Interestingly, the n-propanol rate also increased modestly, perhaps suggesting some pathway exists for conversion of isopropanol to n-propanol. The methanol rate fell with isopropanol addition and no ethanol was seen, suggesting that there is no back reaction to lighter alcohols from isopropanol.

4.9.5 Effect of Carbon Dioxide Feed

The effect of carbon dioxide addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) was examined (16-DMM-64). Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas ratio = 1:1. The results are summarized below:

		Carbon Dioxide Feed (%)		
	No CO2	3%	6%	No CO2
Ref	PR 064	PR 093	PR 160	PR 233
Time on Stream, hrs	64	93	160	233
Sel. Total Alcohols (%)	83	89	89	84
Total Alcohol Rate (g/kg-hr)	192	137	107	165
Methanol Rate (g/kg-hr)	108	102	90	103
Ethanol Rate (g/kg-hr)	1	2	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	18	12	6	12
Isobutanol Rate (g/kg-hr)	64	21	11	51
MeOH/i-BuOH mole ratio	7	19	33	8
Hydrocarbon rate (g/kg-hr)	23	9	6	18

Addition of carbon dioxide to the syngas feed adversely affected the performance of a spinel oxide catalyst 10-DAN-55 (Pd on $ZnCr_2O_4$); the total alcohol rate fell by 44% and the isobutanol rate by 83% on addition of 6% carbon dioxide. In concert, the methanol rate decreased by a modest 17%, such that the methanol/i-butanol ratio rose from 7 to 33.

It should be remembered that the water gas shift (WGS) equilibrium must be taken into account when viewing these results, as these materials are excellent WGS catalysts. The equilibrium

$$CO + H_2O = CO_2 + H_2$$

lies to the right under the reaction conditions employed here (Keq = 8), so the effect of carbon dioxide on catalyst performance cannot be disentangled from that of water: the introduction of carbon dioxide to the system will automatically result in an increase in the water content of the gas mixture.

The inhibition of higher alcohol synthesis by carbon dioxide has been observed in other HAS catalyst systems. This observation is explained by assuming that water rather than carbon dioxide inhibits HAS by competing for adsorption with the intermediate C_1 species on the catalyst surface, preventing the homologation reactions from proceeding.

Methanol formation is thus not as sensitive to the water/carbon dioxide equilibrium and, in addition, the mechanism proposed for methanol synthesis involves carbon dioxide as an intermediate. The extra water produced via the WGS equilibrium may help to drive the alcohol equilibrium back to the left, viz.:

$$n\,CO + 2n\,H_2 = C_nH_{2n+1}OH + (n-1)\,H_2O$$

An advantage of carbon dioxide addition is that the rate of hydrocarbon formation is suppressed to an even greater extent such that the selectivity to total alcohols shows a modest increase from 83% to 89%. The extra water produced via the WGS equilibrium may also help to drive the hydrocarbon equilibrium back to the left, viz.:

$$n\,CO + (2n+1)\,H_2 = C_nH_{2n+2} + n\,H_2O$$

or perhaps water helps to titrate acid sites on the catalysts responsible for hydrocarbon formation.

The catalyst recovered slowly after stopping the addition of carbon dioxide: normally changes in process parameters and alcohol feeds result in a new steady state within 4-8 hours, but on turning off the carbon dioxide feed, the catalyst was still returning to pre-carbon dioxide feed performance after 48 hrs. This suggests some surface intermediate is being slowly lost, perhaps carbonate.

4.9.6 Effect of Water Feed

The effect of water addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) was examined (16-DMM-65). Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas ratio = 1:1. The results are summarized below:

	None	Water Feed 150 g/kg-hr	Water Feed 334 g/kg-hr	Water Feed 490 g/kg-hr
Ref	PR 233	PR 303	PR 328	PR 332
Time on Stream, hrs	233	303	328	332
Sel. Total Alcohols (%)	84	78	86	89
Total Alcohol Rate (g/kg-hr)	165	166	107	92
Methanol Rate (g/kg-hr)	103	125	92	85
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	12	6	3	0
Isobutanol Rate (g/kg-hr)	51	35	12	7
MeOH/i-BuOH mole ratio	8	14	32	48
Hydrocarbon rate (g/kg-hr)	18	24	9	6

Addition of water to the syngas feed adversely affected the performance of the catalyst; the total alcohol rate fell by 44% and the isobutanol rate by 86% on addition of up to 490 g/kg-hr of water. In concert, the methanol rate decreased by only 17%, resulting in an increase in the methanol/i-butanol ratio from 8 to 48.

These results are essentially identical to those obtained through carbon dioxide addition. It should be remembered that the water gas shift (WGS) equilibrium must be taken into account when viewing these results, as these materials are excellent WGS catalysts. The introduction of water to the system will automatically result in an increase in the carbon dioxide content of the gas mixture.

ESCA analysis of the spent catalyst, after water addition, indicated the formation of a carbonate layer on the catalyst surface, supporting this hypothesis.

The WGS activity is potentially beneficial, as it is less expensive to remove carbon dioxide from the recycle stream by extraction than water via distillation.

4.9.7 Aging of Catalyst During Feeding Experiments

A single sample of catalyst 10-DAN-55 was used for the above experiments, and it showed some effects of aging with time on stream (see below). We believe that this is due to loss of palladium surface area with time (total time elapsed = 279 hrs, or about 12 days continuously on stream). Palladium is the major component in the formulation that promotes HAS and we believe that sintering of the metal is responsible for the loss in selectivity. SEM photographs and surface analysis confirm this hypothesis.

Ref.	PR 220	PR 398	PR 499
Time on Stream, hrs	72	403	570
Sel. Total Alcohols (%)	84	72	67
Total Alcohol Rate (g/kg-hr)	115	107	97
Methanol Rate (g/kg-hr)	48	54	54
Ethanol Rate (g/kg-hr)	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0
n-Propanol rate (g/kg-hr)	0	5	3
Isobutanol Rate (g/kg-hr)	57	48	38
MeOH/i-BuOH mole ratio	3.3	4.5	5.8
Hydrocarbon rate (g/kg-hr)	14	25	27

4.10 Preparation of an Improved Catalyst (16-DMM-68)

We set out to prepare an improved version of 10-DAN-54, our previous "best" catalyst for higher alcohol synthesis. This new catalyst, 16-DMM-68, has extra added potassium which should increase its selectivity to total alcohols and allow operation at higher conversions. The catalyst is a Zn/Cr/Mn spinel oxide promoted with Pd and K. (The composition is 2.25 wt% K, 5.9 wt% Pd on the ZnCrMn spinel oxide containing excess ZnO.) The procedure involved the preparation the base spinel oxide via controlled pH precipitation, followed by incipient wetness impregnation of the spinel with solutions of potassium and palladium as the nitrates. This material (16-DMM-68) has acceptable elemental analysis for the expected composition and possesses the desired high surface area of >80 m^2/g. Catalyst 16-DMM-68 was characterized and then tested under standard conditions (400°C, 1000 psi, GHSV = 12000, syngas ratio (H_2/CO) = 1) in order to compare its performance with 10-DAN-54.

4.10.1 Comparison with 10-DAN-54

The results of tests with 16-DMM-68 are summarized below and are compared to 10-DAN-54 under identical conditions (400°C, 1000 psi, GHSV = 12000, H_2/CO = 1):

	16-DMM-68	10-DAN-54
Ref. No.	PR-020	PR-620
Sel. Total Alcohols (%)	84	68
Total Alcohol Rate (g/kg-hr)	233	200
Methanol Rate (g/kg-hr)	119	75
Ethanol Rate (g/kg-hr)	0	0
Isopropanol rate (g/kg-hr)	0	0
n-Propanol rate (g/kg-hr)	12	11
Isobutanol Rate (g/kg-hr)	102	94
MeOH/i-BuOH mole ratio	4.7	3.2
Hydrocarbon rate (g/kg-hr)	26	60

16-DMM-68 was slightly more active and significantly more selective for alcohols than 10-DAN-54, probably due to the extra alkali added. 16-DMM-68 also produced more methanol and, as a consequence, the methanol to isobutanol mole ratio rose from 3.2 (in the case of 10-DAN-54) to 4.7 for 16-DMM-68.

4.10.2 Testing at Higher Temperatures and Pressures

We tested 16-DMM-68 at elevated temperatures (>400°C) and pressures (>1000 psi). GHSV was held constant at 12000 and the syngas ratio was also held constant at 1:1. The results are summarized below:

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1180 psi	T = 440°C P = 1500 psi
Ref. No.	PR-020	PR-113	PR-170	PR-125
Sel. Total Alcohols (%)	84	86	54	64
Total Alcohol Rate (g/kg-hr)	233	407	159	304
Methanol Rate (g/kg-hr)	119	248	35	99
Ethanol Rate (g/kg-hr)	0	7	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	12	21	15	27
Isobutanol Rate (g/kg-hr)	102	130	109	179
MeOH/i-BuOH mole ratio	4.7	7.6	1.3	2.2
Hydrocarbon rate (g/kg-hr)	26	37	94	112
Conversion (%)	14	24	23	28

The data showed that the catalyst was most effective for higher alcohol synthesis (HAS) at elevated temperatures and pressures. Note that the *combination* of high temperature and high pressure is required for optimal for HAS. This is because the sum of the individual effects promotes HAS over both hydrocarbon formation (favored at higher temperatures) and methanol formation (favored at higher pressures).

This catalyst (with extra added alkali as compared with 10-DAN-54) can also operate effectively at syngas conversions up to 28%. (See PR-125 in the table above.) 10-DAN-54 was limited to conversions of < 20%; otherwise hydrocarbon formation became a serious inefficiency.

4.10.3 Modifications of the 10-DMM-68 Composition

A series of catalysts was synthesized using our catalyst 10-DMM-68 as the center point. The support used was the standard Zn/Cr/Mn spinel oxide. The K and Pd levels employed are shown below:

	K Level (wt%)	Pd Level (wt%)
High	3.5	9.0
Mid point (16-DMM-68)	2.25	6.0
Low	1.0	3.0

Four new catalysts were prepared using the high/high, high/low, low/high and low/low combinations of K and Pd. Each catalyst was tested at 4 different process conditions, in the order shown below:

1. 400°C, 1000 psi
2. 400°C, 1500 psi
3. 440°C, 1500 psi
4. 440°C, 1000 psi

Stainless steel tubes were used as reactors for convenience, as it was thought that problems caused by reactor tube walls catalyzing syngas conversion were a cause for concern only at low syngas ratios ($H_2/CO < 1$). This proved to be a false assumption as the data subsequently showed.

The results from this "mini-design" are displayed in Tables 4.10-1 – 4.10-5. Data analysis was performed using Data Desk® software using the following protocol:

Input variables:

K level
Pd level
temperature
pressure

Output variables:

Selectivity to total alcohols
Total alcohol rate
Methanol rate
Ethanol rate
Isopropanol rate
n-Propanol rate
Isobutanol rate
Methanol/isobutanol mole ratio
Total hydrocarbons rate
Conversion

A correlation table between input and output variables was developed which showed little interaction between the input and output variables. The strongest correlation was between hydrocarbon rate and temperature. High temperature operation (at 440°C) results in drastic loss in selectivities to total alcohols (down to 18-30%), and this obscures the effect of the catalyst formulation variables. We had previously observed problems with the tube walls catalyzing syngas conversion at 400°C using a syngas ratio (H_2/CO) = 0.5, but it appears that at higher temperatures (e.g., 440°C), the tube walls can also catalyze syngas conversion with a more hydrogen-rich syngas mix. Comparison with tests in a copper-lined tube with 1:1 syngas confirm this hypothesis (see Table 4.10-6)

The design did suggest that higher Pd loadings would be beneficial for isobutanol synthesis. However, in copper-lined reactors, a test of a high Pd catalyst (9 wt%) did not give superior isobutanol activity as compared with the standard 6 wt% formulation. (See Tables 4.10-6 and 4.10-7).

The 6 wt% Pd formulation and a 9 wt% Pd formulation were tested with 1:2 syngas in copper-lined tubes; see Tables 4.10-8 and 4.10-9). The 6 wt% Pd catalyst, at 440°C and 1500 psi, produced 71 g/kg-hr of isobutanol with a methanol/isobutanol product mole ratio < 1. Under the same conditions, the 9 wt% Pd catalyst was again inferior, producing 52 g/kg-hr of isobutanol with a methanol/isobutanol product mole ratio = 1.7. Of particular interest here is that the 6 wt% Pd catalyst produced more higher alcohols than methanol on a molar basis at good rates using a syngas mix that could be derived from a Shell gasifier.

Table 4.10-1. Catalyst Tests with K/Pd Center Point Catalyst.

2.25 wt% K / 6.0 wt% Pd

Tested in a stainless steel tube

16DMM107

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR268	PR276	PR292	PR300
Sel. Total Alcohols (%)	74	77	45	46
Total Alcohol Rate (g/kg-hr)	192	319	290	192
Methanol Rate (g/kg-hr)	59	147	49	23
Ethanol Rate (g/kg-hr)	3	4	0	10
Isopropanol rate (g/kg-hr)	9	7	29	20
n-Propanol rate (g/kg-hr)	35	48	77	57
Isobutanol Rate (g/kg-hr)	83	109	135	83
MeOH/i-BuOH mole ratio	2.8	5.4	1.4	1.0
Hydrocarbon rate (g/kg-hr)	44	57	250	162
Conversion (%)	20	23	28	22

Table 4.10-2. Catalyst Tests with Low K / Low Pd.

1.0 wt% K / 3.0 wt% Pd

Tested in a stainless steel tube

16DMM102

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR217	PR225	PR241	PR249
Sel. Total Alcohols (%)	55	59	29	27
Total Alcohol Rate (g/kg-hr)	129	243	182	91
Methanol Rate (g/kg-hr)	50	119	44	23
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	11	9	13	5
n-Propanol rate (g/kg-hr)	17	30	45	28
Isobutanol Rate (g/kg-hr)	50	86	79	35
MeOH/i-BuOH mole ratio	4.0	5.5	2.2	2.5
Hydrocarbon rate (g/kg-hr)	66	99	306	170
Conversion (%)	15	18	25	16

Table 4.10-3. Catalyst Tests at High K / Low Pd.

3.5 wt% K / 3.0 wt% Pd

Tested in a stainless steel tube

16DMM102

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR116	PR124	PR146	PR166
Sel. Total Alcohols (%)	78	69	30	27
Total Alcohol Rate (g/kg-hr)	163	352	277	166
Methanol Rate (g/kg-hr)	66	167	40	18
Ethanol Rate (g/kg-hr)	4	14	21	12
Isopropanol rate (g/kg-hr)	5	19	41	28
n-Propanol rate (g/kg-hr)	19	45	50	32
Isobutanol Rate (g/kg-hr)	66	95	119	76
MeOH/i-BuOH mole ratio	4.0	7.0	1.4	1.0
Hydrocarbon rate (g/kg-hr)	29	92	460	330
Conversion (%)	17	24	34	26

Table 4.10-4. Catalyst Tests at Low K / High Pd.

1.0 wt% K / 9.0 wt% Pd

Tested in a stainless steel tube

16DMM105

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR218	PR246	PR242	PR250
Sel. Total Alcohols (%)	60	60	31	31
Total Alcohol Rate (g/kg-hr)	191	347	339	191
Methanol Rate (g/kg-hr)	70	152	58	32
Ethanol Rate (g/kg-hr)	2	5	1	0
Isopropanol rate (g/kg-hr)	8	18	53	31
n-Propanol rate (g/kg-hr)	28	43	96	61
Isobutanol Rate (g/kg-hr)	83	129	130	66
MeOH/i-BuOH mole ratio	3.4	4.7	1.8	2.0
Hydrocarbon Rate (g/kg-hr)	82	142	529	306
Conversion (%)	21	26	37	27

Table 4.10-5. Catalyst Tests at High K / High Pd.

3.5 wt% K / 9.0 wt% Pd

Tested in a stainless steel tube

16DMM101

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR115	PR125	PR145	PR165
Sel. Total Alcohols (%)	82	78	23	18
Total Alcohol Rate (g/kg-hr)	115	264	197	101
Methanol Rate (g/kg-hr)	54	126	28	16
Ethanol Rate (g/kg-hr)	0	7	6	8
Isopropanol rate (g/kg-hr)	2	18	29	6
n-Propanol rate (g/kg-hr)	15	37	47	23
Isobutanol Rate (g/kg-hr)	43	67	84	48
MeOH/i-BuOH mole ratio	5.2	7.5	1.3	1.3
Hydrocarbon rate (g/kg-hr)	15	46	487	331
Conversion (%)	11	18	31	24

Table 4.10-6. Catalyst Tests with K / Pd Center Point Catalyst.

2.25 wt% K / 6.0 wt% Pd

Tested in a copper lined tube

16DMM78

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	PR020	PR113	PR125	PR170
Sel. Total Alcohols (%)	84	86	64	54
Total Alcohol Rate (g/kg-hr)	233	407	304	159
Methanol Rate (g/kg-hr)	119	248	99	35
Ethanol Rate (g/kg-hr)	0	7	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	12	21	27	15
Isobutanol Rate (g/kg-hr)	102	130	179	109
MeOH/i-BuOH mole ratio	4.7	7.6	2.2	1.3
Hydrocarbon rate (g/kg-hr)	26	37	94	112
Conversion (%)	14	24	28	28

Table 4.10-7. Catalyst Tests at Low K / High Pd.

1.0 wt% K / 9.0 wt% Pd

16DMM108

Tested in a copper lined tube

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	PR321	-	PR329	-
Sel. Total Alcohols (%)	69	-	52	-
Total Alcohol Rate (g/kg-hr)	164	-	237	-
Methanol Rate (g/kg-hr)	63	-	65	-
Ethanol Rate (g/kg-hr)	0	-	15	-
Isopropanol rate (g/kg-hr)	0	-	7	-
n-Propanol rate (g/kg-hr)	10	-	28	-
Isobutanol Rate (g/kg-hr)	91	-	122	-
MeOH/i-BuOH mole ratio	2.8	-	2.1	-
Hydrocarbon Rate (g/kg-hr)	48	-	145	-
Conversion (%)	15	-	22	-

Table 4.10-8. Catalyst Tests with K / Pd Center Point Catalyst.

2.25 wt% K / 6.0 wt% Pd

Tested in a copper lined tube with 1:2 syngas

16DMM110

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	-	-	PR344	-
Sel. Total Alcohols (%)	-	-	63	-
Total Alcohol Rate (g/kg-hr)	-	-	96	-
Methanol Rate (g/kg-hr)	-	-	14	-
Ethanol Rate (g/kg-hr)	-	-	0	-
Isopropanol rate (g/kg-hr)	-	-	3	-
n-Propanol rate (g/kg-hr)	-	-	8	-
Isobutanol Rate (g/kg-hr)	-	-	71	-
MeOH/i-BuOH mole ratio	-	-	0.8	-
Hydrocarbon rate (g/kg-hr)	-	-	41	-
Conversion (%)	-	-	26	-

Table 4.10-9. Catalyst Tests at Low K / High Pd.

1.0 wt% K / 9.0 wt% Pd

Tested in a copper lined tube with 1:2 syngas

16DMM108

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1500psi	T = 440°C P = 1000 psi
Ref	-	-	PR345	-
Sel. Total Alcohols (%)	-	-	47	-
Total Alcohol Rate (g/kg-hr)	-	-	92	-
Methanol Rate (g/kg-hr)	-	-	22	-
Ethanol Rate (g/kg-hr)	-	-	5	-
Isopropanol rate (g/kg-hr)	-	-	0	-
n-Propanol rate (g/kg-hr)	-	-	13	-
Isobutanol Rate (g/kg-hr)	-	-	52	-
MeOH/i-BuOH mole ratio	-	-	1.7	-
Hydrocarbon Rate (g/kg-hr)	-	-	69	-
Conversion (%)	-	-	20	-