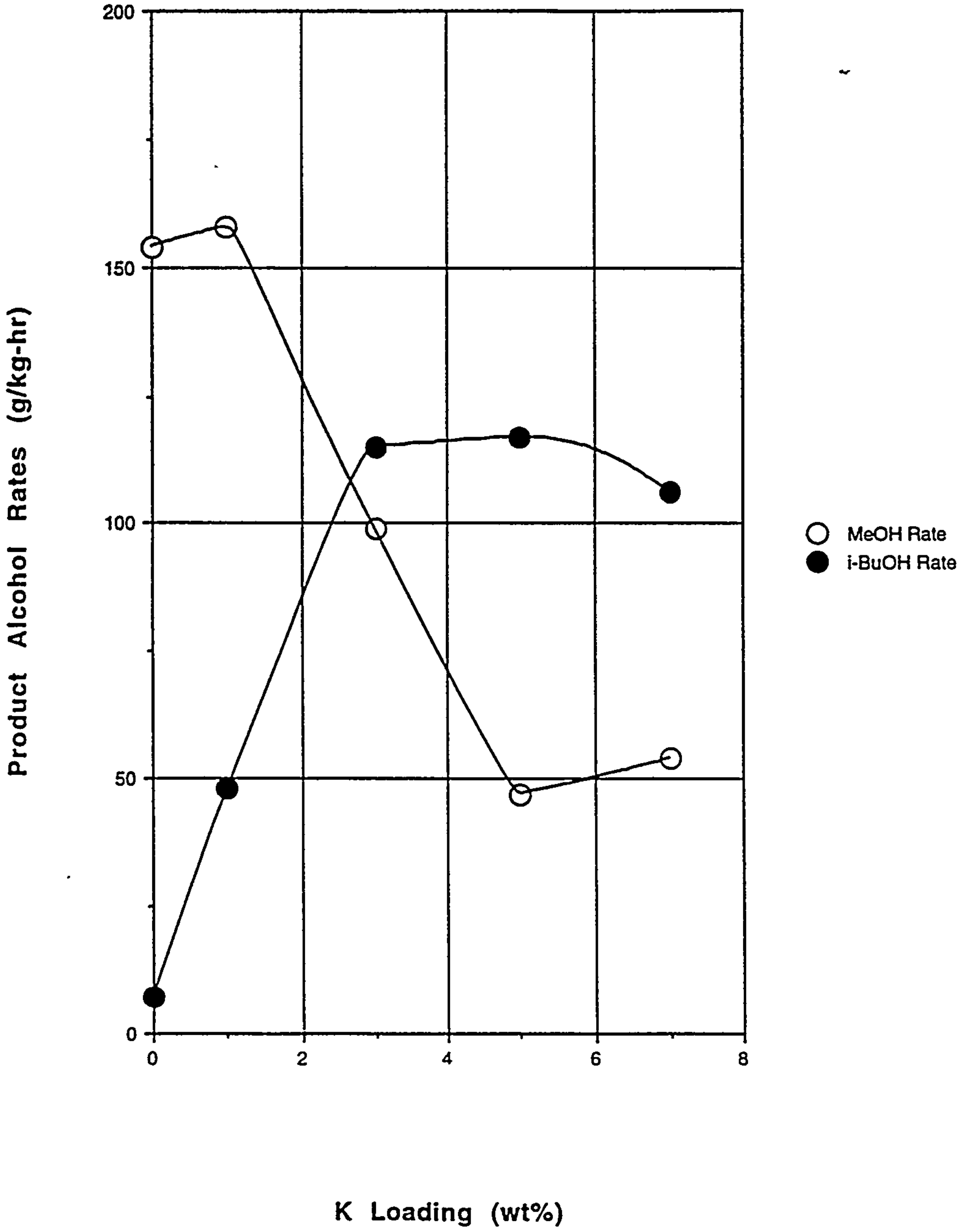


Figure 4.11-4. Selectivity to total alcohols vs. K loading for 6 wt% Pd on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

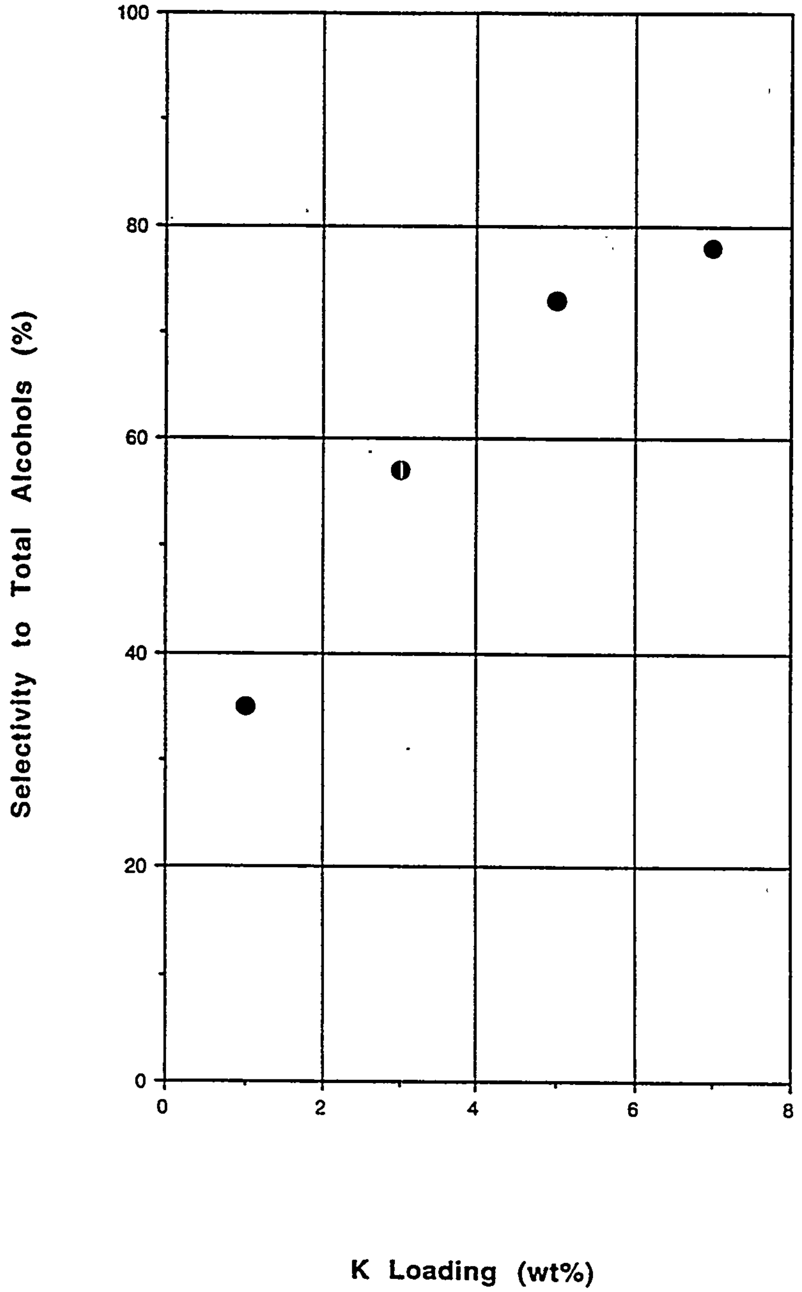


Figure 4.11-5. Rate to total alcohols vs. K loading for 6 wt% Pd on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

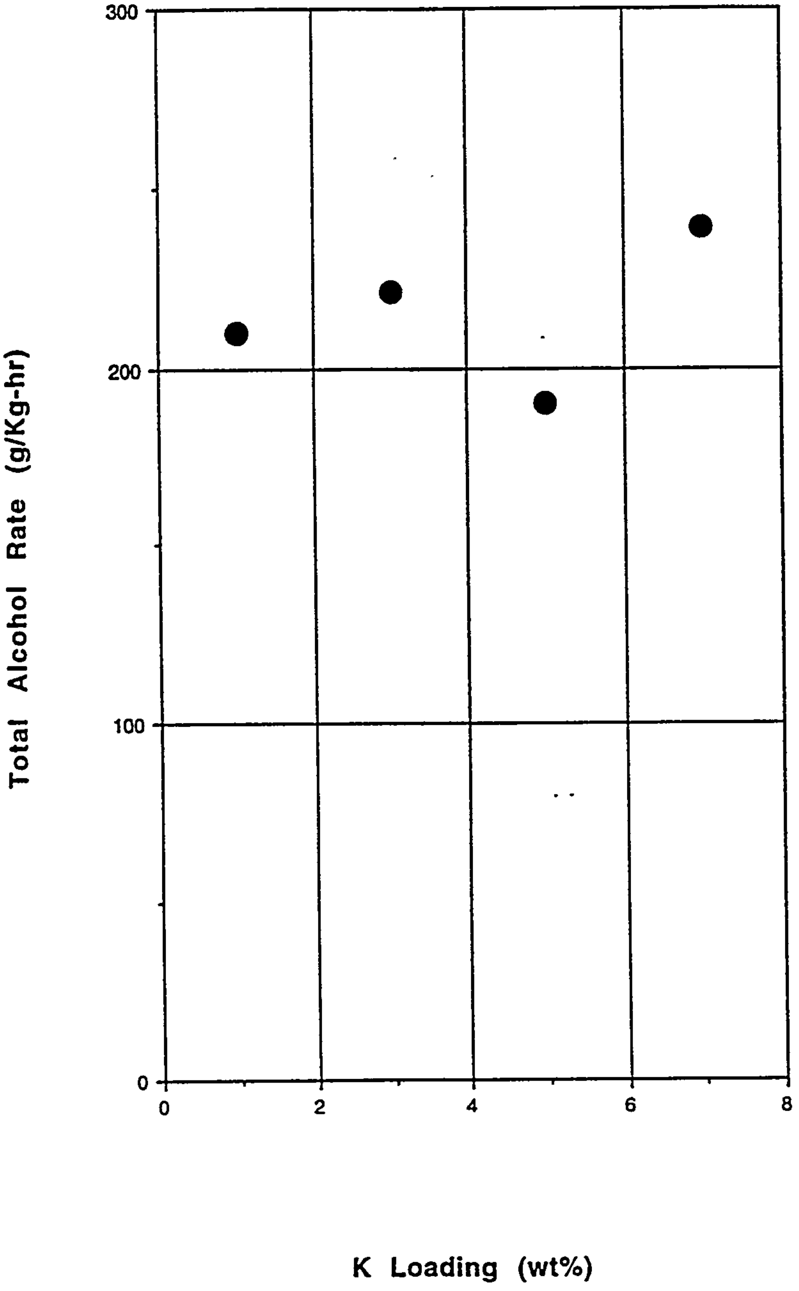


Figure 4.11-6. Rates to methanol and isobutanol vs. K loading for 6 wt% Pd on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

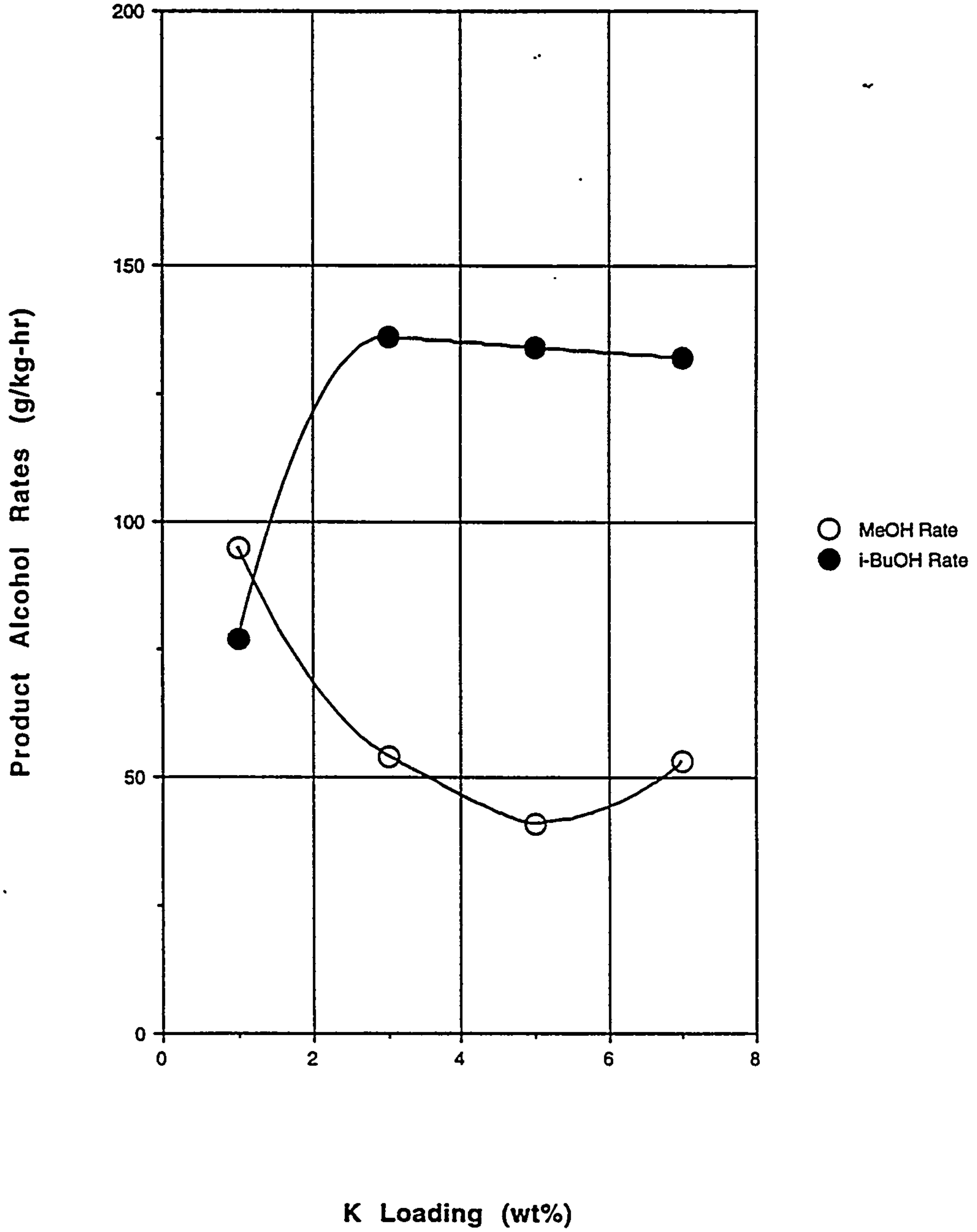


Table 4.11-1. ZnCr support with excess Zn, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR516 T = 400°C P = 1000 psi	PR524 T = 400°C P = 1500 psi	PR540 T = 440°C P=1500 psi	PR548 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	50	61	29	29
Total Alcohol Rate (g/kg-hr)	164	292	170	118
Methanol Rate (g/kg-hr)	160	285	154	101
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	4	2
n-Propanol rate (g/kg-hr)	0	1	5	6
Isobutanol Rate (g/kg-hr)	2	6	7	8
MeOH/i-BuOH mole ratio	269	191	86	48
Hydrocarbon rate (g/kg-hr)	82	91	216	150
Conversion (%)	17	20	21	18

Table 4.11-2. ZnCr support with excess Zn and 1% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR017 T = 400°C P = 1000 psi	PR025 T = 400°C P = 1500 psi	PR043 T = 440°C P=1500 psi	PR049 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	70	76	41	41
Total Alcohol Rate (g/kg-hr)	185	327	217	135
Methanol Rate (g/kg-hr)	176	308	158	115
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	2	0
n-Propanol rate (g/kg-hr)	0	0	9	4
Isobutanol Rate (g/kg-hr)	9	18	48	16
MeOH/i-BuOH mole ratio	77	30	13	29
Hydrocarbon rate (g/kg-hr)	38	51	167	101
Conversion (%)	11	15	16	13

Table 4.11-3. ZnCr support with excess Zn and 3% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR018 T = 400°C P = 1000 psi	PR026 T = 400°C P = 1500 psi	PR042 T = 440°C P=1500 psi	PR050 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	83	87	49	41
Total Alcohol Rate (g/kg-hr)	168	298	231	151
Methanol Rate (g/kg-hr)	126	229	99	84
Ethanol Rate (g/kg-hr)	0	1	0	3
Isopropanol rate (g/kg-hr)	0	0	7	6
n-Propanol rate (g/kg-hr)	2	8	9	5
Isobutanol rate (g/kg-hr)	40	60	115	51
MeOH/i-BuOH mole ratio	12	15	3.5	6.7
Hydrocarbon rate (g/kg-hr)	18	23	149	149
Conversion (%)	17	19	23	20

Table 4.11-4. ZnCr support with excess Zn and 5% K, tested in a copper-lined tube with GHSV 12000 and H_2/CO = 1

	PR146 T = 400°C P = 1000 psi	PR171 T = 400°C P = 1500 psi	PR195 T = 440°C P=1500 psi	PR211 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	84	87	71	70
Total Alcohol Rate (g/kg-hr)	134	254	178	106
Methanol Rate (g/kg-hr)	68	157	47	19
Ethanol Rate (g/kg-hr)	0	1	0	1
Isopropanol rate (g/kg-hr)	0	1	5	3
n-Propanol rate (g/kg-hr)	5	11	10	5
Isobutanol Rate (g/kg-hr)	61	84	117	78
MeOH/i-BuOH mole ratio	4.4	7.5	1.6	0.94
Hydrocarbon rate (g/kg-hr)	15	22	48	33
Conversion (%)	15	14	14	15

Table 4.11-5. ZnCr support with excess Zn and 7% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR360 T = 400°C P = 1000 psi	PR368 T = 400°C P = 1500 psi	PR384 T = 440°C P=1500 psi	PR392 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	97	96	85	87
Total Alcohol Rate (g/kg-hr)	124	254	189	103
Methanol Rate (g/kg-hr)	72	165	54	20
Ethanol Rate (g/kg-hr)	0	0	1	0
Isopropanol rate (g/kg-hr)	1	2	6	3
n-Propanol rate (g/kg-hr)	14	23	22	10
Isobutanol Rate (g/kg-hr)	37	64	106	69
MeOH/i-BuOH mole ratio	7.8	10.3	2.0	1.2
Hydrocarbon rate (g/kg-hr)	3	6	22	11
Conversion (%)	9	17	18	16

Table 4.11-6. ZnCr support with excess Zn, 5.9% Pd and 1% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR445 T = 400°C P = 1000 psi	PR453 T = 400°C P = 1500 psi	PR469 T = 440°C P=1500 psi	PR477 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	44	59	35	26
Total Alcohol Rate (g/kg-hr)	113	264	210	96
Methanol Rate (g/kg-hr)	76	184	95	47
Ethanol Rate (g/kg-hr)	1	3	16	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	2	6	20	12
Isobutanol Rate (g/kg-hr)	34	72	77	36
MeOH/i-BuOH mole ratio	9.0	10.3	4.8	5.2
Hydrocarbon rate (g/kg-hr)	81	102	235	166
Conversion (%)	12	16	18	13

Table 4.11-7. ZnCr support with excess Zn, 5.9% Pd and 3% K, tested in a copper-lined tube with GHSV 12000 and H_2/CO = 1

	PR444 T = 400°C P = 1000 psi	PR452 T = 400°C P = 1500 psi	PR470 T = 440°C P=1500 psi	PR478 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	70	77	57	55
Total Alcohol Rate (g/kg-hr)	159	294	221	136
Methanol Rate (g/kg-hr)	73	155	54	24
Ethanol Rate (g/kg-hr)	1	4	8	8
Isopropanol rate (g/kg-hr)	1	1	5	6
n-Propanol rate (g/kg-hr)	4	12	18	14
Isobutanol Rate (g/kg-hr)	81	121	136	84
MeOH/i-BuOH mole ratio	3.6	5.1	1.6	1.1
Hydrocarbon rate (g/kg-hr)	43	51	111	78
Conversion (%)	17	21	23	18

Table 4.11-8. ZnCr support with excess Zn, 5.9% Pd and 5% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR517 T = 400°C P = 1000 psi	PR525 T = 400°C P = 1500 psi	PR539 T = 440°C P=1500 psi	PR547 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	86	87	73	85
Total Alcohol Rate (g/kg-hr)	137	240	190	161
Methanol Rate (g/kg-hr)	54	129	41	48
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	1
n-Propanol rate (g/kg-hr)	9	17	15	9
Isobutanol Rate (g/kg-hr)	74	94	134	102
MeOH/i-BuOH mole ratio	2.9	5.5	1.2	1.9
Hydrocarbon rate (g/kg-hr)	14	21	50	20
Conversion (%)	12	15	17	15

Table 4.11-9. ZnCr support with excess Zn, 5.9% Pd and 7% K, tested in a copper-lined tube with GHSV 12000 and H_2/CO = 1

	PR292 T = 400°C P = 1000 psi	PR300 T = 400°C P = 1500 psi	PR316 T = 440°C P=1500 psi	PR324 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	91	91	78	80
Total Alcohol Rate (g/kg-hr)	171	313	239	158
Methanol Rate (g/kg-hr)	76	180	53	21
Ethanol Rate (g/kg-hr)	0	2	3	0
Isopropanol rate (g/kg-hr)	3	3	10	5
n-Propanol rate (g/kg-hr)	24	36	42	47
Isobutanol Rate (g/kg-hr)	69	93	132	85
MeOH/i-BuOH mole ratio	4.5	7.8	1.6	1.0
Hydrocarbon rate (g/kg-hr)	11	18	45	29
Conversion (%)	14	15	15	16

Table 4.11-10. Catalyst tests of Zn/Cr support with excess Zn.

10 wt% Cs Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 361	T = 400°C P = 1500 psi Run PR 369	T = 440°C P=1500psi Run PR 385	T = 440°C P = 1000 psi Run PR 393
Sel. Total Alcohols (%)	94	95	76	71
Total Alcohol Rate (g/kg-hr)	97	196	133	66
Methanol Rate (g/kg-hr)	62	141	41	15
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	2	0
n-Propanol rate (g/kg-hr)	11	21	20	14
Isobutanol Rate (g/kg-hr)	24	38	72	37
MeOH/i-BuOH mole ratio	10	15	2.3	1.6
Hydrocarbon rate (g/kg-hr)	4	6	28	19
Conversion (%)	7	12	13	10

Table 4.11-11. Catalyst tests of support with excess Zn.

7.5 wt% Cs Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR293	T = 400°C P = 1500 psi Run PR 299	T = 440°C P=1500psi Run PR 317	T = 440°C P = 1000 psi Run PR 323
Sel. Total Alcohols (%)	96	96	74	74
Total Alcohol Rate (g/kg-hr)	105	203	129	89
Methanol Rate (g/kg-hr)	61	142	40	16
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	2	0
n-Propanol rate (g/kg-hr)	11	15	15	14
Isobutanol Rate (g/kg-hr)	33	46	73	60
MeOH/i-BuOH mole ratio	7.3	12	2.2	1.0
Hydrocarbon rate (g/kg-hr)	2	4	29	23
Conversion (%)	10	11	9	12

Table 4.11-12. Catalyst tests of Zn/Cr support with excess Zn.

5 wt% Cs Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 243	T = 400°C P = 1500 psi Run PR 249	T = 440°C P=1500psi Run PR 267	T = 420°C P = 1000 psi Run PR 273
Sel. Total Alcohols (%)	94	94	81	91
Total Alcohol Rate (g/kg-hr)	128	217	141	116
Methanol Rate (g/kg-hr)	64	141	39	23
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	10	14	14	11
Isobutanol Rate (g/kg-hr)	54	60	87	83
MeOH/i-BuOH mole ratio	4.7	9.4	1.8	1.1
Hydrocarbon rate (g/kg-hr)	5	8	22	8
Conversion (%)	10	9	9	10

Table 4.11-13. Catalyst tests of Zn/Cr support with excess Zn.

3 wt% Cs Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 466	T = 400°C P = 1500 psi Run PR 474	T = 440°C P=1500psi Run PR 490	T = 440°C P = 1000 psi Run PR 498
Sel. Total Alcohols (%)	88	90	77	79
Total Alcohol Rate (g/kg-hr)	187	315	248	172
Methanol Rate (g/kg-hr)	85	177	58	41
Ethanol Rate (g/kg-hr)	0	2	0	0
Isopropanol rate (g/kg-hr)	0	1	5	3
n-Propanol rate (g/kg-hr)	9	17	14	8
Isobutanol Rate (g/kg-hr)	93	118	171	120
MeOH/i-BuOH mole ratio	3.7	6	1.4	1.4
Hydrocarbon rate (g/kg-hr)	15	20	52	31
Conversion (%)	15	16	18	13

Table 4.11-14. Catalyst tests of Zn/Cr support with excess Zn.

1 wt% Cs Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 467	T = 400°C P = 1500 psi Run PR 475	T = 440°C P=1500psi Run PR 491	T = 440°C P = 1000 psi Run PR 499
Sel. Total Alcohols (%)	58	68	40	31
Total Alcohol Rate (g/kg-hr)	146	277	192	87
Methanol Rate (g/kg-hr)	113	217	90	38
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	2	4	16	11
Isobutanol Rate (g/kg-hr)	31	56	86	38
MeOH/i-BuOH mole ratio	14	15	4.2	4.1
Hydrocarbon rate (g/kg-hr)	57	69	172	117
Conversion (%)	11	12	15	9

Table 4.11-15. Catalyst tests of Zn/Cr support with excess Zn.

1.0 wt% Cs / 5.9% Pd Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 565	T = 400°C P = 1500 psi Run PR 573	T = 440°C P=1500psi Run PR 585	T = 440°C P = 1000 psi Run PR 597
Sel. Total Alcohols (%)	52	62	43	48
Total Alcohol Rate (g/kg-hr)	120	230	184	132
Methanol Rate (g/kg-hr)	75	158	64	51
Ethanol Rate (g/kg-hr)	0	0	9	7
Isopropanol rate (g/kg-hr)	0	0	4	0
n-Propanol rate (g/kg-hr)	0	4	16	12
Isobutanol Rate (g/kg-hr)	44	68	91	62
MeOH/i-BuOH mole ratio	6.8	9.3	2.8	3.3
Hydrocarbon rate (g/kg-hr)	63	77	154	89
Conversion (%)	11	13	17	10

Table 4.11-16. Catalyst tests of Zn/Cr support with excess Zn.

3.0 wt% Cs / 5.9% Pd Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 516	T = 400°C P = 1500 psi Run PR 522	T = 440°C P=1500psi Run PR 536	T = 440°C P = 1000 psi Run PR 546
Sel. Total Alcohols (%)	85	84	67	77
Total Alcohol Rate (g/kg-hr)	193	282	238	228
Methanol Rate (g/kg-hr)	71	150	48	32
Ethanol Rate (g/kg-hr)	1	3	0	0
Isopropanol rate (g/kg-hr)	1	2	7	4
n-Propanol rate (g/kg-hr)	15	22	22	23
Isobutanol Rate (g/kg-hr)	105	105	161	170
MeOH/i-BuOH mole ratio	2.7	5.7	1.2	0.75
Hydrocarbon rate (g/kg-hr)	22	31	84	49
Conversion (%)	17	18	20	19

Table 4.11-17. Catalyst tests of Zn/Cr support with excess Zn.

5.0 wt% Cs / 5.9% Pd Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 566	T = 400°C P = 1500 psi Run PR 574	T = 440°C P=1500psi Run PR 584	T = 440°C P = 1000 psi Run PR 598
Sel. Total Alcohols (%)	91	91	81	88
Total Alcohol Rate (g/kg-hr)	188	276	233	212
Methanol Rate (g/kg-hr)	82	156	45	23
Ethanol Rate (g/kg-hr)	0	1	0	0
Isopropanol rate (g/kg-hr)	2	3	10	7
n-Propanol rate (g/kg-hr)	19	26	29	28
Isobutanol Rate (g/kg-hr)	84	90	150	154
MeOH/i-BuOH mole ratio	3.9	7.0	1.2	0.58
Hydrocarbon rate (g/kg-hr)	11	31	39	22
Conversion (%)	19	18	19	18

Table 4.11-18. Catalyst tests of Zn/Cr/Mn support with excess Zn.

1 wt% Cs Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 615	T = 400°C P = 1500 psi Run PR 623	T = 440°C P=1500psi Run PR 639	T = 440°C P = 1000 psi Run PR 647
Sel. Total Alcohols (%)	71	80	67	63
Total Alcohol Rate (g/kg-hr)	122	219	153	93
Methanol Rate (g/kg-hr)	72	146	50	26
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	0	3	6	7
Isobutanol Rate (g/kg-hr)	50	70	96	60
MeOH/i-BuOH mole ratio	5.7	8.3	2.1	1.8
Hydrocarbon rate (g/kg-hr)	28	30	49	36
Conversion (%)	11	13	16	10

Table 4.11-19 Catalyst tests of Zn/Cr/Mn support with excess Zn.

3 wt% Cs Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 616	T = 400°C P = 1500 psi Run PR 624	T = 440°C P=1500psi Run PR 640	T = 440°C P = 1000 psi Run PR 648
Sel. Total Alcohols (%)	98	97	85	82
Total Alcohol Rate (g/kg-hr)	115	206	158	103
Methanol Rate (g/kg-hr)	78	153	55	21
Ethanol Rate (g/kg-hr)	0	0	1	0
Isopropanol rate (g/kg-hr)	0	0	6	4
n-Propanol rate (g/kg-hr)	9	14	15	7
Isobutanol Rate (g/kg-hr)	28	38	79	70
MeOH/i-BuOH mole ratio	11	16	2.8	1.2
Hydrocarbon rate (g/kg-hr)	2	3	18	16
Conversion (%)	14	15	17	15

Table 4.11-20. Catalyst tests of Zn/Cr/Mn support with excess Zn.

5 wt% Cs Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 417	T = 400°C P = 1500 psi Run PR 425	T = 440°C P=1500psi Run PR 441	T = 440°C P = 1000 psi Run PR 448
Sel. Total Alcohols (%)	96	96	84	85
Total Alcohol Rate (g/kg-hr)	99	166	111	72
Methanol Rate (g/kg-hr)	71	129	41	27
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	9	10	16	16
Isobutanol Rate (g/kg-hr)	19	26	54	30
MeOH/i-BuOH mole ratio	15	20	3.1	3.6
Hydrocarbon rate (g/kg-hr)	2	4	13	8
Conversion (%)	6	10	14	5

Table 4.11-21. Catalyst tests of Zn/Cr/Mn support with excess Zn.

1 wt% Cs, 6 wt% Pd Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 717	T = 400°C P = 1500 psi Run PR 725	T = 440°C P=1500psi Run PR 731	T = 440°C P = 1000 psi Run PR 749
Sel. Total Alcohols (%)	72	76	54	59
Total Alcohol Rate (g/kg-hr)	117	189	146	118
Methanol Rate (g/kg-hr)	38	88	32	17
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	5	10	14	12
Isobutanol Rate (g/kg-hr)	73	92	101	89
MeOH/i-BuOH mole ratio	2.1	3.8	1.3	0.76
Hydrocarbon rate (g/kg-hr)	30	38	88	115
Conversion (%)	9	15	18	13

Table 4.11-22. Catalyst tests of Zn/Cr/Mn support with excess Zn.

3 wt% Cs, 6 wt% Pd Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 716	T = 400°C P = 1500 psi Run PR 724	T = 440°C P=1500psi Run PR 732	T = 440°C P = 1000 psi Run PR 748
Sel. Total Alcohols (%)	82	85	58	67
Total Alcohol Rate (g/kg-hr)	133	231	203	156
Methanol Rate (g/kg-hr)	47	115	32	15
Ethanol Rate (g/kg-hr)	0	0	1	1
Isopropanol rate (g/kg-hr)	5	5	14	11
n-Propanol rate (g/kg-hr)	24	38	44	31
Isobutanol Rate (g/kg-hr)	56	74	113	98
MeOH/i-BuOH mole ratio	3.5	6.2	1.1	0.6
Hydrocarbon rate (g/kg-hr)	18	25	105	56
Conversion (%)	13	18	22	15

Table 4.11-23. Catalyst tests of Zn/Cr/Mn support with excess Zn.

5 wt% Cs, 6 wt% Pd Catalyst

Tested in a copper lined tube

	T = 400°C P = 1000 psi Run PR 817	T = 400°C P = 1500 psi Run 825	T = 440°C P=1500psi Run PR 841	T = 440°C P = 1000 psi Run PR 849
Sel. Total Alcohols (%)	87	89	71	77
Total Alcohol Rate (g/kg-hr)	93	164	142	131
Methanol Rate (g/kg-hr)	38	89	22	9
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	9
n-Propanol rate (g/kg-hr)	20	26	24	25
Isobutanol Rate (g/kg-hr)	35	48	96	87
MeOH/i-BuOH mole ratio	4.4	7.5	0.94	0.41
Hydrocarbon rate (g/kg-hr)	9	13	42	30
Conversion (%)	12	12	14	13

Table 4.11-24. Catalyst tests of Zn/Cr/Mn support with excess Zn.

5 wt% Cs, 5.9 wt% Pd Catalyst

Tested in a copper lined tube

	T = 440°C P = 1000 psi Run PR 875	T = 450°C P = 1000 psi Run 883	T = 460°C P=1000psi Run PR 899
Sel. Total Alcohols (%)	73	69	61
Total Alcohol Rate (g/kg-hr)	82	85	92
Methanol Rate (g/kg-hr)	10	8	7
Ethanol Rate (g/kg-hr)	0	0	0
Isopropanol rate (g/kg-hr)	1	8	10
n-Propanol rate (g/kg-hr)	21	20	20
Isobutanol Rate (g/kg-hr)	43	49	55
MeOH/i-BuOH mole ratio	0.96	0.66	0.51
Hydrocarbon rate (g/kg-hr)	22	29	44
Conversion (%)	10	9	11

Table 4.11-25. Catalyst tests of ZnO prepared via precipitation at constant pH = 10 from K(OH/CO_3) (calcined).

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 667	T = 400°C P = 1500 psi PR 675	T = 440°C P=1500psi PR 691	T = 440°C P = 1000 psi PR 697
Sel. Total Alcohols (%)	57	68	23	15
Total Alcohol Rate (g/kg-hr)	74	164	59	23
Methanol Rate (g/kg-hr)	74	164	59	23
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	0	0	0	0
Isobutanol Rate (g/kg-hr)	0	0	0	0
MeOH/i-BuOH mole ratio	-	-	-	-
Hydrocarbon rate (g/kg-hr)	28	38	100	67
Conversion (%)	9	10	11	8

Table 4.11-26. Catalyst tests of ZnO prepared via precipitation at constant pH = 10 from $K(OH/CO_3)$ (calcined).

1% K

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 115	T = 400°C P = 1500 psi PR 123	T = 440°C P=1500psi PR 141	T = 440°C P = 1000 psi PR 149
Sel. Total Alcohols (%)	84	91	70	72
Total Alcohol Rate (g/kg-hr)	72	157	85	41
Methanol Rate (g/kg-hr)	63	142	42	15
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	2	6	6	0
Isobutanol Rate (g/kg-hr)	7	8	38	26
MeOH/i-BuOH mole ratio	35	72	4.5	2.3
Hydrocarbon rate (g/kg-hr)	7	7	23	10
Conversion (%)	7	8	8	7

Table 4.11-27. Catalyst tests of ZnO prepared via precipitation at constant pH = 10 from K(OH/CO_3) (calcined).

3% K

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 116	T = 400°C P = 1500 psi PR 124	T = 440°C P=1500psi PR 140	T = 440°C P = 1000 psi PR 148
Sel. Total Alcohols (%)	95	98	82	76
Total Alcohol Rate (g/kg-hr)	79	156	100	46
Methanol Rate (g/kg-hr)	69	142	63	20
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	2	1
n-Propanol rate (g/kg-hr)	6	0	14	5
Isobutanol Rate (g/kg-hr)	4	14	22	20
MeOH/i-BuOH mole ratio	68	41	11	4.1
Hydrocarbon rate (g/kg-hr)	2	2	12	9
Conversion (%)	9	10	11	9

Table 4.11-28. Catalyst tests of ZnO prepared via precipitation at constant pH = 10 from K(OH/CO_3) (calcined).

5% K

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 151	T = 400°C P = 1500 psi PR 189	T = 440°C P=1500psi PR 201	T = 440°C P = 1000 psi PR 217
Sel. Total Alcohols (%)	96	98	87	88
Total Alcohol Rate (g/kg-hr)	56	95	68	25
Methanol Rate (g/kg-hr)	52	91	49	13
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	2	0	0	0
n-Propanol rate (g/kg-hr)	4	4	13	3
Isobutanol Rate (g/kg-hr)	0	0	6	9
MeOH/i-BuOH mole ratio	-	-	31	5.4
Hydrocarbon rate (g/kg-hr)	1	1	6	2
Conversion (%)	7	7	7	7

Table 4.11-29. Catalyst tests of ZnCr support.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 917	T = 400°C P = 1500 psi PR 925	T = 440°C P=1500psi PR 941	T = 440°C P = 1000 psi PR 947
Sel. Total Alcohols (%)	73	84	56	39
Total Alcohol Rate (g/kg-hr)	117	248	161	71
Methanol Rate (g/kg-hr)	116	243	153	70
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	1
n-Propanol rate (g/kg-hr)	0	0	0	0
Isobutanol Rate (g/kg-hr)	1	5	8	0
MeOH/i-BuOH mole ratio	332	191	78	-
Hydrocarbon rate (g/kg-hr)	21	24	63	53
Conversion (%)	9	10	9	10

Table 4.11-30. Catalyst tests of Zn/Cr Support plus 1% K.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 916	T = 400°C P = 1500 psi PR 924	T = 440°C P=1500psi PR 940	T = 440°C P = 1000 psi PR 948
Sel. Total Alcohols (%)	77	85	49	33
Total Alcohol Rate (g/kg-hr)	129	248	131	53
Methanol Rate (g/kg-hr)	103	208	72	28
Ethanol Rate (g/kg-hr)	0	0	2	1
Isopropanol rate (g/kg-hr)	0	0	3	4
n-Propanol rate (g/kg-hr)	0	0	3	2
Isobutanol Rate (g/kg-hr)	26	40	51	18
MeOH/i-BuOH mole ratio	16	21	5.7	6.3
Hydrocarbon rate (g/kg-hr)	20	22	78	62
Conversion (%)	13	13	12	10

Table 4.11-31. Catalyst tests of Zn/Cr Support plus 3% K.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 015	T = 400°C P = 1500 psi PR 023	T = 440°C P=1500psi PR 039	T = 440°C P = 1000 psi PR 049
Sel. Total Alcohols (%)	86	91	64	69
Total Alcohol Rate (g/kg-hr)	91	200	131	84
Methanol Rate (g/kg-hr)	49	130	39	16
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	2	0
n-Propanol rate (g/kg-hr)	0	4	0	0
Isobutanol Rate (g/kg-hr)	42	66	90	68
MeOH/i-BuOH mole ratio	4.6	7.8	1.8	6.3
Hydrocarbon rate (g/kg-hr)	8	12	47	62
Conversion (%)	9	10	11	10

Table 4.11-32. Catalyst tests of Zn/Cr Support plus 5% K.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 016	T = 400°C P = 1500 psi PR 024	T = 440°C P=1500psi PR 040	T = 440°C P = 1000 psi PR 048
Sel. Total Alcohols (%)	92	93	78	79
Total Alcohol Rate (g/kg-hr)	88	179	143	77
Methanol Rate (g/kg-hr)	58	132	46	17
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	2	1
n-Propanol rate (g/kg-hr)	5	9	7	4
Isobutanol Rate (g/kg-hr)	25	38	88	55
MeOH/i-BuOH mole ratio	9.2	14	2.1	1.2
Hydrocarbon rate (g/kg-hr)	4	7	26	15
Conversion (%)	10	12	13	10

Table 4.11-33. Catalyst tests of Zn/Cr Support plus 1% Cs.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 265	T = 400°C P = 1500 psi PR 273	T = 440°C P=1500psi PR 289	T = 440°C P = 1000 psi PR 297
Sel. Total Alcohols (%)	83	89	54	40
Total Alcohol Rate (g/kg-hr)	110	234	123	53
Methanol Rate (g/kg-hr)	80	181	54	19
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	1	2
n-Propanol rate (g/kg-hr)	0	0	0	0
Isobutanol Rate (g/kg-hr)	30	53	68	32
MeOH/i-BuOH mole ratio	11	14	3.2	2.4
Hydrocarbon rate (g/kg-hr)	12	15	65	50
Conversion (%)	9	10	10	8

Table 4.11-34. Catalyst tests of Zn/Cr Support plus 3% Cs.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 266	T = 400°C P = 1500 psi PR 274	T = 440°C P=1500psi PR 290	T = 440°C P = 1000 psi PR 298
Sel. Total Alcohols (%)	87	91	44	34
Total Alcohol Rate (g/kg-hr)	138	263	200	132
Methanol Rate (g/kg-hr)	79	177	48	15
Ethanol Rate (g/kg-hr)	0	0	5	3
Isopropanol rate (g/kg-hr)	0	1	16	13
n-Propanol rate (g/kg-hr)	7	11	13	10
Isobutanol Rate (g/kg-hr)	54	74	121	91
MeOH/i-BuOH mole ratio	6.0	9.5	1.6	0.68
Hydrocarbon rate (g/kg-hr)	12	14	179	194
Conversion (%)	12	13	20	17

Table 4.11-35. Catalyst tests of Zn/Cr Support plus 5% Cs.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 363	T = 400°C P = 1500 psi PR 371	T = 440°C P=1500psi PR 389	T = 440°C P = 1000 psi PR 409
Sel. Total Alcohols (%)	91	91	59	72
Total Alcohol Rate (g/kg-hr)	79	160	242	78
Methanol Rate (g/kg-hr)	49	113	74	10
Ethanol Rate (g/kg-hr)	0	0	0	5
Isopropanol rate (g/kg-hr)	0	0	3	3
n-Propanol rate (g/kg-hr)	6	8	32	7
Isobutanol Rate (g/kg-hr)	24	38	133	53
MeOH/i-BuOH mole ratio	8.3	12	2.2	0.76
Hydrocarbon rate (g/kg-hr)	4	8	112	22
Conversion (%)	6	8	24	6

Table 4.11-36. Catalyst tests of Zn/Cr Support plus 1% Cs and 5.9% Pd.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 316	T = 400°C P = 1500 psi PR 324	T = 440°C P=1500psi PR 340	T = 440°C P = 1000 psi PR 348
Sel. Total Alcohols (%)	45	58	36	28
Total Alcohol Rate (g/kg-hr)	133	280	196	77
Methanol Rate (g/kg-hr)	62	138	60	20
Ethanol Rate (g/kg-hr)	0	0	5	1
Isopropanol rate (g/kg-hr)	3	4	14	3
n-Propanol rate (g/kg-hr)	6	19	28	12
Isobutanol Rate (g/kg-hr)	62	119	90	41
MeOH/i-BuOH mole ratio	4.0	4.7	2.7	2.0
Hydrocarbon rate (g/kg-hr)	103	128	228	136
Conversion (%)	15	19	19	14

Table 4.11-37. Catalyst tests of Zn/Cr Support plus 3 wt % Cs and 5.9% Pd.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 364	T = 400°C P = 1500 psi PR 372	T = 440°C P=1500psi PR 392	T = 440°C P = 1000 psi PR 410
Sel. Total Alcohols (%)	70	78	59	55
Total Alcohol Rate (g/kg-hr)	166	292	207	117
Methanol Rate (g/kg-hr)	56	128	39	13
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	3	4	7	8
n-Propanol rate (g/kg-hr)	28	41	19	9
Isobutanol Rate (g/kg-hr)	80	120	142	87
MeOH/i-BuOH mole ratio	2.8	4.3	1.1	0.59
Hydrocarbon rate (g/kg-hr)	48	52	102	70
Conversion (%)	13	15	23	11

Table 4.11-38. Catalyst tests of Zn/Cr Support plus 5 wt % Cs and 5.9% Pd.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 466	T = 400°C P = 1500 psi PR 474	T = 440°C P=1500psi PR 490	T = 440°C P = 1000 psi PR 498
Sel. Total Alcohols (%)	79	81	68	71
Total Alcohol Rate (g/kg-hr)	168	279	227	187
Methanol Rate (g/kg-hr)	58	127	36	16
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	7	7	13	12
n-Propanol rate (g/kg-hr)	54	69	35	33
Isobutanol Rate (g/kg-hr)	49	75	142	126
MeOH/i-BuOH mole ratio	4.7	6.7	1.0	0.5
Hydrocarbon rate (g/kg-hr)	30	40	77	57
Conversion (%)	13	21	22	14

Table 4.11-39. Catalyst tests of Zn/Cr Engelhard Commercial Support.

(calcined @ 325°C)

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 017	T = 400°C P = 1500 psi PR 025	T = 440°C P=1500psi PR 041	T = 440°C P = 1000 psi PR 049
Sel. Total Alcohols (%)	65	77	43	27
Total Alcohol Rate (g/kg-hr)	111	236	133	59
Methanol Rate (g/kg-hr)	105	223	102	41
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	3
n-Propanol rate (g/kg-hr)	0	0	18	10
Isobutanol Rate (g/kg-hr)	6	13	13	5
MeOH/i-BuOH mole ratio	73	68	31	36
Hydrocarbon rate (g/kg-hr)	30	35	94	86
Conversion (%)	8	14	14	9

Table 4.11-40. Catalyst tests of Zn/Cr Engelhard Commercial Support plus 1 wt% K.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 015	T = 400°C P = 1500 psi PR 026	T = 440°C P=1500psi PR 042	T = 440°C P = 1000 psi PR 048
Sel. Total Alcohols (%)	61	75	53	53
Total Alcohol Rate (g/kg-hr)	133	251	167	129
Methanol Rate (g/kg-hr)	78	170	49	70
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	6	5
n-Propanol rate (g/kg-hr)	8	0	9	6
Isobutanol Rate (g/kg-hr)	47	81	103	47
MeOH/i-BuOH mole ratio	6.6	8.4	1.9	6.0
Hydrocarbon rate (g/kg-hr)	48	46	101	65
Conversion (%)	12	19	19	13

Table 4.11-41. Catalyst tests of Zn/Cr Engelhard Commercial Support plus 3 wt% K.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 115	T = 400°C P = 1500 psi PR 123	T = 440°C P=1500psi PR 134	T = 440°C P = 1000 psi PR 147
Sel. Total Alcohols (%)	80	88	70	70
Total Alcohol Rate (g/kg-hr)	75	159	99	67
Methanol Rate (g/kg-hr)	38	92	26	8
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	1	6	2
n-Propanol rate (g/kg-hr)	4	10	0	0
Isobutanol Rate (g/kg-hr)	34	57	67	57
MeOH/i-BuOH mole ratio	4.5	6.4	1.5	0.54
Hydrocarbon rate (g/kg-hr)	11	12	29	21
Conversion (%)	10	12	13	11

4.11-42. Catalyst tests of Zn/Cr Engelhard Commercial Support plus 5 wt% K.

Tested in a copper lined tube

	T = 400°C P = 1000 psi PR 116	T = 400°C P = 1500 psi PR 124	T = 440°C P=1500psi PR 140	T = 440°C P = 1000 psi PR 148
Sel. Total Alcohols (%)	96	97	84	83
Total Alcohol Rate (g/kg-hr)	82	159	130	70
Methanol Rate (g/kg-hr)	59	123	47	16
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	1	9	5
n-Propanol rate (g/kg-hr)	0	0	23	10
Isobutanol Rate (g/kg-hr)	23	34	51	38
MeOH/i-BuOH mole ratio	10	14	3.7	1.7
Hydrocarbon rate (g/kg-hr)	2	3	15	10
Conversion (%)	13	14	15	13

4.12 Surface Science Analysis of Spinel Oxide Based Catalysts

This work was performed in collaboration with Professor Gar Hoflund and his research group in the Department of Chemical Engineering at the University of Florida.

4.12.1 Techniques employed

A number of surface science techniques were employed to investigate the composition and nature of freshly prepared and used catalytic materials. Ion Scattering Spectroscopy (ISS), Auger Electron Spectroscopy (AES), X-Ray Photoelectron Spectroscopy (XPS), and Electron Stimulated Desorption (ESD) were used to probe the surface of both fresh and used catalysts. Each technique provides a specific type of information about the these complex catalysts. The information is complementary, and when taken together, yields an improved understanding of the composition and chemical nature of the materials.

ISS, AES and XPS provide compositional information with varying degrees of surface sensitivity. ISS is highly surface sensitive, detecting atoms only in the outermost layer. AES and XPS are much less surface sensitive, generally probing 40-60 angstroms beneath the surface, depending on the kinetic energies of the electrons being detected and the experimental geometry. In general, AES probes less deeply (i.e., is more surface sensitive) than XPS. High resolution XPS data can provide chemical state information about the elements present in the near surface region.

ESD allows the detection of surface hydrogen. The role of surface hydrogen, which is a very important component of the catalytic reaction, is not well understood or even usually examined because of detection difficulties. ESD uses 1 KeV electrons to cause emission of ionic and neutral species. The m/e spectra (ESD) and ion energy distribution (ESDIED) of the desorbing ions are obtained using a quadrupole mass spectrometer with an energy prefilter.

4.12.2 ISS, AES and XPS Data

2.25 wt% K, 5.9 wt% Pd on ZnCrMn spinel oxide with excess ZnO (16-DMM-68)

The "as prepared" catalyst was examined "as is" and after reduction *in situ* using 1.4 x 10^{-5} Torr of hydrogen while ramping the temperature from 20°C to 350°C over a 100 minute time period. The "as prepared" catalyst is relatively featureless, mainly showing ZnO. Dramatic changes occur during the reduction step. Both K and Pd become highly concentrated near the surface, and the data suggest that they are closely associated in the same particle. Sputtering of the sample shows increasing Cr and Mn concentrations in the subsurface region.

Surface analysis of the fresh vs. spent catalyst shows that alkali, Cr and Mn concentrations increase and Pd and Zn concentrations decrease during operation. Potassium is observed, as expected, but sodium, an impurity, is also seen — probably carried over from the metal nitrate salts during catalyst preparation.

5 wt% K, 5.9 wt% Pd on ZnCr spinel oxide with excess ZnO

Zinc, oxygen and small amounts of Pd, K and Cr are present in the near surface region. Zn is present as ZnO and there is a significant concentration of hydroxyl groups bound to the Zn. No carbon is present on the sample surface.

Reduction of the sample results in a significant increase in the surface Pd concentration, and the K appears to be associated with the Pd. Zn is still present as ZnO but the hydroxyl group concentration bound to the Zn has diminished substantially.

Surface analysis of the fresh vs. used catalyst shows a reduction in the surface Pd. The potassium promoter is spread uniformly over the outermost surface of the used catalysts. In fact, the outermost atomic layer consists of Zn and K. As the sample is sputtered, the K concentration decreases and the O and Pd concentrations increase until a Pd rich layer is found; then the Pd concentration decreases. A substantial amount of carbon has appeared. There are less hydroxyl groups present: zinc is present primarily as Zn metal and oxygen associated with zinc is present as hydroxyl groups. The Cr has been reduced to Cr metal and its concentration has increased in the near surface region.

7 wt% K, 5.9 wt% Pd on ZnCr spinel oxide with excess ZnO

The fresh catalyst is similar to the 5 wt% material: zinc, oxygen and small amounts of Pd, K and Cr are present in the near surface region. Zn is present as ZnO and there is a significant concentration of hydroxyl groups bound to the Zn. No carbon is present on the sample surface.

Reduction of the sample results in the formation of multiple forms of Zn; this differs from the 5 wt% K catalysts where only ZnO was present. There is also more oxygen present in the near surface region.

The used sample shows a reduction in the surface Pd. The outermost atomic layer consists of Zn and K, but Pd and Na are also present. As the sample is sputtered, the K concentration decreases and the O and Pd concentrations increase until a Pd rich layer is found; then the Pd concentration decreases. A longer sputtering time was necessary to reach the Pd-rich layer than for the 5 wt% K catalyst. A substantial amount of carbon has appeared. Zinc is present primarily as Zn metal and zinc oxide. The Cr has been reduced to Cr metal and its concentration has increased in the near surface region.

3 wt% Cs, 5.9 wt% Pd on ZnCr spinel oxide with excess ZnO

The fresh catalyst shows that zinc, oxygen and small amounts of Pd, Cs and Cr are present in the near surface region. Zn is present as ZnO and hydroxyl groups are also observed. A small amount of carbon is already present on the sample surface.

Reduction of the sample under hydrogen removes the carbon and enriches the near surface region in Cs. More hydroxyl groups are seen. Zinc is still present as ZnO.

The used catalyst has Zn, O, Cs and Cr in the near surface region. Some of the ZnO has been reduced to Zn metal. The surface is further enriched in Cs and the Pd concentration has decreased. The outermost atomic layer consists mainly of oxygen with Cs, Pd and Cr present as well. As the sample is sputtered, the Cs and Pd concentrations increase until a steady Pd concentration is reached; this Pd layer contains significant amounts of Cs and Cr. The Pd is concentrated in the outermost layers and diminishes with continued sputtering.

4.12.3 ESD/ESDIED Data

Four samples were examined:

1. ZnCrMn spinel oxide with excess ZnO, with K and Na impurities
2. 16-DMM-68 fresh catalyst (composition 1 promoted with extra K and with Pd)
3. 16-DMM-68 used catalyst
4. A ZnCr spinel oxide with excess ZnO, with K and Na impurities

The ions desorbing consisted of H^+, H_2^+, O^+, OH^+, H_3O^+, CO^+ and Cl^+. Most of the H-containing ions may relate to the surface acidity and all originate from the outermost atomic layer of the samples. Differences in the relative sizes of the m/e spectra and the peak shapes in the ion energy distribution indicate differences in the chemical nature of the surface with regard to hydrogen.

The two support surfaces are similar with respect to the H^+ ion energy distribution, but the width is greater for sample 4, and the H^+/H_3O^+ ratio is larger suggesting higher acidity for ZnCr spinel oxide versus ZnCrMn spinel oxide.

Addition of Pd to the ZnCrMn spinel oxide results in large changes: in addition to hydrogen chemical states associated with the spinel, two other, higher kinetic energy states are present corresponding to hydrogen adsorbed on palladium.

Under reaction conditions, the amount of hydrogen associated with the support is decreased and that associated with the palladium has increased. These results show that the chemical state of the hydrogen adsorbed on the catalyst surface can be observed and changes can be correlated with catalytic performance.

4.12.4 Conclusions from the Surface Science Analysis

- The surface of the catalysts is predominately ZnO and alkali.
- ZnO is reduced to Zn metal with use.
- The palladium forms a layer lying just beneath the outermost atomic layer.
- Sodium is carried over from the spinel oxide preparation.
- The alkali is initially associated with the Pd, but with use becomes spread out over the surface of the Pd/spinel. Too thick (or too thin) a layer results in inefficient higher alcohol synthesis.
- Cesium associates with the Pd in used catalysts to a greater extent than does K.
- Chromium migrates to the surface with time, and is probably responsible for increased hydrocarbon formation due to increased surface acidity. Mn addition tends to lower overall spinel acidity.
- Hydrogen can be observed on the catalyst surface. Hydrogen on the active catalyst is associated with the palladium.

5. Experimental Details

5.1 Catalyst Preparation

The ZnCr and ZnCrMn oxides were prepared by coprecipitating the metal nitrate salts in aqueous medium at a constant pH. An aqueous solution containing the metal nitrate salts and a basic solution were dripped slowly into ~200 mL of the basic solution using two peristaltic pumps. Care is taken to assure that the resulting solution is well stirred during the addition and the pH of the solution is monitored continuously. The flow of the basic solution is adjusted to keep the solution at a constant pH. The resulting mixture is then heated for a given time and then solid precipitate is filtered and washed with at least three liters of water, mixing well during the washing. The solid is dried at 110-120°C overnight and calcined for the desired time at the appropriate temperature. The catalysts were impregnated using the incipient wetness method.

5.2 Catalyst Testing

The reactor tubes were made from 1/4 inch copper tube inserted into 3/8 inch stainless steel tubes. The copper tubing was rinsed well with acetone before use. (Experiments not noted to have been run in copper reactors were conducted in reactors constructed of 1/4 inch stainless steel tubing that had been treated overnight with a 50/50 solution of hydrochloric acid and water. The tubes were rinsed with water for 5 minutes followed by an acetone rinse.) Reactors were dried under vacuum. One gram of catalyst was mixed with 3 cm^3 of glass beads until the mixture was uniform. The reactors were then loaded while tapping on the sides of reactor tube. Due to the V-like nature of the reactor tubes, each side of the V was loaded with one-half of the catalyst mixture at a time. Glass wool was then put into place on both sides of the reactor. The catalysts were reduced with 5% hydrogen in nitrogen for four hours at the desired temperature.

The reduced catalysts were then loaded into the sand bath and the system was pressurized with nitrogen. Once the reactor reached the correct temperature, the nitrogen was turned off and the syngas feedstream was turned on and adjusted to the correct pressure.

5.3 Microreactor System for Screening Catalysts

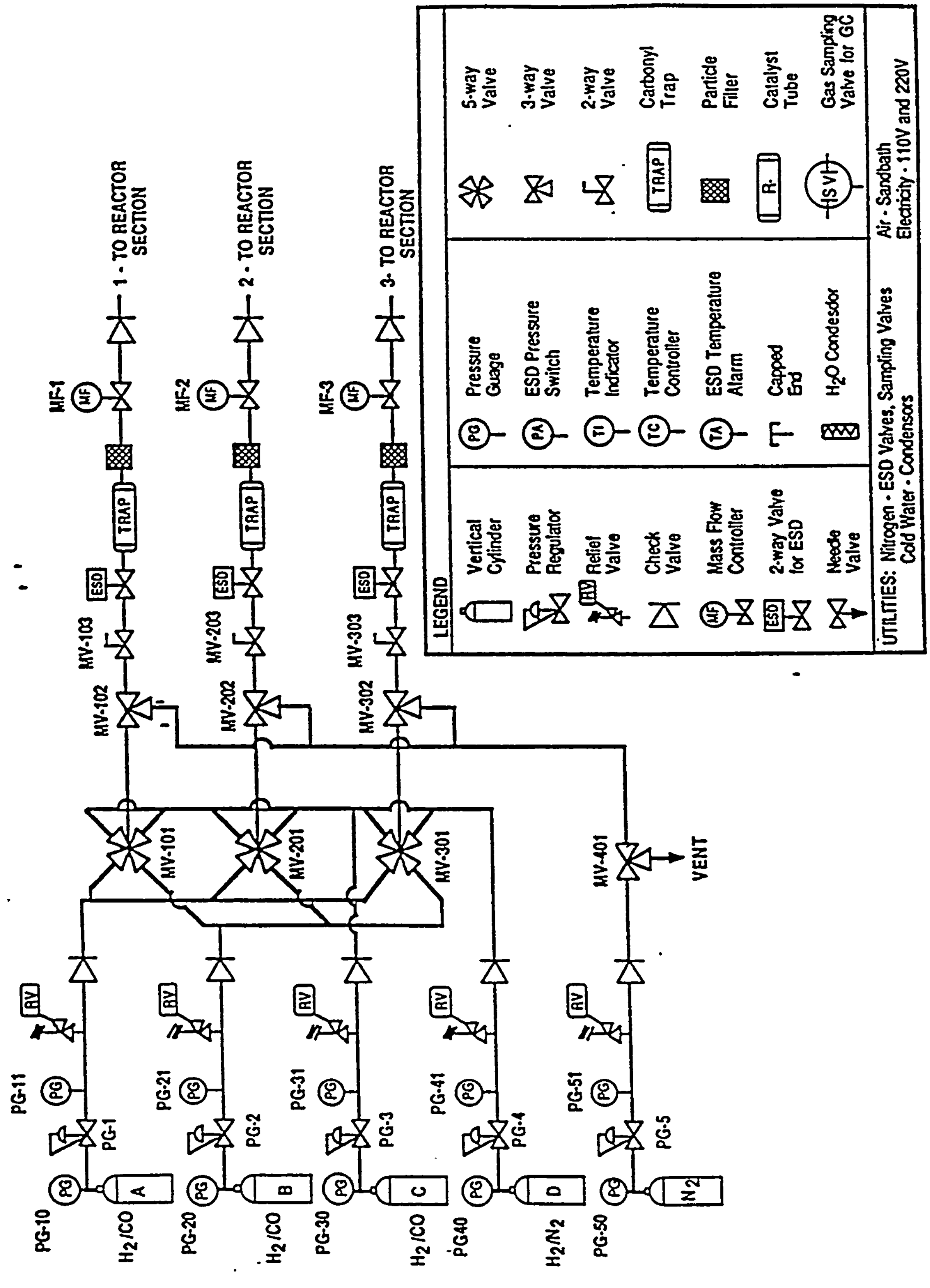
The Syngas Microreactor system was designed to screen heterogeneous catalysts for the conversion of synthesis gas to methanol and higher alcohols over a pressure range of 15-1500 psig, a temperature range of 25-400°C, and feed gas flow rate range of 50-1000 sccm. Up to three fixed-bed reactor tubes may be operated independently, except for reaction temperature. The unit consists of three sections: the feed section, the reaction section, and the analytical section (Figures 5.3-1, 5.3-2, and 5.3-3).

1. Feed Section. The feed section is designed to allow the operator to select any one of four premixed feed gases independently for any reaction tube. In addition, a nitrogen purge and pressure testing stream is available for selection. After stream selection, the feed gas for a reaction tube is passed through a molecular sieve/activated carbon trap to remove water and metal carbonyl contaminants. The purified gas then passes through a mass flow meter and into the reaction tube inlet.

2. Reaction Section. Each reaction tube is manufactured from 0.5" stainless steel and can hold up to ten milliliters of catalyst. The reaction tubes are heated using an air fluidized sandbath which is operated by a PID controller that senses the process temperature via a thermocouple positioned directly in the sandbath. The temperature of each reaction tube is also monitored using a thermocouple positioned axially inside the reaction tube. The reaction tube offgas passes into a spring-loaded back pressure regulator (used to elevate reaction pressure) equipped with a bypass valve.

3. Analytical Section. From the back pressure regulator, the product gas stream enters into the analytical section of the unit. The analytical section consists of automated, air-actuated, gas sampling valves (GSVs) to provide on-line offgas sampling, followed by knock-out drums to collect liquid product for future analyses. In a modification of the unit after initial construction, an aluminum box was fabricated to house the gas sampling system components. These included the back pressure regulators, gas sampling valves (GSV-1& GSV-2), reactor down-stream pressure gauges and the calib./ gas sample 3-way valves. Independent block heaters were used on the gas sampling valves and provide some of the heat required by the box. However, the majority of heat is provided by a 4 ft section of heat tape attached to the inside of the box cover and regulated by a Payne Controller.

Figure 5.3-1. Feed System of Syngas Microreactor System



Feed System of Syngas Microreactor System.

Figure 5.3-2. Reactor System of Syngas Microreactor System

Reactor Section of Syngas Microreactor System.

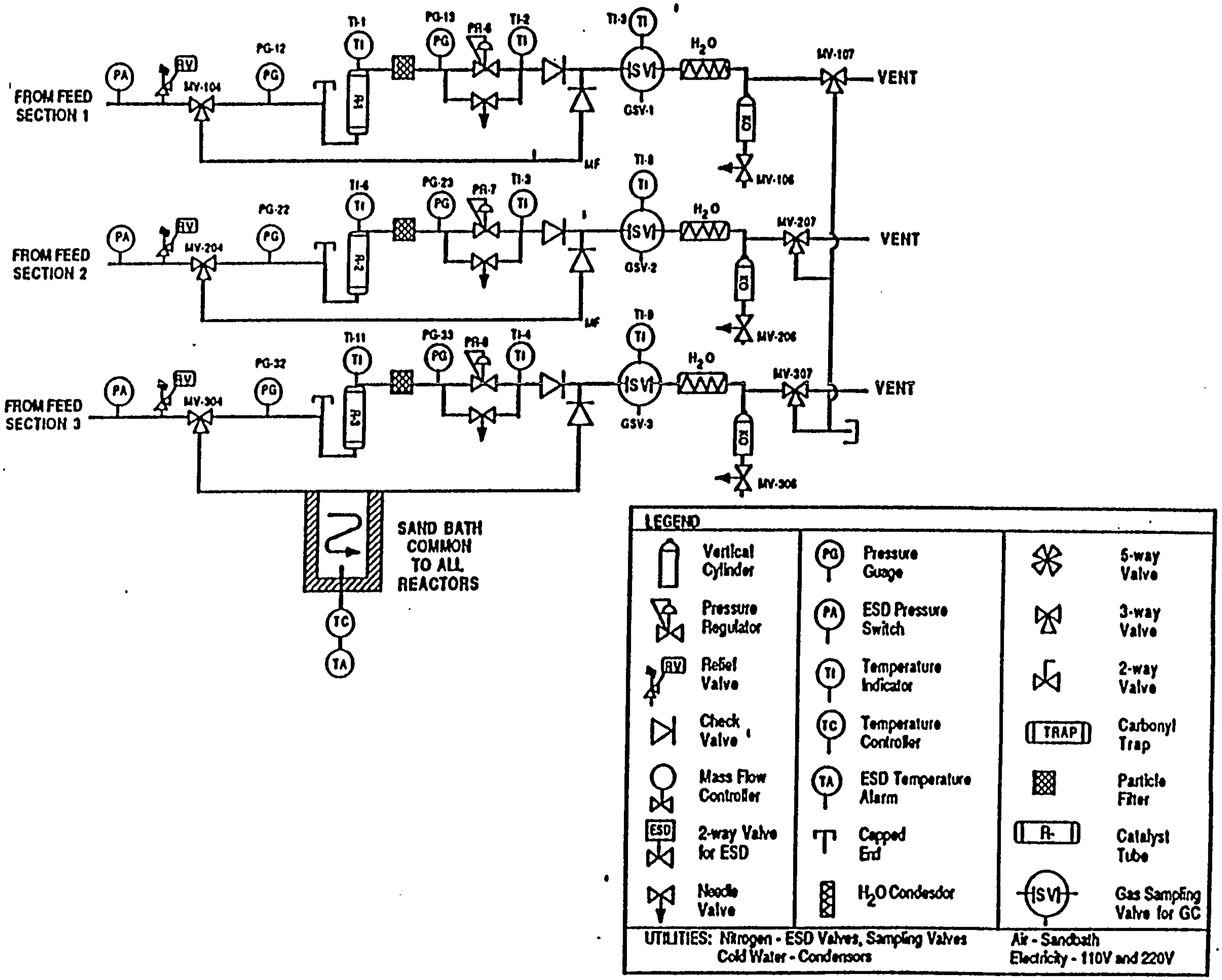
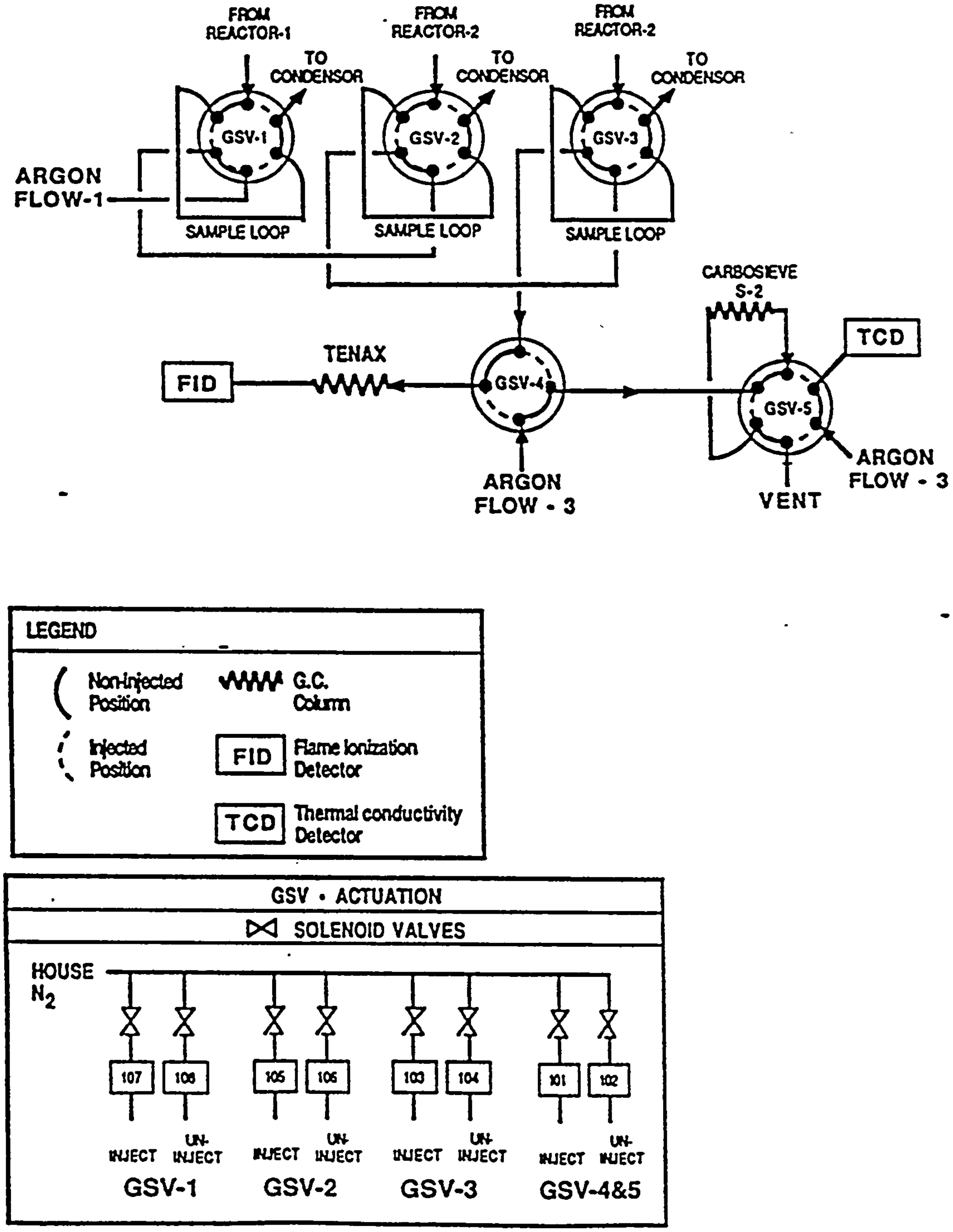


Figure 5.3-3. Analytical System of Syngas Microreactor System



5.4 Product Analysis

Each reaction line in the microreactor system passes through an independent six port, two position, gas sampling valve (GSV-1, GSV-2, or GSV-3). These valves alternatingly provide 0.6 ml reactor offgas samples to a Varian 3700 gas chromatograph. All valves are pneumatically actuated using a collection of solenoid valves controlled via the UCC computer automated laboratory system (CALS).

Once a sample enters the argon carrier gas stream (see Figure 5.3-3), it is transported outside of the fume hood to a four-port two-position air-actuated switching valve (GSV-4) located at the GC. This valve directs the sample to either the organics separation (Tenax column) and detection leg of the analysis scheme or to the inorganics separation (Carbosieve S-2 column) and detection section. While GSV-4 is directing samples to the Tenax column, GSV-5, a six-port two-position gas sampling valve back-flushes the Carbosieve column of accumulated organic compounds from previous analyses. GSV-4 and GSV-5 are bridged so that they actuate at the same moment. The analytical section is designed to have GSV-1, 2 or 3 send two samples to the GC two minutes apart. The first sample goes to the organics analysis section. On the second sampling, GSV-4 and 5 are actuated to divert the second gas sample to the inorganics analysis section.

5.5 Gas Chromatographic Analyses

A single Varian 3700 gas chromatograph equipped with two detectors is used for offgas analysis. Inorganics (H_2, N_2, CO, and CO_2) are separated on a 10'x1/8" 80/100 mesh Carbosieve S-2 column purchased from Supelco and detected by thermal conductivity. All organic products are resolved on a 12'x1/8" 80/100 mesh Tenax column obtained from Alltech and detected using flame ionization. The Tenax column has been calibrated on an absolute weight basis using quantified mixtures of C_1-C_6 normal hydrocarbons, normal and branched alcohols, and normal aldehydes. Argon is used as the carrier gas for both columns. The following parameters are used for the GC oven and the two columns and detectors:

Temperature ramp: 50°C to 225°C at 8°C/min with a 10 minute hold at the upper temperature

Column	Flow Rate	Injector Temp.
Tenax	20 sccm	220°C
Carbosieve (sample)	20 sccm	170°C
Carbosieve (reference)	20 sccm	170°C

Detector	Temperature	Sensitivity	Attenuation	Other
TCD	200°C	5.0 mV	4X	Filament Temp. = 350°C
FID	250°C	10^{-10}	8X	H_2 flow = 30 sccm Air flow = 300 sccm

5.6 Data Analysis

Upon collecting the dual channel GC chromatogram for a reactor tube, CALS determines the identity and area of all components eluted and passes the results to a VAX mainframe computer. The operator accesses the VAX using a terminal in the laboratory and enters a FORTRAN program that has been written to provide further data analysis. The operator inputs the feed and offgas flow rates, reaction conditions, and catalyst reference numbers. The program calculates the catalyst activity and selectivity as well as performing carbon, hydrogen, and oxygen mass balances. In general, the oxygen and hydrogen mass balance is not 100% because the analytical system is unable to quantitate the H_2O concentration in the offgas. A summary of the results may then be printed in a convenient format.