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)

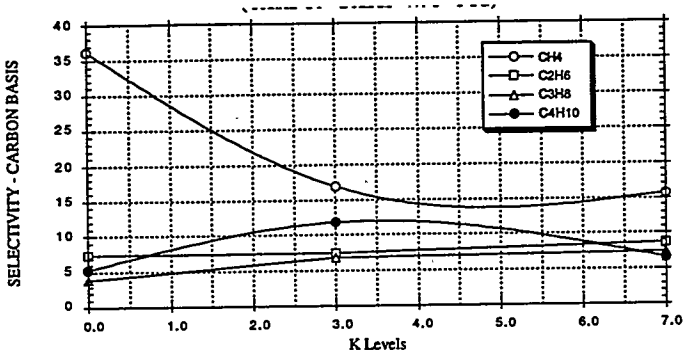


Figure 4.6-2. Alcohol Selectivity as a Function of K Loading (CO_2-free basis)

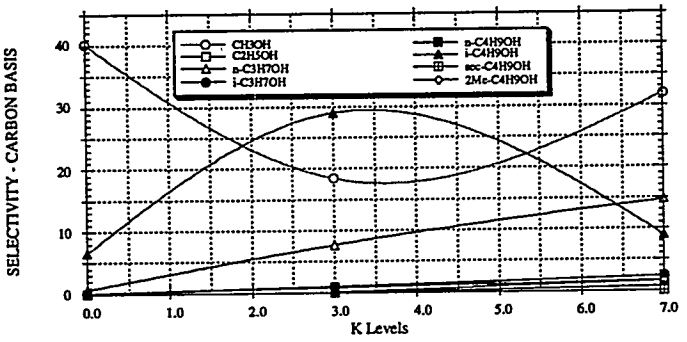
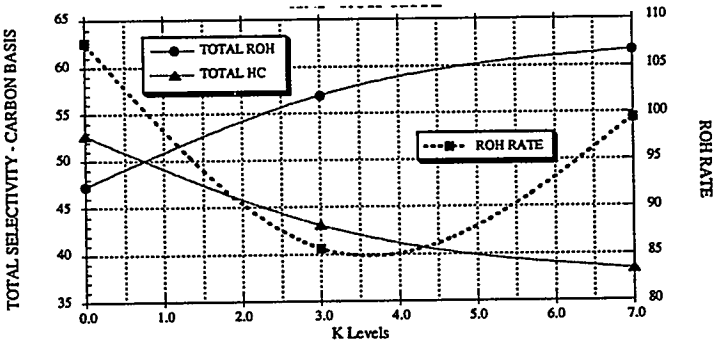


Figure 4.6-3. Total Hydrocarbon and Alcohol Selectivity and Alcohol Rate



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)

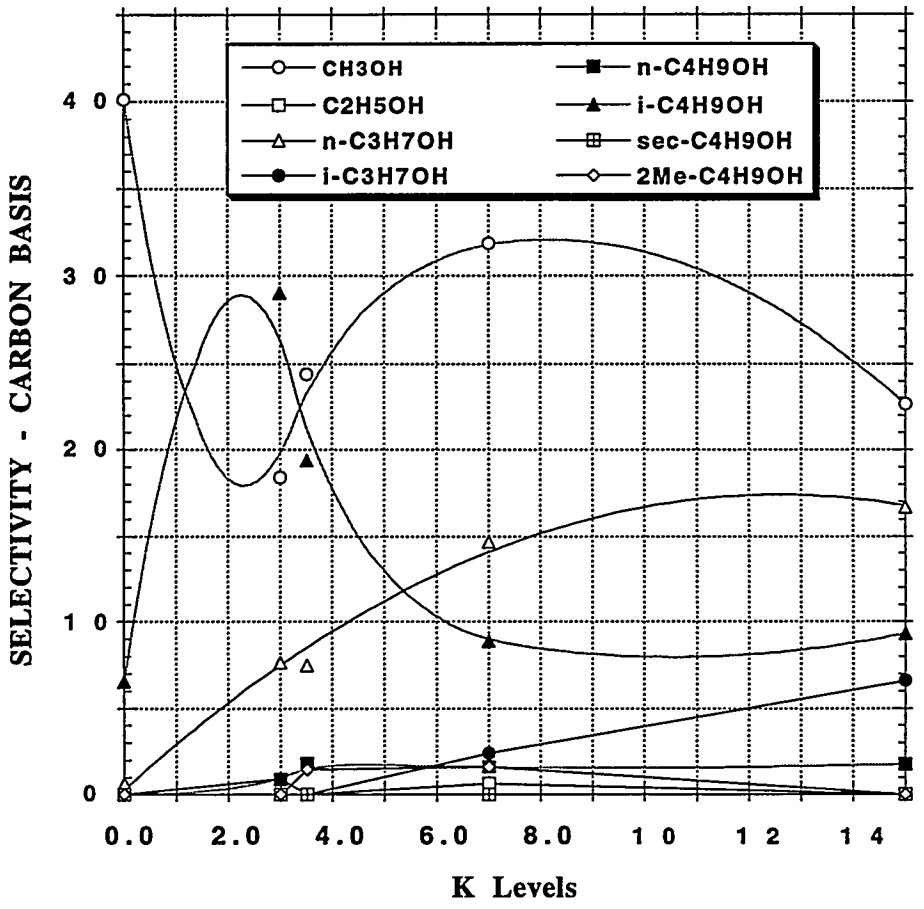


Figure 4.6-5. Hydrocarbon Selectivity as a Function of K Loading (Carbon Basis w/o CO_2)

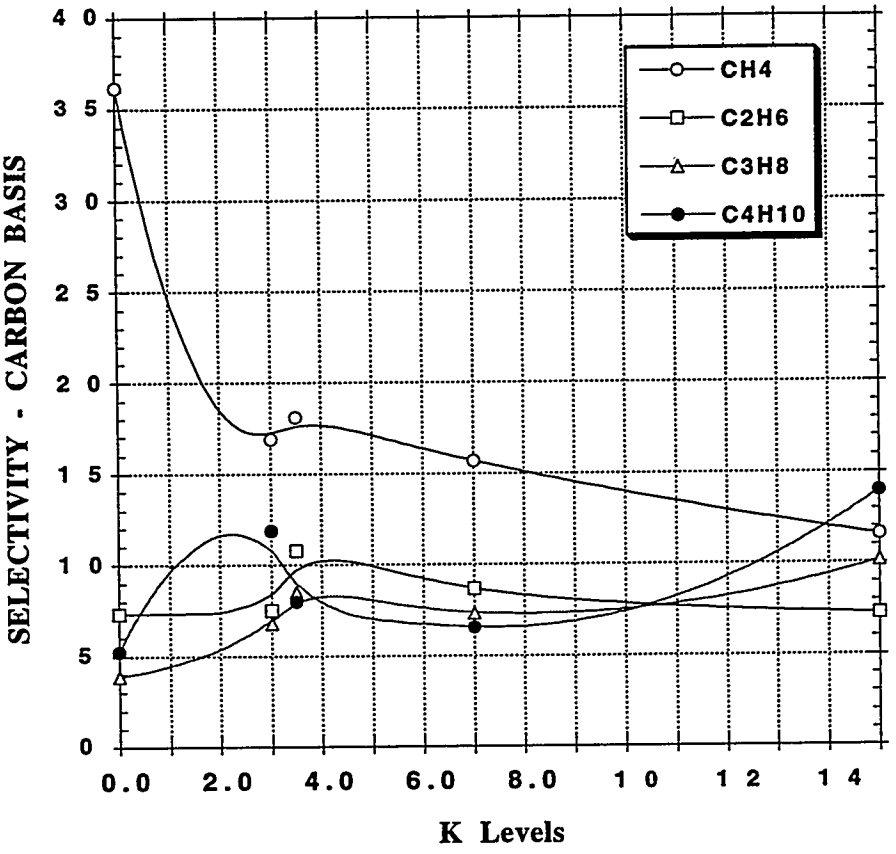
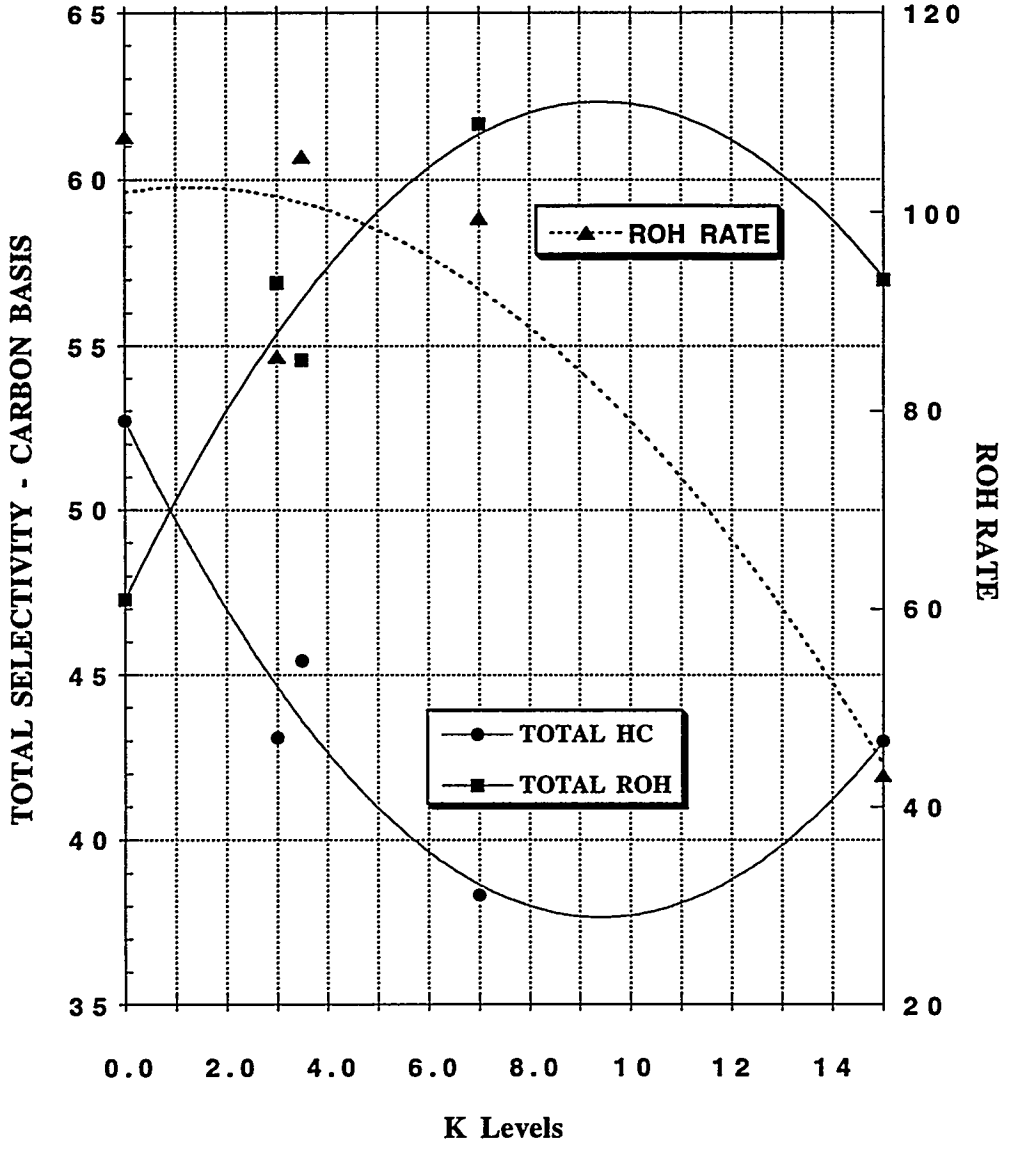


Figure 4.6-6. Alcohol Rate and Total Hydrocarbon and Alcohol Selectivity



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)

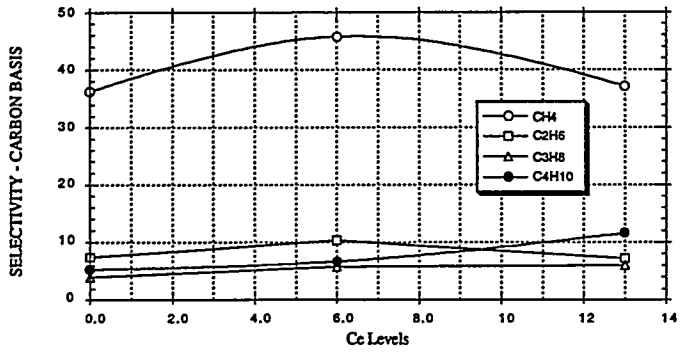


Figure 4.7-2. Alcohol Selectivity as a Function of Ce Loading (CO_2-free basis)

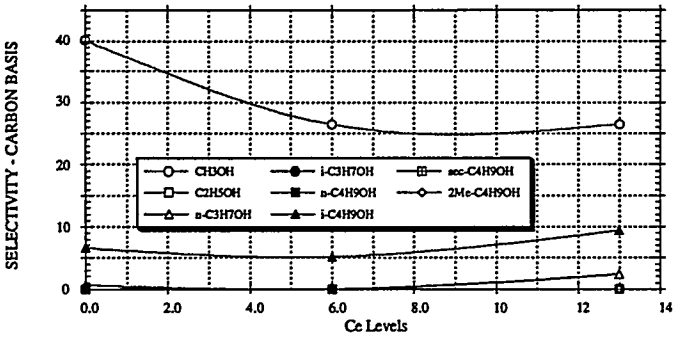
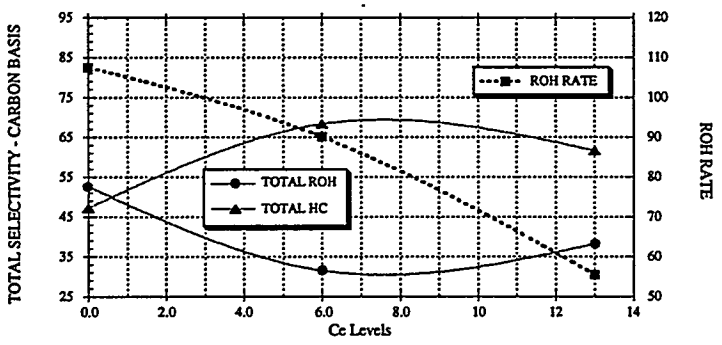


Figure 4.7-3. Total Hydrocarbon and Alcohol Selectivity and Alcohol Rate



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.

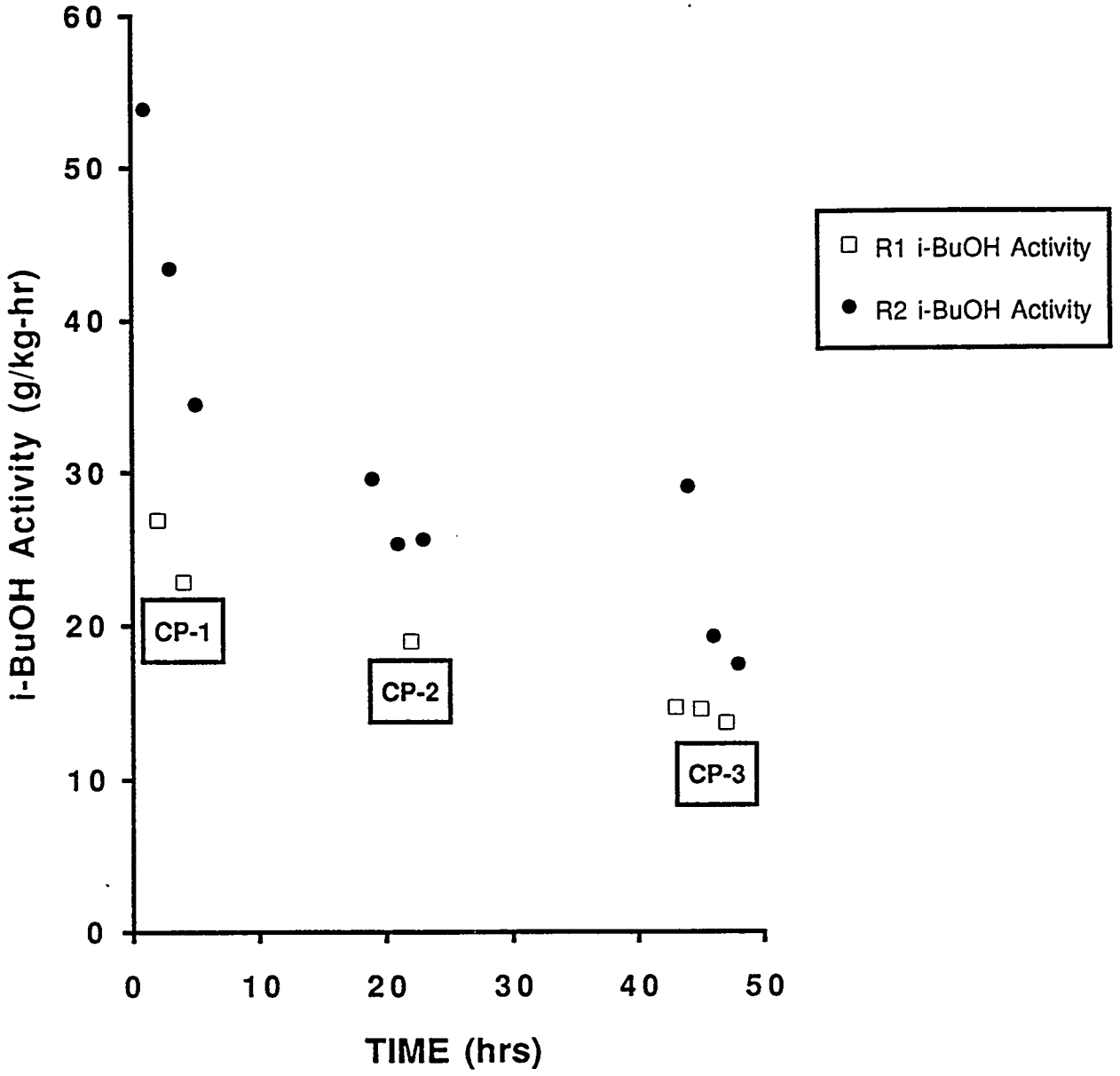


Figure 4.8-2. Typical alcohol distribution from process design experiments (10DAN135, charge 1).

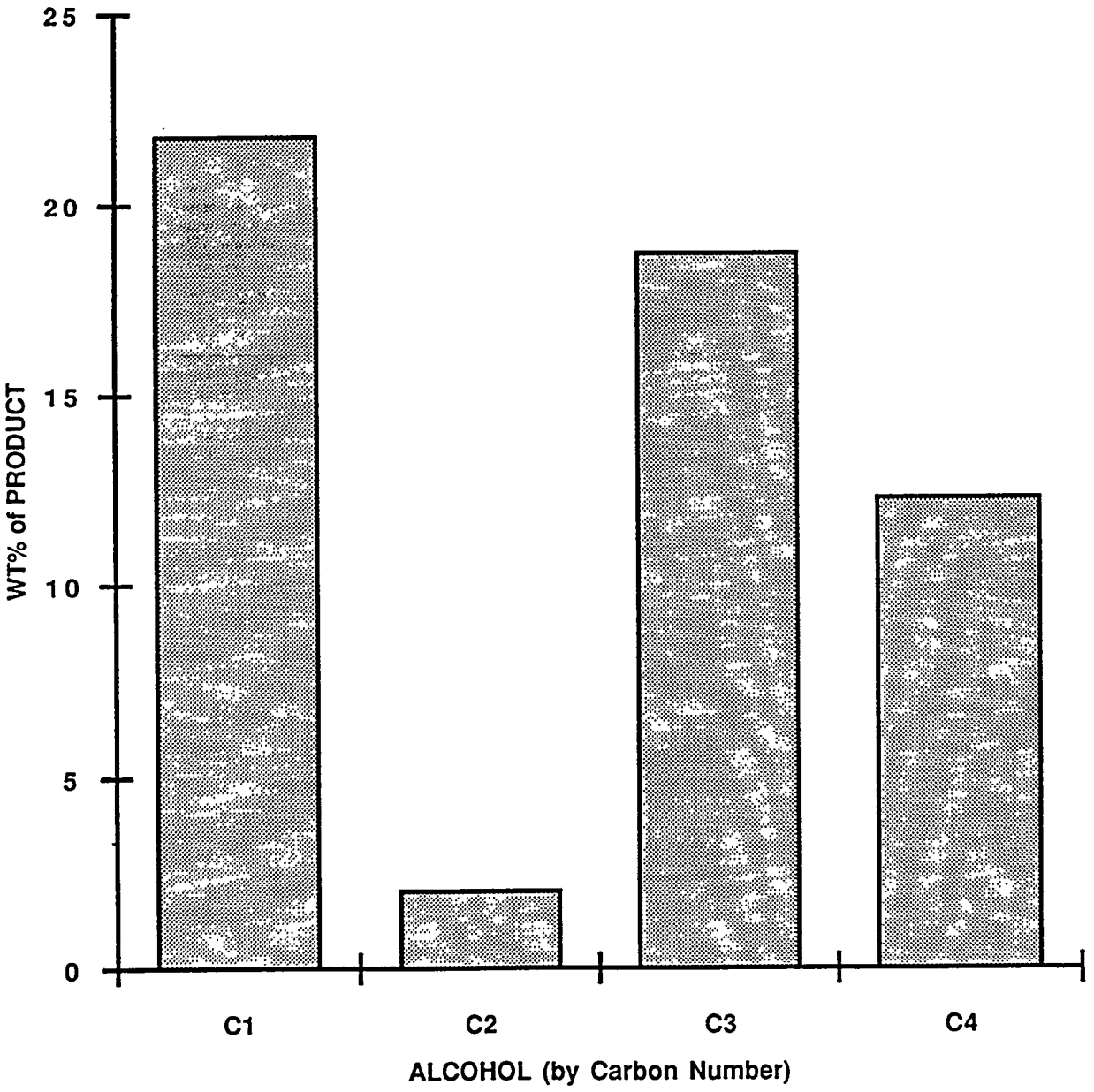


Figure 4.8-3. Typical alcohol distribution from catalyst formulation design (10DAN54).

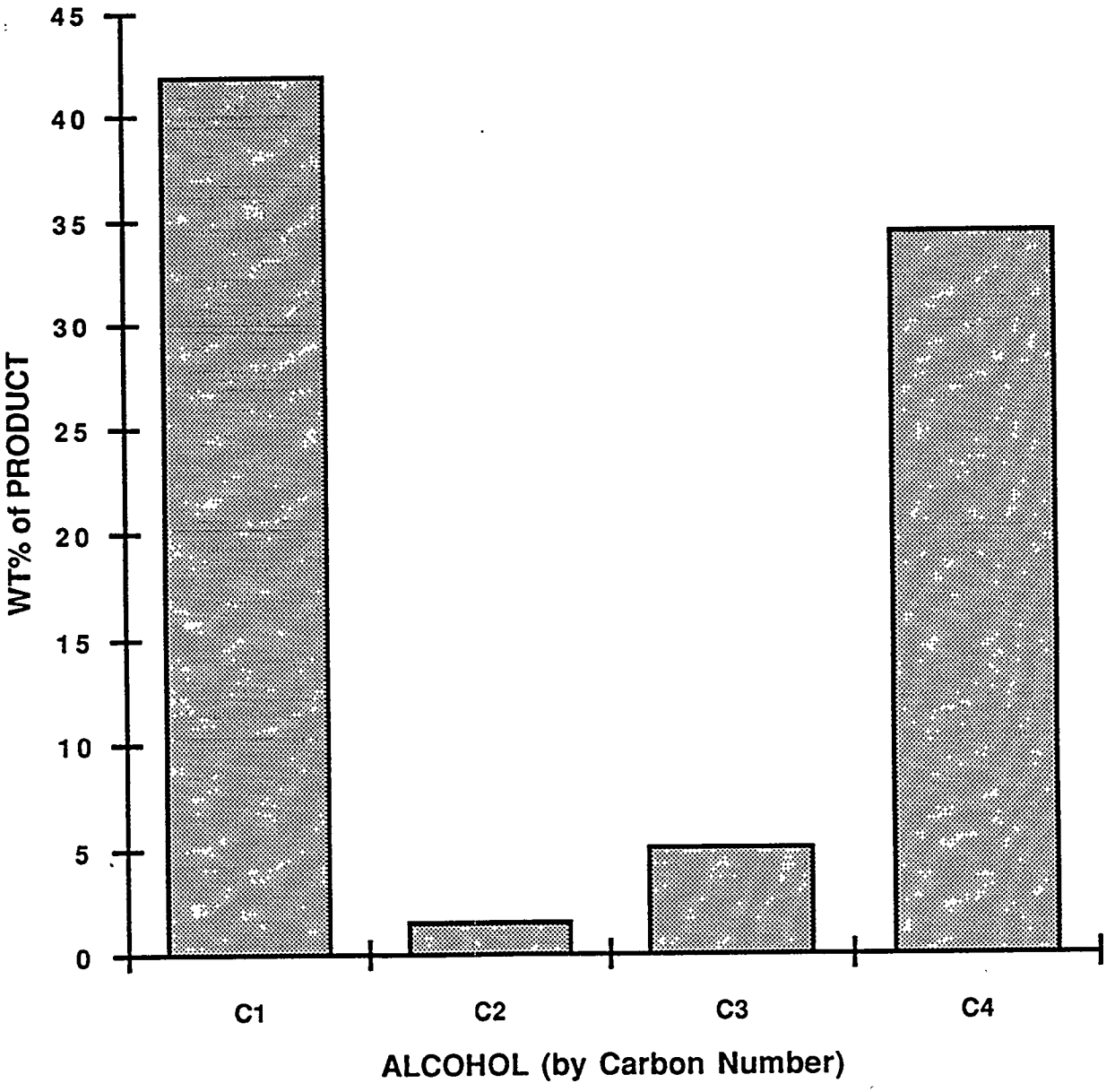


Figure 4.8-4. Process design center points after replacing catalyst with a fresh charge.

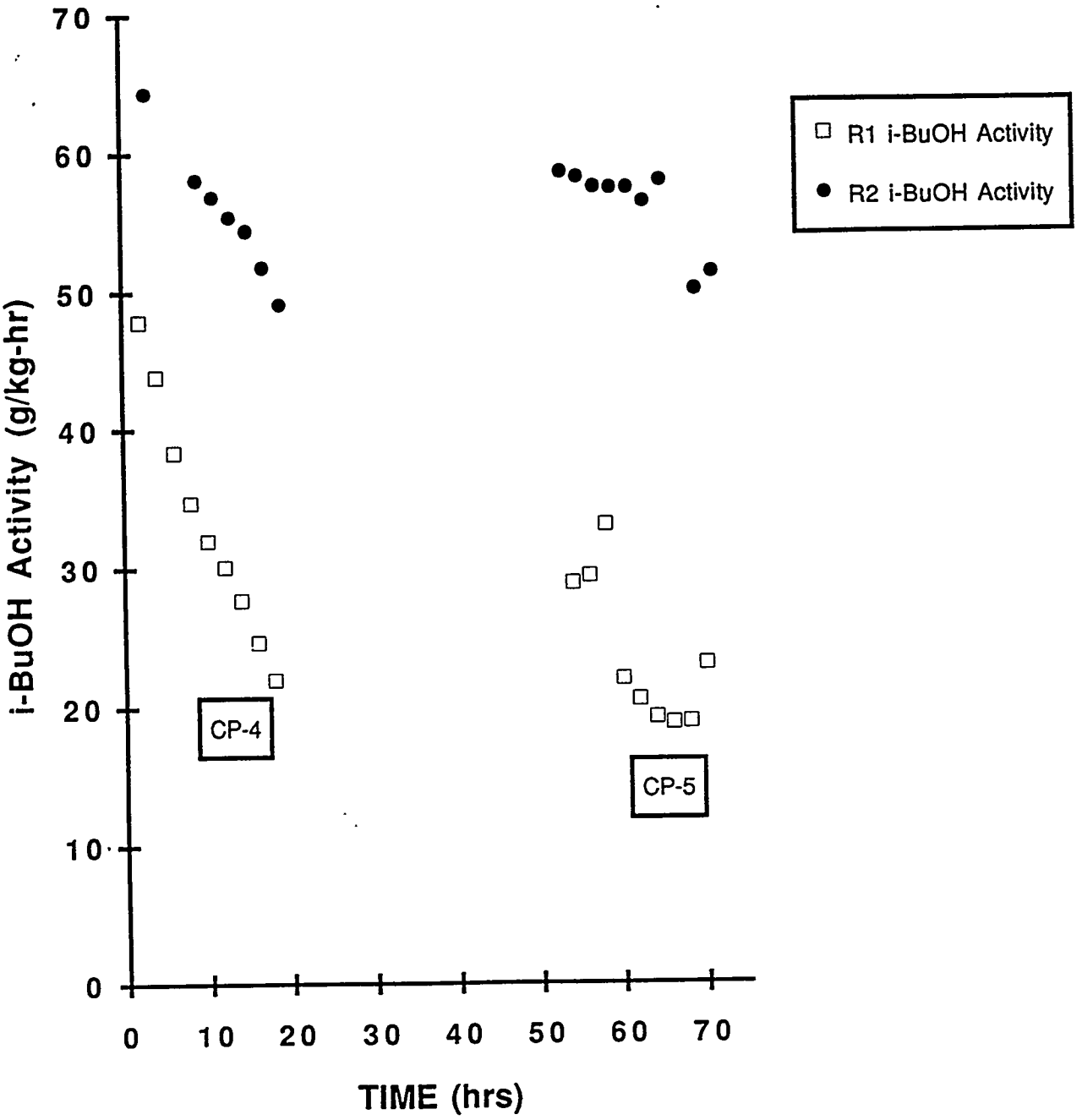


Figure 4.8-5 Alcohol distribution for second charge of catalyst.