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HETEROGENEOUS CATALYTIC PROCESS FOR ALCOHOL FUELS FROM SYNGAS

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1. Executive Summary

The principal objectives of this project are to discover and evaluate novel heterogeneous catalysts for conversion of syngas to oxygenates having use as fuel enhancers, to explore novel reactor and process concepts applicable in this process, and to develop the best total process for converting syngas to liquid fuels.

Among our previous best catalysts was the family consisting of potassium-promoted Pd on a Zn/Cr spinel oxide prepared via controlled pH precipitation. We have now 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 best support.

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, demonstrating the effectiveness of zinc oxide addition to the spinel support.

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. The commercial 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.

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. Hydrogen can be observed on the catalyst surface by surface science studies. Hydrogen on the active catalyst is associated with the palladium.

2. Project Objectives

- To discover, study, and evaluate novel heterogeneous catalytic systems for the production of oxygenated fuel enhancers from synthesis gas. In particular, novel heterogeneous catalysts will be studied and optimized for the production of: (a) C₁-C₅ alcohols using conventional methanol synthesis conditions, and (b) methanol and isobutanol mixtures which may be used for the downstream synthesis of MTBE or related oxygenates.
- To explore, analytically and on the bench scale, novel reactor and process concepts for use in converting syngas to liquid fuel products.
- To develop on the bench scale the best combination of chemistry, catalyst, reactor, and total process configuration to achieve the minimum product cost for the conversion of syngas to liquid products.

3. Project Organization

This project has been divided into two tasks.

Task 1 is concerned with catalyst identification, preparation, performance evaluation, and characterization. This work is being largely conducted by catalyst chemists and analytical specialists. Chemical studies to support the engineering effort in Task 2 are included in this task, but fundamental aspects of the catalytic chemistry are emphasized in this effort.

Task 2 includes process conceptualization and economics, and bench-scale process evaluation of systems developed in Task 1. This is largely an engineering activity.

4. Technical Progress

4.1. Task 1 - Catalyst Studies

4.1.1. Introduction

It is well known that the addition of alkali promoters to ZnCrO , MnCrO , and ZnMnCrO systems will modify the selectivity of high temperature methanol catalysts towards C_2+ alcohols. Interest in higher alcohol synthesis (HAS) from syngas has stemmed from the desire to use the alcohol mixtures as high-octane blending stock for gasoline. Currently refining modifications and the use of oxygenated petrochemicals such as methyl-tert-butyl-ether (MTBE) have become favored 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 ethers related to MTBE. One could also envision dehydrating the isobutanol to isobutene, followed by reaction with methanol to form MTBE. We have been investigating a series of promoted Zn/Cr/Mn spinel oxide materials as promising catalysts for this process.

One of our better catalysts 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. This catalyst is designated as 16-DMM-68. The major components/variables involved 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
- the addition of Pd

In order to determine the scope of this discovery, we have prepared comparative catalysts based on Zn/Cr spinel oxide support that does not contain excess ZnO and ZnO by itself, both prepared by controlled pH precipitation. These materials are the components that go into making our current best catalyst and their overall performance should be inferior to our best catalyst.

Spinel oxide catalysts promoted with cesium and both cesium and palladium have also 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, thus this comparison should demonstrate that the presence of excess ZnO gives a superior catalyst.

Finally, our best catalysts are prepared by controlled pH precipitation of the spinel oxide. Comparison of potassium promoted catalysts made via this procedure with potassium promoted materials derived from a commercial Zn/Cr spinel used for methanol synthesis prepared via an alternative procedure should demonstrate the benefit of the controlled pH precipitation method in catalyst preparation.

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

We have attempted to answer the following questions:

- In terms of catalyst performance, is the combination of the catalyst components (the complete catalyst) superior to the individual parts ?
- Does the presence of excess ZnO result in better catalyst performance ?
- Does the method of catalyst preparation make a difference in catalyst performance ?

4.1.2. Potassium Promotion of Zn/Cr/O and ZnO

We have 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 1-8. 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 Potassium¹
440°C, 1500 psi, GHSV = 12000, H₂/CO = 1:1

	Zn/Cr <u>3 wt% K</u> PR039	ZnO <u>1 wt% K</u> PR141	Zn/Cr/O w. ex.ZnO <u>5 wt% K</u> 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 m²/g, while that of the ZnO is < 20 m²/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 m²/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.

4.1.3. Presence and Absence of 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 9-11. 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, H₂/CO=1

	<u>Zn/Cr w ex.ZnO</u> <u>with 3 wt% Cs¹</u>	<u>Zn/Cr only</u> <u>with 3 wt% Cs</u>
	PR490	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 12-14. 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, H₂/CO=1. Test results for representative catalysts on the two supports are shown below:

	<u>Zn/Cr w ex.ZnO</u> <u>with 5 wt% Cs</u> <u>and 6 wt% Pd¹</u>	<u>Zn/Cr only</u> <u>with 5 wt% Cs</u> <u>and 6 wt% Pd</u>
	PR598	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.

4.1.4. Comparison with Catalysts Based on Commercial Material

We have examined the effect of potassium promotion on higher alcohol synthesis using a commercial 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 15-18. 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 Potassium¹
440°C, 1500 psi, GHSV = 12000, H₂/CO = 1:1

	A <u>1 wt% K</u> PR042	B <u>3 wt% K</u> PR039	C <u>5 wt% K</u> 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.

4.1.5. 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.

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 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.

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 1.4×10^{-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.

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.

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.

4.1.6. Experimental

4.1.6.1. 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.

4.1.6.2. 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. Reactors were dried

under vacuum. One gram of catalyst was mixed with 3 cm³ 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.

4.1.7. Task 1 Conclusions

- 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.
- Differences in relative surface areas help to explain why the spinels are more active for isobutanol synthesis and require more potassium promoter for the maximum isobutanol rate.
- 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.
- 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.
- 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.
- Hydrogen can be observed on the catalyst surface by surface science studies. Hydrogen on the active catalyst is associated with the palladium.

TABLE 1

**ZnO - Prepared via precipitation at constant pH = 10 from K(OH/CO₃)
(calcined)**

Tested in a copper lined tube

	T = 400°C <u>P = 1000 psi</u> PR 667	T = 400°C <u>P = 1500 psi</u> PR 675	T = 440°C <u>P=1500psi</u> PR 691	T = 440°C <u>P = 1000 psi</u> 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 2

**ZnO - Prepared via precipitation at constant pH = 10 from K(OH/CO₃)
(calcined)**

1% K

Tested in a copper lined tube

	T = 400°C <u>P = 1000 psi</u> PR 115	T = 400°C <u>P = 1500 psi</u> PR 123	T = 440°C <u>P=1500psi</u> PR 141	T = 440°C <u>P = 1000 psi</u> 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 3

**ZnO - Prepared via precipitation at constant pH = 10 from K(OH/CO₃)
(calcined)**

3% K

Tested in a copper lined tube

	T = 400°C <u>P = 1000 psi</u> PR 116	T = 400°C <u>P = 1500 psi</u> PR 124	T = 440°C <u>P=1500psi</u> PR 140	T = 440°C <u>P = 1000 psi</u> 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

**ZnO - Prepared via precipitation at constant pH = 10 from K(OH/CO₃)
(calcined)**

5% K

Tested in a copper lined tube

	T = 400°C <u>P = 1000 psi</u> PR 151	T = 400°C <u>P = 1500 psi</u> PR 189	T = 440°C <u>P=1500psi</u> PR 201	T = 440°C <u>P = 1000 psi</u> 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 5

Zn/Cr Support**Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 917	T = 400°C <u>P = 1500 psi</u> PR 925	T = 440°C <u>P=1500psi</u> PR 941	T = 440°C <u>P = 1000 psi</u> 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 6**Zn/Cr Support plus 1% K****Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 916	T = 400°C <u>P = 1500 psi</u> PR 924	T = 440°C <u>P=1500psi</u> PR 940	T = 440°C <u>P = 1000 psi</u> 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 7

Zn/Cr Support plus 3% K**Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 015	T = 400°C <u>P = 1500 psi</u> PR 023	T = 440°C <u>P=1500psi</u> PR 039	T = 440°C <u>P = 1000 psi</u> 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 8

Zn/Cr Support plus 5% K**Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 016	T = 400°C <u>P = 1500 psi</u> PR 024	T = 440°C <u>P=1500psi</u> PR 040	T = 440°C <u>P = 1000 psi</u> 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 9

Zn/Cr Support plus 1% Cs**Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 265	T = 400°C <u>P = 1500 psi</u> PR 273	T = 440°C <u>P=1500psi</u> PR 289	T = 440°C <u>P = 1000 psi</u> 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 10**Zn/Cr Support plus 3% Cs****Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 266	T = 400°C <u>P = 1500 psi</u> PR 274	T = 440°C <u>P = 1500 psi</u> PR 290	T = 440°C <u>P = 1000 psi</u> 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 11

Zn/Cr Support plus 5% Cs**Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 363	T = 400°C <u>P = 1500 psi</u> PR 371	T = 440°C <u>P=1500psi</u> PR 389	T = 440°C <u>P = 1000 psi</u> 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 12

Zn/Cr Support**1.0 wt% Cs / 5.9% Pd Catalyst****Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 316	T = 400°C <u>P = 1500 psi</u> PR 324	T = 440°C <u>P=1500psi</u> PR 340	T = 440°C <u>P = 1000 psi</u> 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 13**Zn/Cr Support****3.0 wt% Cs / 5.9% Pd Catalyst****Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 364	T = 400°C <u>P = 1500 psi</u> PR 372	T = 440°C <u>P=1500psi</u> PR 392	T = 440°C <u>P = 1000 psi</u> 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 14**Zn/Cr Support****5.0 wt% Cs / 5.9% Pd Catalyst****Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 466	T = 400°C <u>P = 1500 psi</u> PR 474	T = 440°C <u>P=1500psi</u> PR 490	T = 440°C <u>P = 1000 psi</u> 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 15

Zn/Cr Engelhard Commercial Support (calcined @ 325°C)**Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 017	T = 400°C <u>P = 1500 psi</u> PR 025	T = 440°C <u>P=1500psi</u> PR 041	T = 440°C <u>P = 1000 psi</u> 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 16

Zn/Cr Engelhard Commercial Support plus 1 wt% K**Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 015	T = 400°C <u>P = 1500 psi</u> PR 026	T = 440°C <u>P=1500psi</u> PR 042	T = 440°C <u>P = 1000 psi</u> 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 17

Zn/Cr Engelhard Commercial Support plus 3 wt% K**Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 115	T = 400°C <u>P = 1500 psi</u> PR 123	T = 440°C <u>P=1500psi</u> PR 134	T = 440°C <u>P = 1000 psi</u> 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

TABLE 18

Zn/Cr Engelhard Commercial Support plus 5 wt% K**Tested in a copper lined tube**

	T = 400°C <u>P = 1000 psi</u> PR 116	T = 400°C <u>P = 1500 psi</u> PR 124	T = 440°C <u>P = 1500 psi</u> PR 140	T = 440°C <u>P = 1000 psi</u> 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