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HETEROGENEOUS CATALYTIC PROCESS FOR ALCOHOL FUELS FROM SYNGAS

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Contributors to this report: D. M. Minahan

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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.

Our previous best catalysts consisted of potassium-promoted Pd on a Zn/Cr spinel oxide prepared via controlled pH precipitation. We have now examined the effect of cesium addition to the Zn/Cr spinel oxide support. Surprisingly, cesium levels required for optimum performance are similar to those for potassium on a wt% basis. The addition of 3 wt% cesium gives isobutanol rates > 170 g/kg-hr 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 our best Pd/K catalyst.

The addition of both cesium and palladium to a Zn/Cr spinel oxide support gives further performance improvements. The 5 wt% cesium, 5.9 wt% Pd formulation gives isobutanol rates > 150 g/kg-hr at 440°C and only 1000 psi with a selectivity to total alcohols of 88% and with a methanol/isobutanol mole ratio of 0.58: this is our best overall performance to date.

The addition of both cesium and palladium to a Zn/Cr/Mn spinel oxide support that contains excess Zn has also been examined. This spinel was the support used in the synthesis of 10-DAN-54, our benchmark catalyst. Formulations made on this support show a lower overall total alcohol rate than those using the spinel without Mn present, and require less cesium for optimal performance.

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) C_1-C_5 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.

Our current best catalyst 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 10-DAN-54. 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 in the form of potassium
- the addition of Pd

In order to better define the important variables, we have prepared a comparative Zn/Cr spinel oxide support that contains excess ZnO and have looked at the catalytic performance of (a) cesium only and (b) cesium and palladium promoters on both a Zn/Cr spinel oxide and a Zn/Cr/Mn spinel oxide, both prepared by controlled pH precipitation.

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

4.1.2. 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 contains 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 1-3. 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 and 5. 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.

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

We have examined the effect of adding palladium in addition to cesium to a Zn/Cr spinel oxide support that contains excess Zn. Three catalysts containing 1, 3 and 5 wt% cesium and 5.9 wt% Pd were prepared and tested — see Tables 6-8.

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 is our best overall performance to date.

4.1.4. 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 show a lower overall total alcohol rate than those using the spinel without Mn present — see Tables 9-11. 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).

4.1.5. 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 12-14. 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 15.

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.

4.1.6. 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 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.

4.1.7. Task 1 Conclusions

- Cesium is a more effective promoter than potassium for higher alcohol synthesis for the Zn/Cr spinel oxide containing excess zinc oxide system.

- 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.

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

Our future plans are to continue formulation screening using alkali and palladium formulations on:

(a) ZnO by itself
(b) Zn/Cr spinel *without* excess ZnO prepared conventionally and via controlled pH precipitation
(c) Zn/Cr/Mn spinel *without* excess ZnO prepared via controlled pH precipitation.

TABLE 1

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 2

Zn/Cr 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 3

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

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 5

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

TABLE 5

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 6

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 7

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 8

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 9

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 11

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

TABLE 11

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 12

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 13

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 14

Zn/Cr/Mn Support with excess Zn

5 wt% Cs, 6 wt% Pd Catalyst

Tested in a copper lined tube

	T = 400°C	T = 400°C	T = 440°C	T = 440°C
	P = 1000 psi	P = 1500 psi	P=1500psi	P = 1000 psi
	Run PR 817	Run 825	Run PR 841	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 15

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