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	B	C
	1 wt% K	3 wt% K	5 wt% K
	PR042	PR039	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 $H_2/CO = 1$

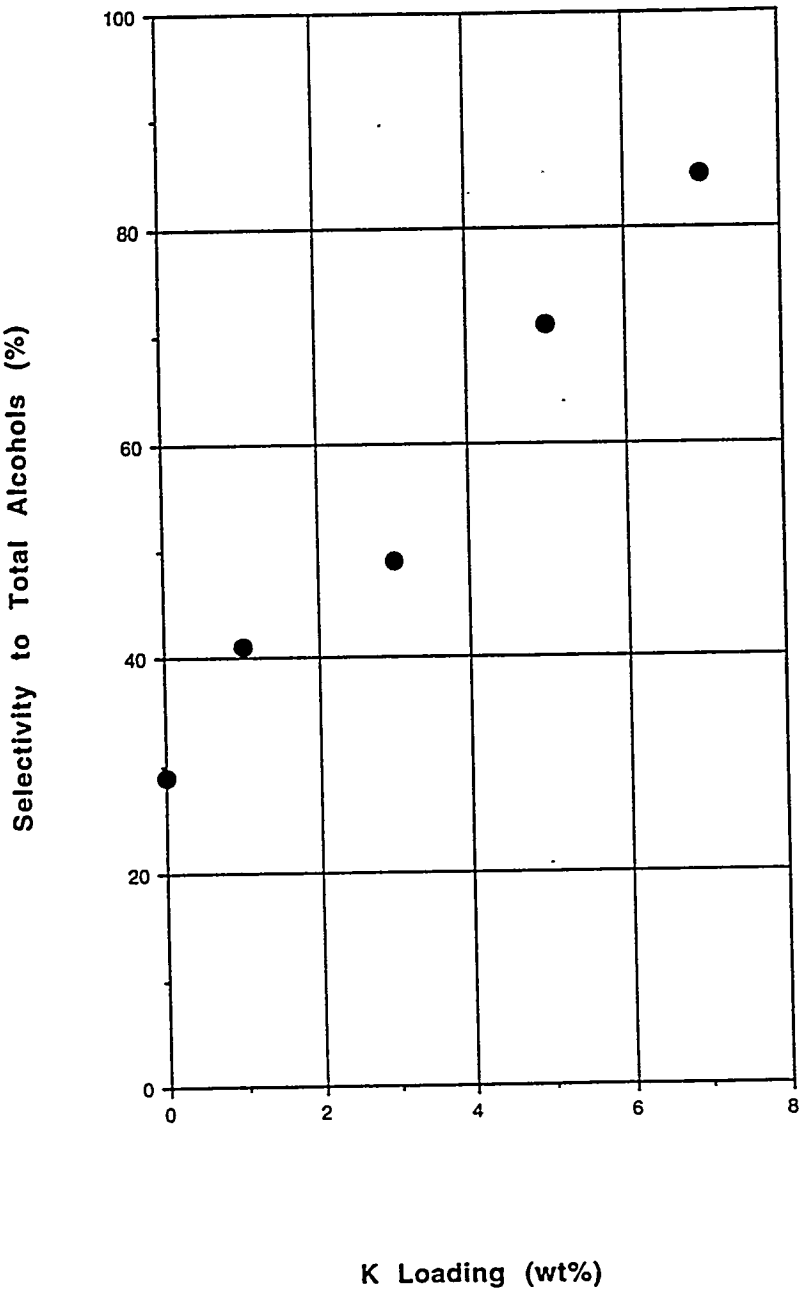

Figure 4.11-2. Rate to total alcohols vs. K loading on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

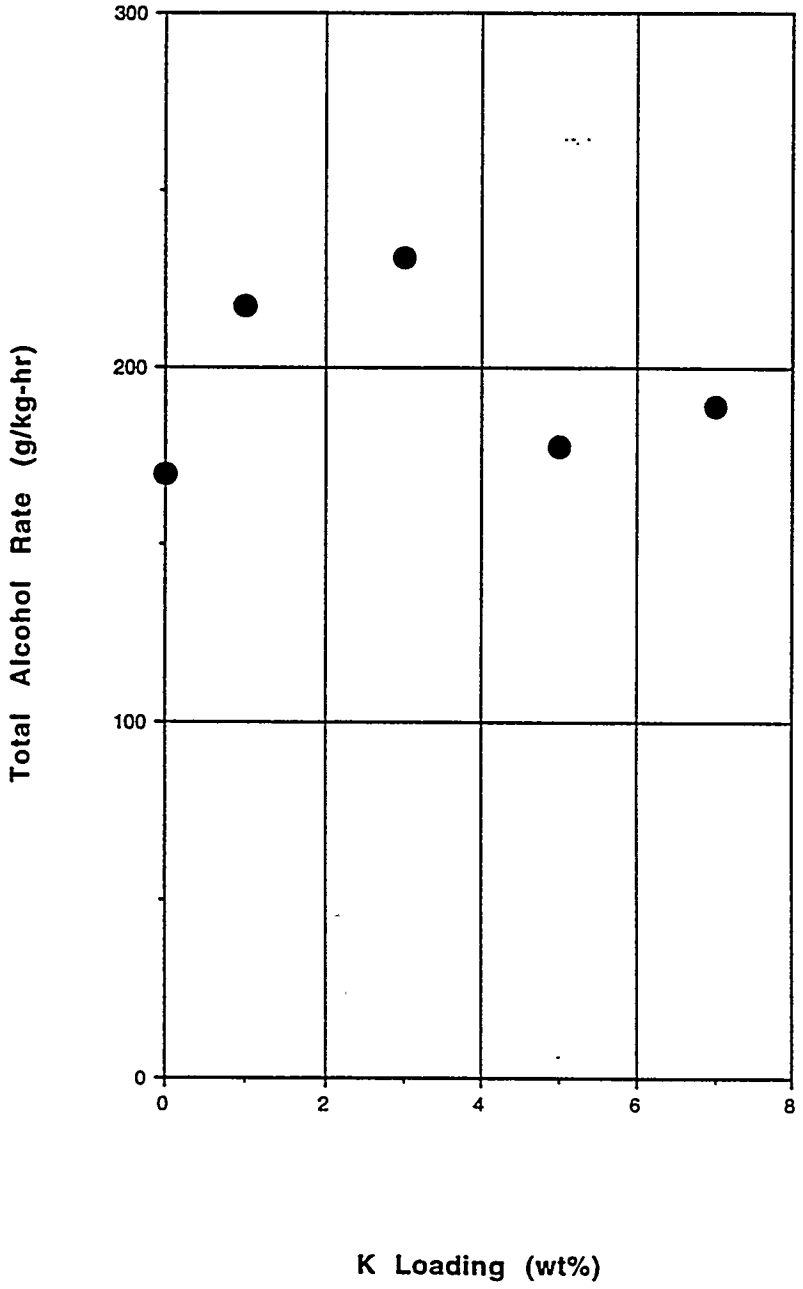

Figure 4.11-3. Rates to methanol and isobutanol vs. K loading on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

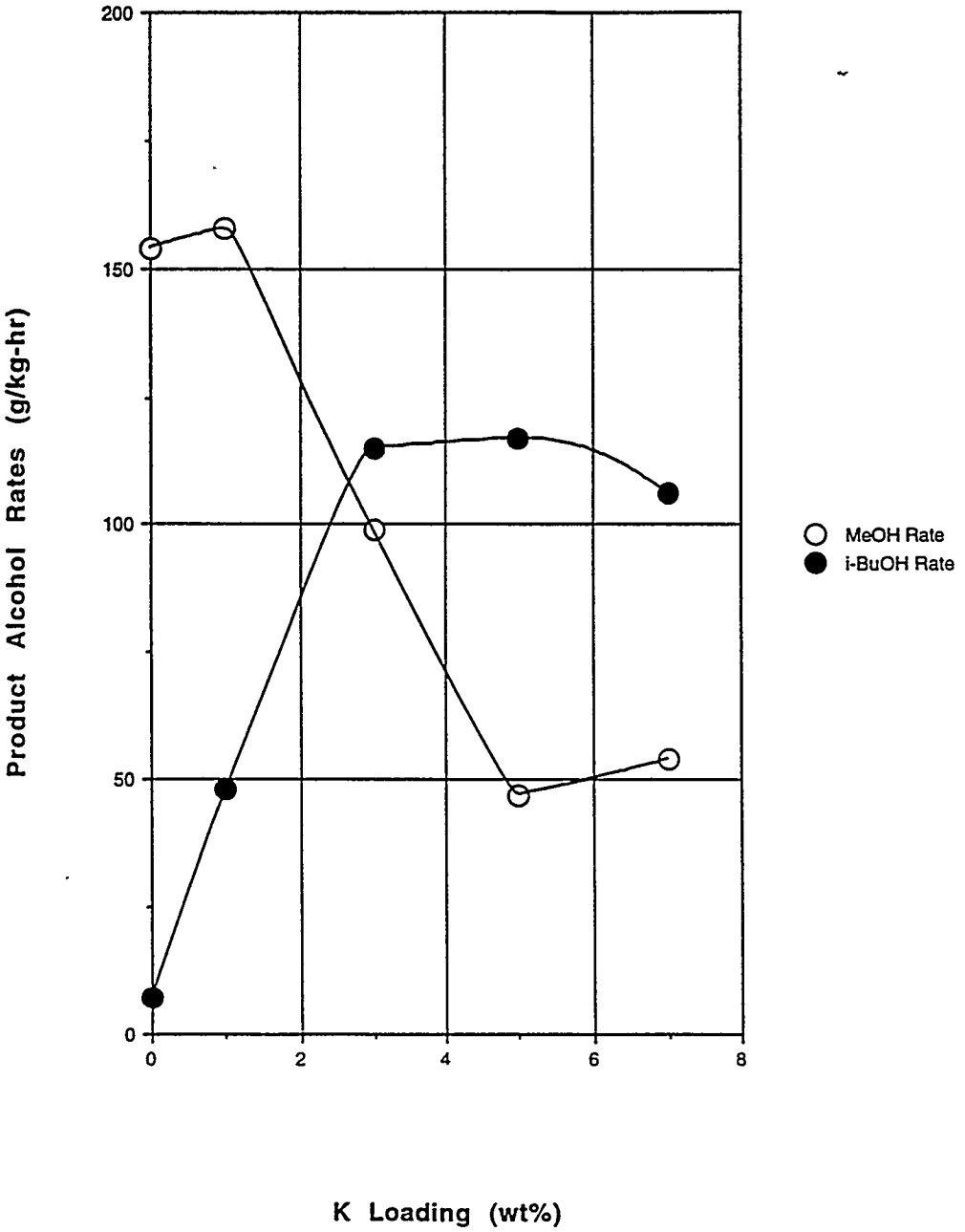

Figure 4.11-4. Selectivity to total alcohols vs. K loading for 6 wt% Pd on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

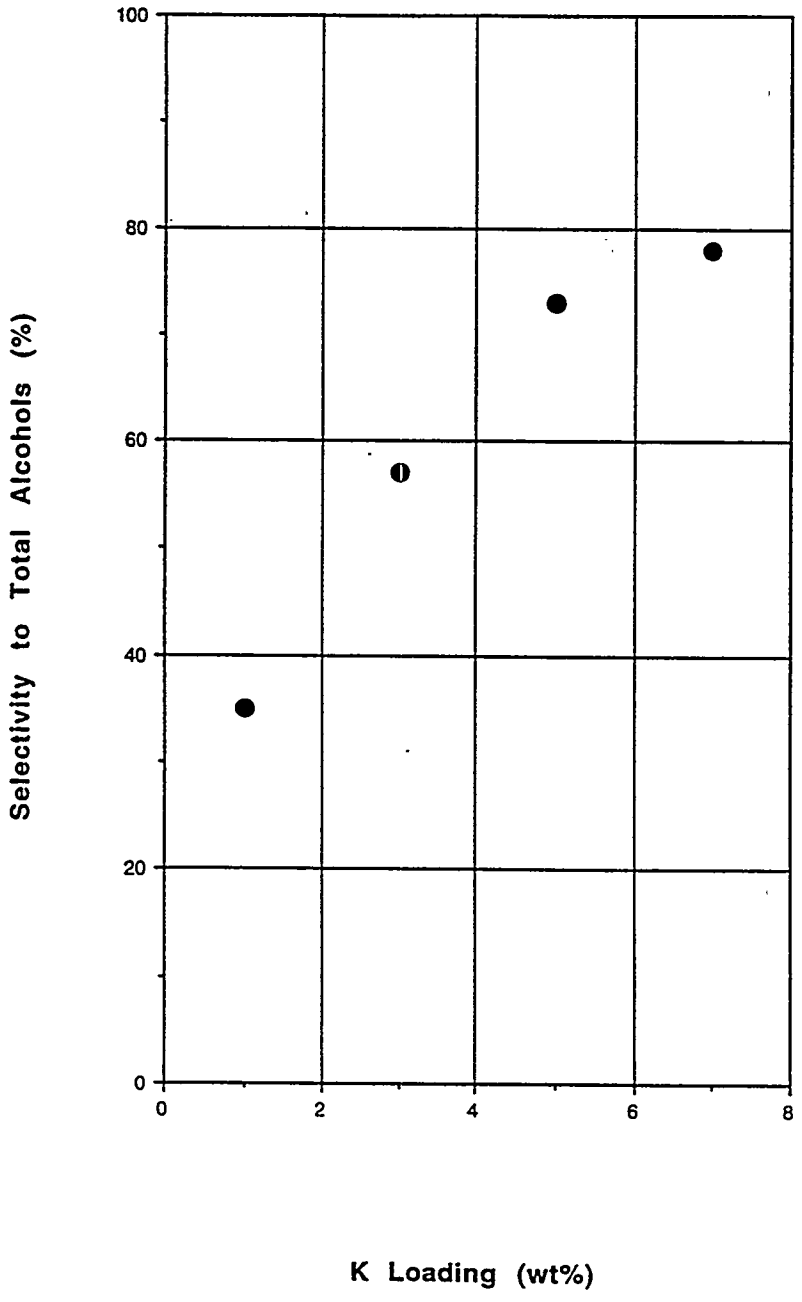

Figure 4.11-5. Rate to total alcohols vs. K loading for 6 wt% Pd on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

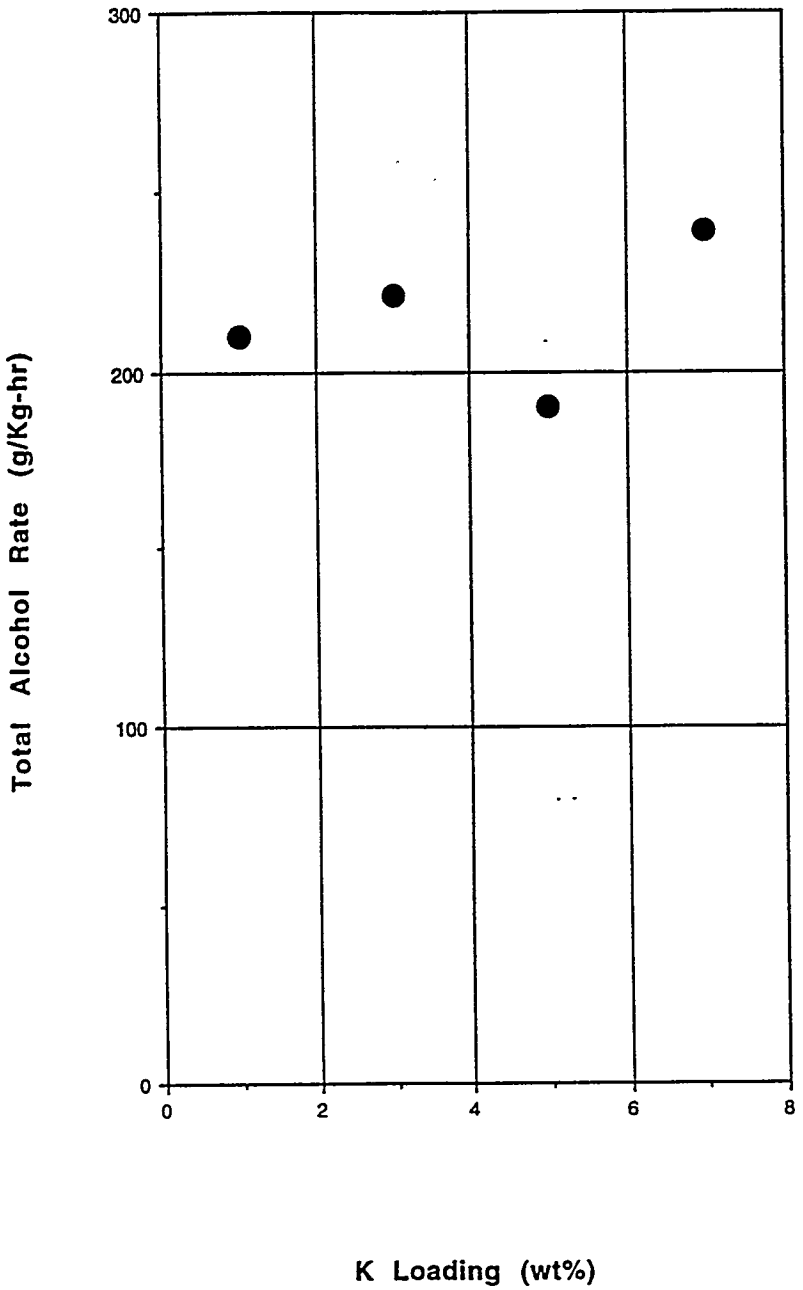

Figure 4.11-6. Rates to methanol and isobutanol vs. K loading for 6 wt% Pd on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

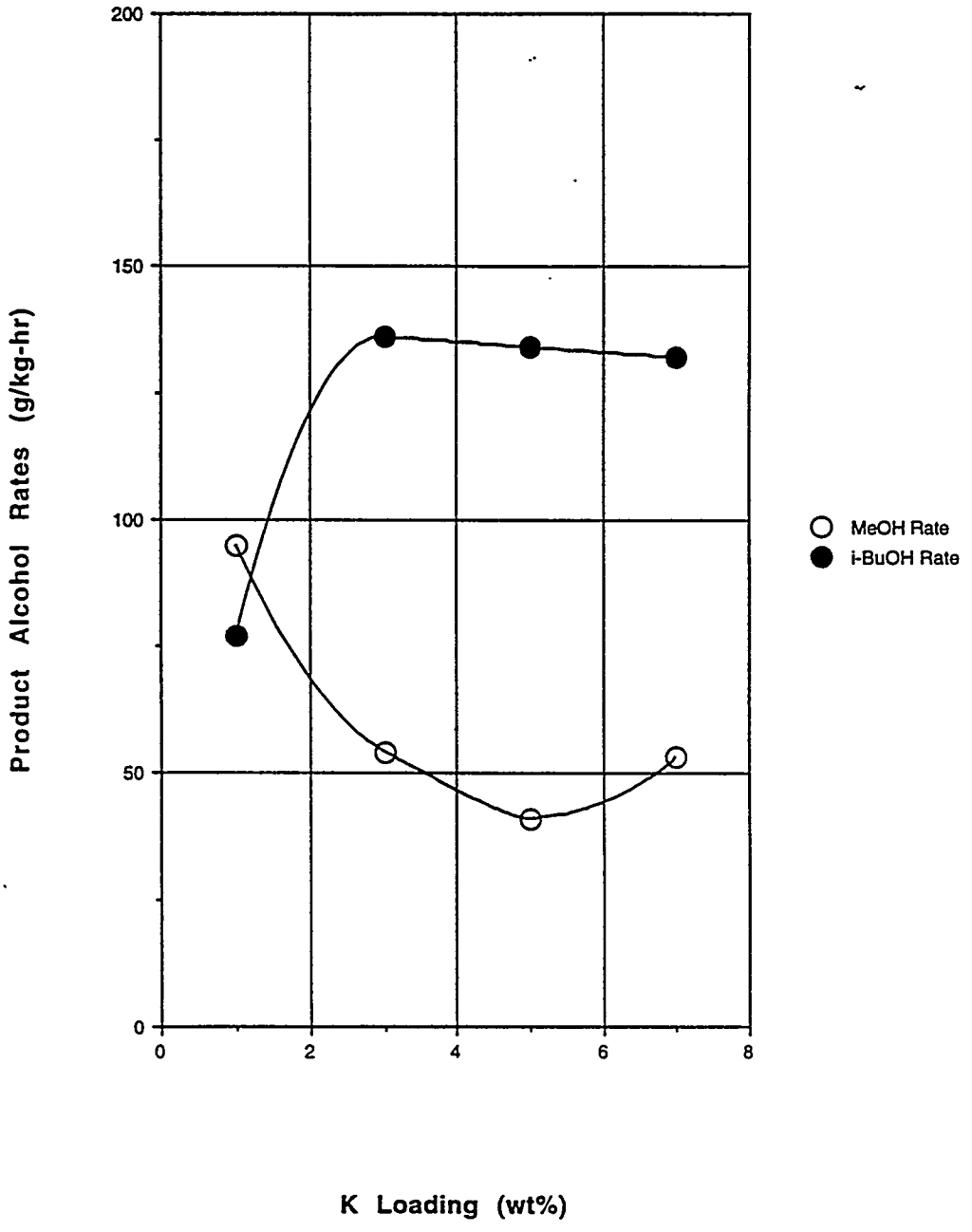

Table 4.11-1. ZnCr support with excess Zn, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	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