4.3 Isobutanol Catalyst Formulation and Preparation - Design #2

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

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

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

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

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

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

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

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

Table 4.3-1 Catalyst Support Compositions

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

Table 4.3-2. Catalyst Composition and Metal Loadings

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

Basis for Design #2

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

Center-Point Catalysts

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

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

Scope of the Design

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

Design Models

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

Alcohol Product Distribution

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

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

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

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

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

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

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

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

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

[1] ACTIVITY= lbs/ft3-hr

[2] SELECTIVITY= wt%

[3] product is almost exclusively n-propanol

[4] product is almost exclusively iso-butanol

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

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

$R^2 = 0.542$

Total Alcohols = No Model Found

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

$$-\underset{(2.3)}{0.0354}*(\text{Calcination Temperature})$$

$R^2 = 0.561$

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

$R^2 = 0.174$

C3 Alcohol = No Model Found

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

$$- \underset{(2.3)}{0.029}*(\text{Calcination Temperature})$$

$R^2 = 0.726$

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

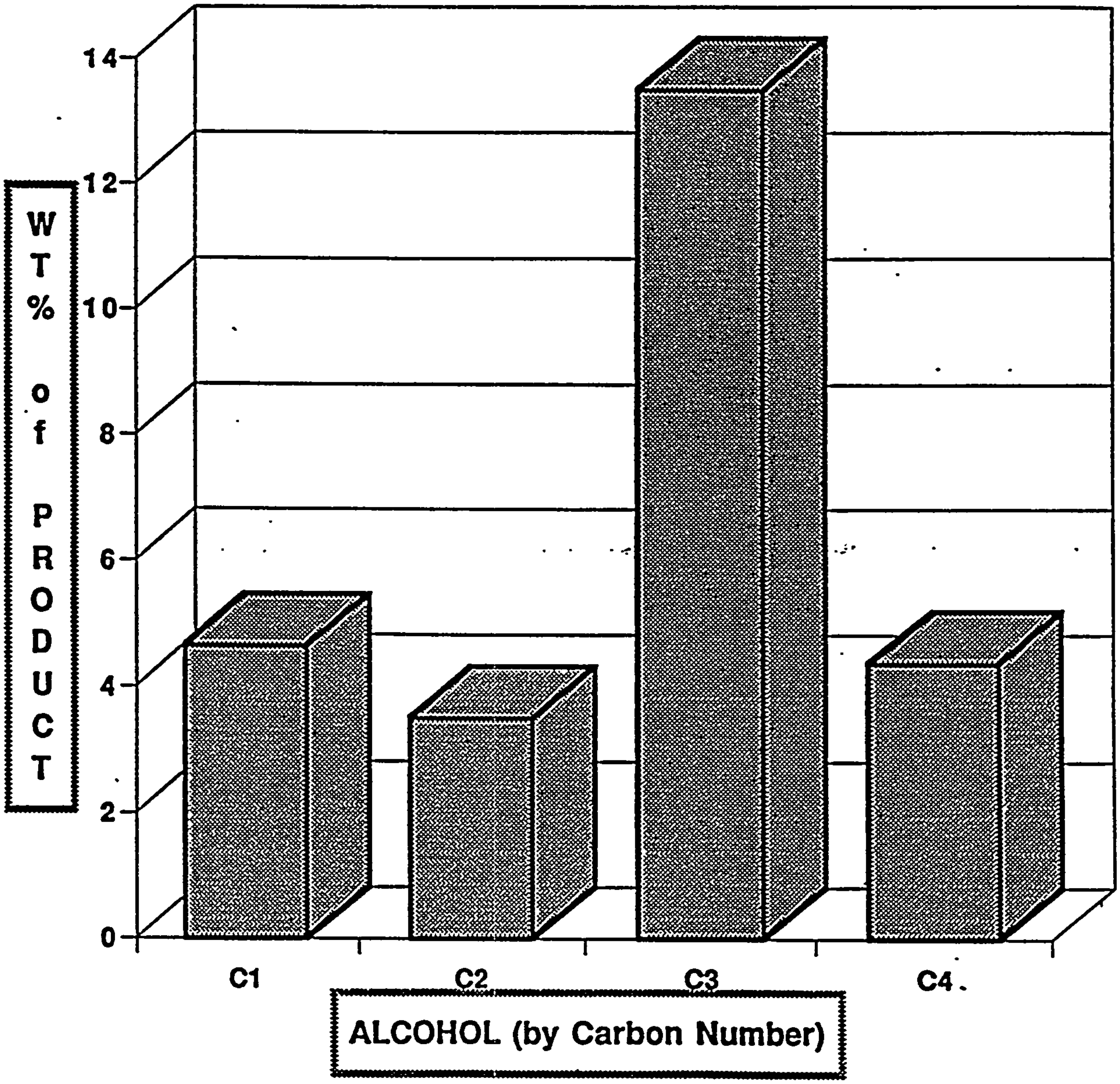


Figure 4.3-2. Product Distribution for 10DAN47 (Zn, Cr, Mn Spinel with Excess Zn plus Potassium)

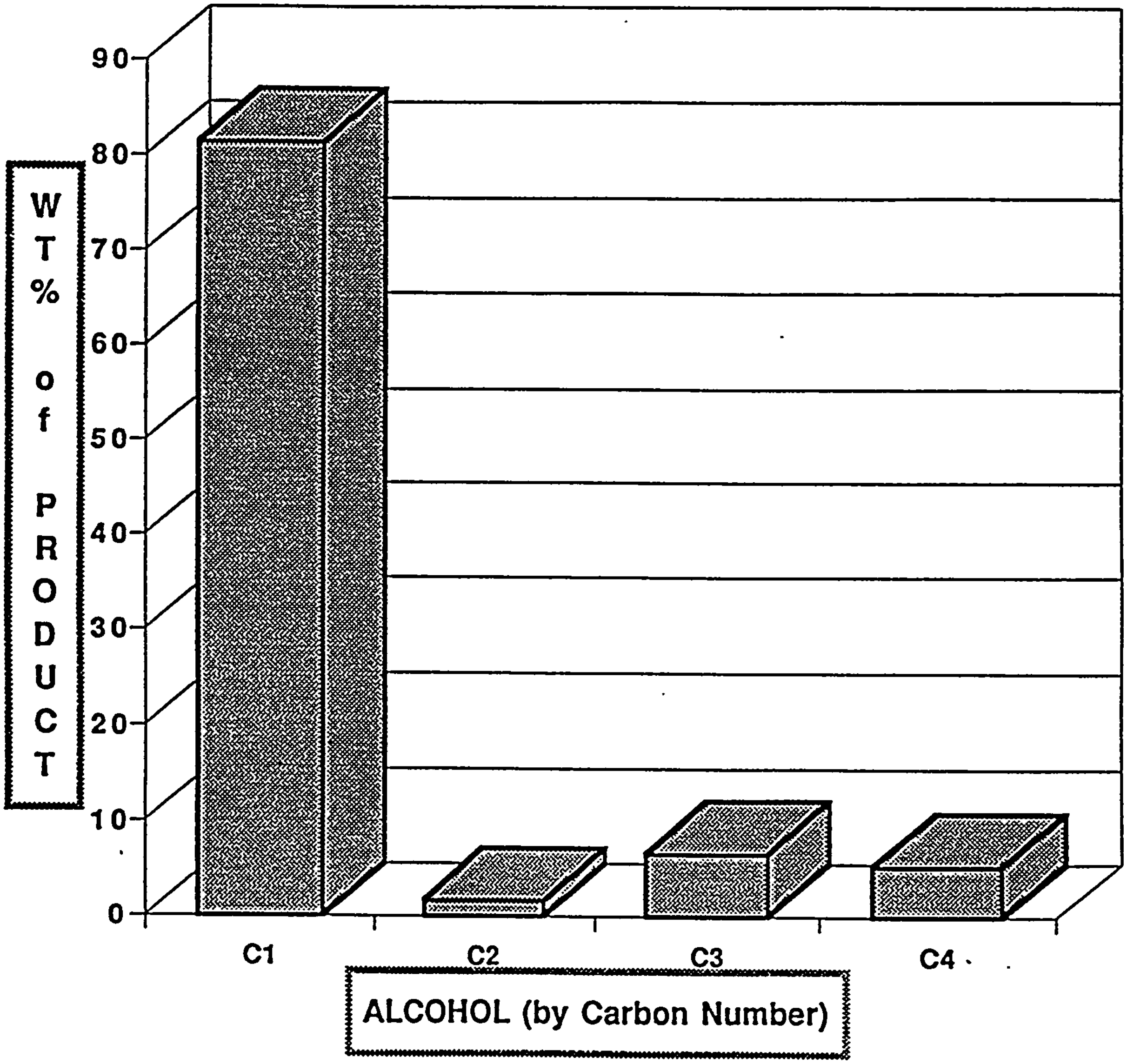


Figure 4.3-3. Product Distribution for 10DAN52 (Zn, Cr, Mn Spinel with Excess Zn plus Cerium)

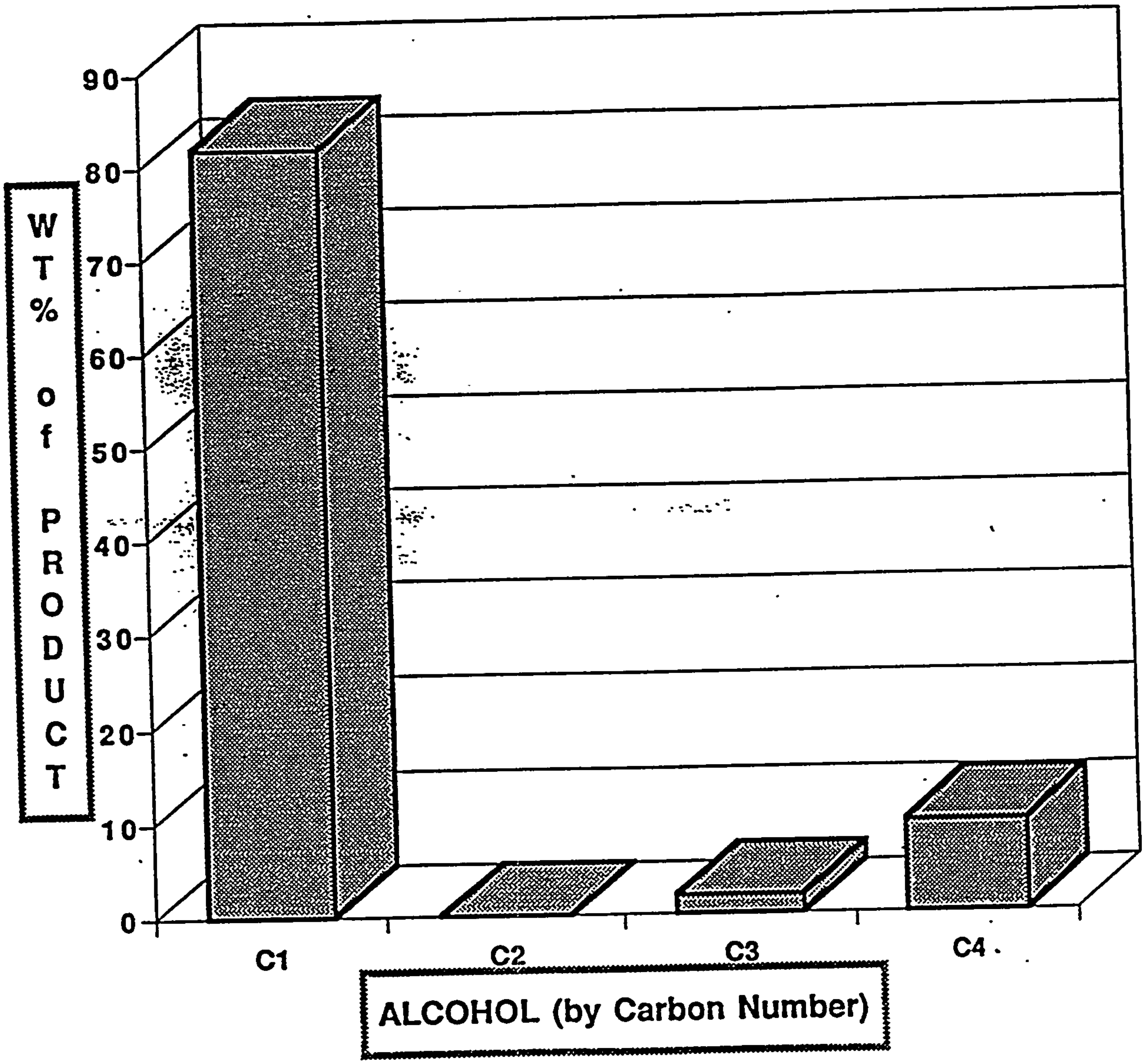
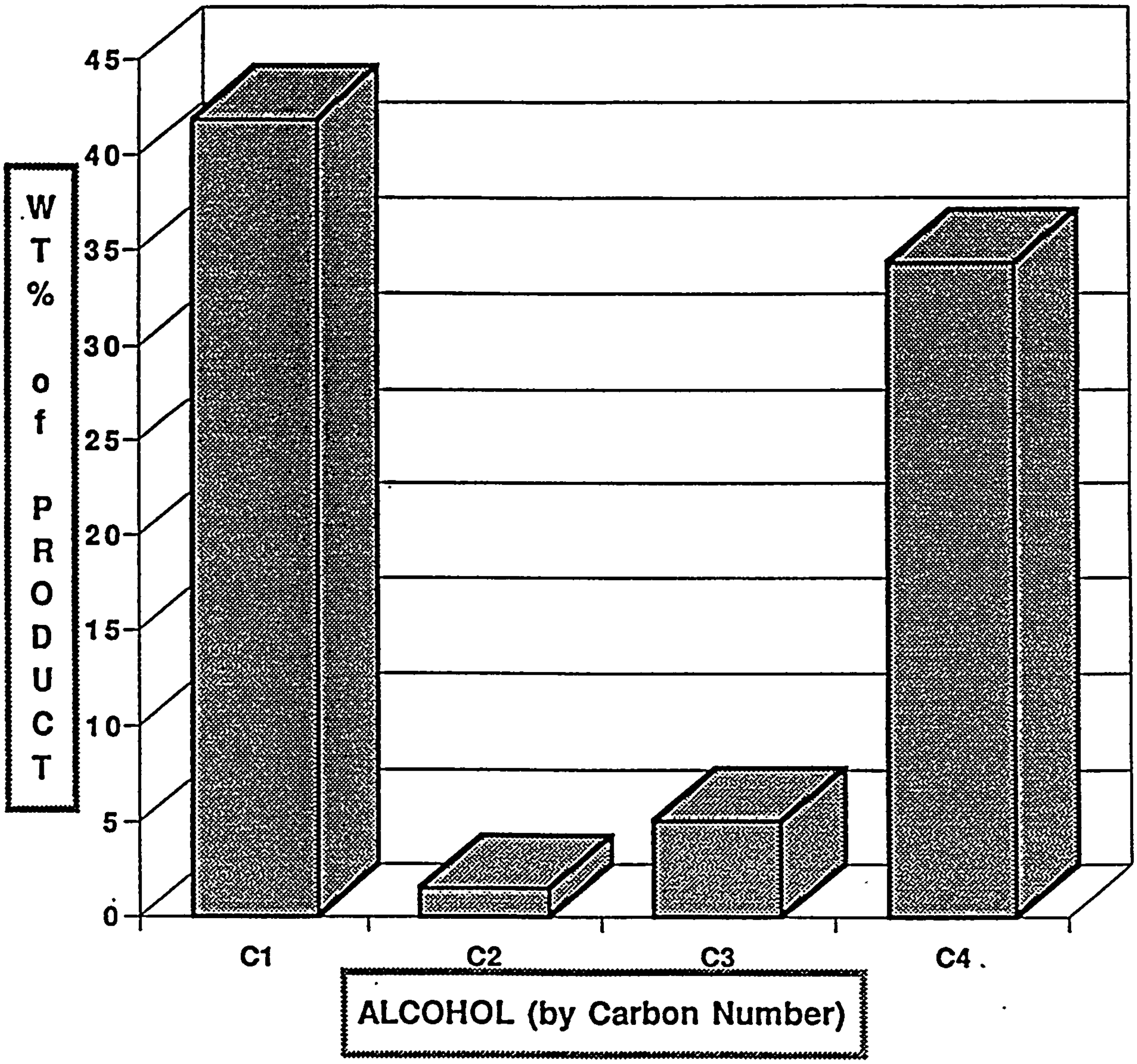


Figure 4.3-4. Product Distribution for 10DAN54 (Zn, Cr, Mn Spinel with Excess Zn plus Palladium)



4.4 "Potassium-Free" Isobutanol Catalysts

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

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

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

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

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

*By weight

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

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

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

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

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

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

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

11DAN69
1 - Zn3MnCr.5-NH4OH

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

11DAN73
2 - Zn3Mn1.5Cr-NH4OH

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

11DAN65
3 - ZnMn1.5Cr - NH4OH

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

11DAN59
4 - Zn3MnCr-NH4OH

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

11DAN62
5 - ZnMnCr.5 - NH4OH

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

10DAN126
6 - Zn2MnCr-(NH4)2CO3

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

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

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

10DAN119
8 - ZnMnCr-(NH4)2CO3

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

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

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

11DAN92
10 - ZnMnCr.5-KOH/K2CO3

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

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

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

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

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

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

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

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

4.5 Precipitation Agent and pH Effects

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

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

Sample Variables and TPR Data

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

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

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

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

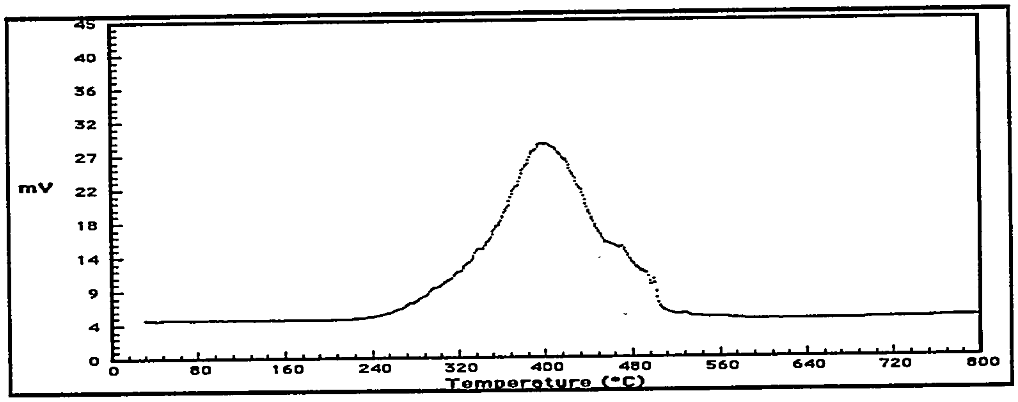


Figure 4.5-2. TPR of 3DAN69, pH 9.5

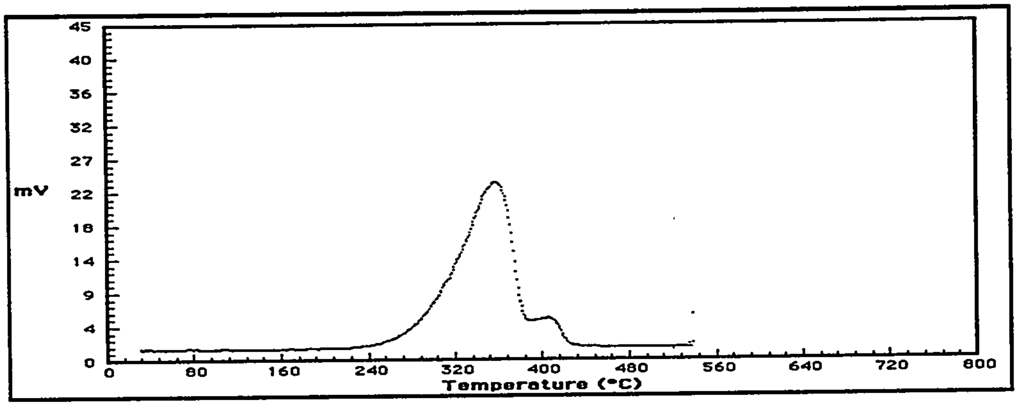
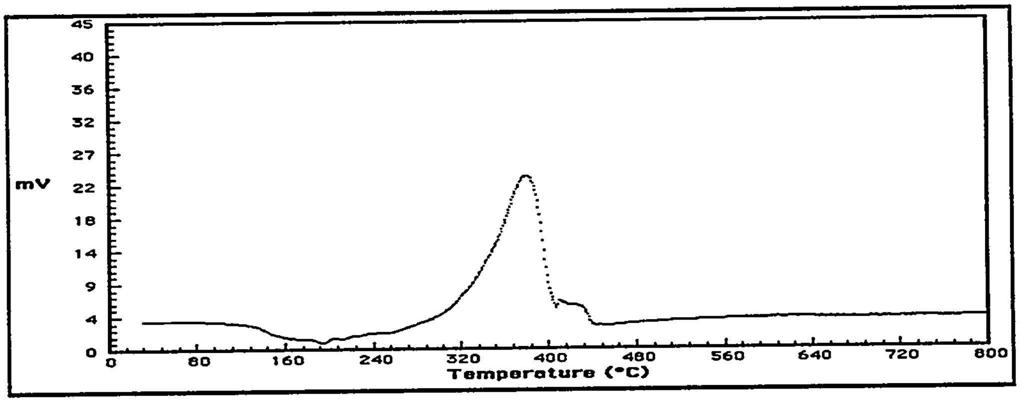


Figure 4.5-3. TPR of 3DAN75, pH 11.0



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

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

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

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

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

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

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

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

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

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

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

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

BULK COMPOSITION - ICP - OES RESULTS

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

SURFACE COMPOSITION - ESCA RESULTS

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

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

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