4.11 Studies of Zn-Cr Spinel Supports

The catalyst that we investigated in many of our studies because of its good performance (16-DMM-68) is a formulation that contains 2.25 wt% K, 5.9 wt% Pd on a ZnCrMn spinel oxide that contains excess ZnO prepared via controlled pH precipitation. The significant features of this composition may be summarized as follows:

- the substitution of Mn for Cr
- the presence of excess ZnO
- the controlled pH precipitation of the spinel/ZnO
- the addition of alkali in the form of potassium
- the addition of Pd

In order to more critically study the effects of some of these features on catalyst performance, we prepared a comparative Zn/Cr spinel oxide support that contained excess ZnO and looked at the catalytic performance of:

(1) the bare Zn/Cr support,
(2) a potassium traverse on the bare Zn/Cr support to determine the effect of alkali addition in the absence of Pd,
(3) a potassium traverse on the Zn/Cr support impregnated with 6 wt% Pd, determined to be the optimum level on the Zn/Cr/Mn support,
(4) a cesium traverse on the bare support,
(5) cesium and palladium promoters on the Zn/Cr support,
(6) cesium addition to the Zn/Cr/Mn spinel oxide,
(7) Cs and Pd addition to the Zn/Cr/Mn spinel oxide,
(8) potassium promotion of Zn/Cr and ZnO supports,
(9) presence and absence of excess ZnO in the Zn/Cr spinel, and
(10) similar catalysts based in commercial Zn/Cr support.

Each catalyst was examined at 4 different process conditions:

- 400°C, 1000 psi
- 400°C, 1500 psi
- 440°C, 1500 psi
- 440°C, 1000 psi

4.11.1 Zn/Cr Spinel With Excess Zn (Bare Support)

The bare support was an inefficient methanol catalyst, producing alcohols at a total rate of 164 g/kg-hr, with a specific methanol rate of 160 g/kg-hr at 1000 psi, 400°C, 12000 GHSV and a syngas ratio (H_2/CO) = 1; see Table 4.11-1. The isobutanol rate was barely detectable at 2 g/kg-hr. Selectivity to total alcohols was only 50%.

Increasing pressure resulted in an increase in overall selectivity to total alcohols (from 50% to 61%) and in total alcohol productivity (the rate almost doubled from 164 g/kg-hr to 292 g/kg-hr), mainly through an increase in the methanol rate. Increasing temperature and pressure resulted in a minor increase in the isobutanol rate to 7 g/kg-hr, but total alcohol selectivity fell to only 29%.

4.11.2 Addition of K to the Zn/Cr Spinel with Excess Zn

Alkali addition (in the form of potassium at 1, 3, 5 and 7 wt%) resulted in an increase in selectivity to total alcohols vs. the bare support and a dramatic increase in higher alcohol synthesis. The data appear in Tables 4.11-2 – 4.11-5. For the 7 wt% K formulation, isobutanol could be made at rates > 100 g/kg-hr at 440°C and 1500 psi with selectivity to total alcohols of 85% and with a methanol/isobutanol mole ratio of 2.0. Under the same conditions, the bare support exhibited an isobutanol rate of 7 g/kg-hr, with selectivity to total alcohols of 29% and with a methanol/isobutanol mole ratio of 86 !

The lowest methanol/isobutanol mole ratio was obtained with the 5 wt% K formulation (1.6 at 440°C, 1500 psi and 0.94 at 440°C, 1000 psi).

The catalysts are compared at 440°C and 1500 psi in Figures 4.11-1 – 4.11-3.

4.11.3 Addition of K to 6 wt% Pd on Zn/Cr Spinel with Excess Zn

Pd additions resulted in further improvements in performance: isobutanol rates of > 130 g/kg-hr were observed at 440°C and 1500 psi for the 3, 5 and 7 wt% K catalysts, suggesting a broad optimum in the K loading. Selectivities increased with K loading. The data appear in Tables 4.11-6 – 4.11-9. The catalysts are compared at 440°C and 1500 psi in Figures 4.11-4 – 4.11-6. The lowest methanol/isobutanol mole ratio was obtained with the 5 wt% K formulation (1.2 at 440°C and 1500 psi).

The 5 wt% K, 5.9 wt% Pd catalyst produced > 100 g/kg-hr of isobutanol at 440°C and only 1000 psi, with 85% selectivities to total alcohols and with a methanol/isobutanol mole ratio of < 2.

The 7 wt% K, 5.9 wt% Pd catalyst at 440°C and 1000 psi produced isobutanol at 85 g/kg-hr, with a selectivity to total alcohols of 80% and a methanol/isobutanol mole ratio of 1.0.

4.11.4 Cesium Addition to a Zn/Cr Spinel With Excess Zn

A set of experiments was designed to determine whether cesium is a more effective promoter than potassium for higher alcohol synthesis and what level of cesium is preferred. We examined the effect of cesium addition to a Zn/Cr spinel oxide support that contained excess ZnO. Five catalysts containing 10, 7.5, 5, 3 and 1 wt% cesium were prepared and tested. The high-cesium catalysts (5, 7.5 and 10 wt%) were very efficient alcohol synthesis catalysts (>94% selective to total alcohols at 400°C, 1000 psi, GHSV = 12000, $H_2/CO = 1$), but were inactive (total alcohol rates < 130 g/kg-hr) — see Tables 4.11-10 – 4.11-12. These results were somewhat surprising, since the total number of atoms of Cs/m^2 of support at these wt% levels is in the same range as the optimum number of atoms for potassium addition (atomic wt K = 39, atomic wt Cs = 133). This implies that atomic size effects, not just acid site neutralization, are important. The highest isobutanol rate observed for these formulations was 87 g/kg-hr at 440°C, 1500 psi, GHSV = 12000, $H_2/CO = 1$ at the lowest cesium loading (5 wt%).

Follow-up tests at lower cesium loadings (1 and 3 wt%) yielded catalysts of very different performance — see Tables 4.11-13 and 4.11-14. The 1 wt% cesium formulation was relatively unselective at 400°C, 1000 psi, GHSV = 12000, $H_2/CO = 1$, with a total alcohol selectivity of only 58%, a clear indication of under-promotion. The isobutanol rate was also low, at only 31 g/kg-hr. The 3 wt% cesium gave a more selective (88% selectivity to total alcohols) and more active (isobutanol rate = 93 g/kg-hr) catalyst under the same conditions.

Operation of the 3 wt% cesium catalyst at higher temperatures and pressures gave impressive results: isobutanol rates > 170 g/kg-hr were observed at 440°C and 1500 psi with selectivity to total alcohols of 77% and with a methanol/isobutanol mole ratio of 1.4: this performance is as good as that of our best Pd/K catalyst.

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

We examined the effect of adding palladium in addition to cesium to a Zn/Cr spinel oxide support that contained excess Zn. Three catalysts containing 1, 3 and 5 wt% cesium and 5.9 wt% Pd were prepared and tested — see Tables 4.11-15 – 4.11-17.

The low-cesium catalyst (1% Cs, 5.9% Pd) was clearly under-promoted, with a 43% selectivity to total alcohols, a total alcohol rate = 120 g/kg-hr, an isobutanol rate of < 100 g/kg-hr and a methanol/isobutanol mole ratio = 2.8 at 440°C, 1500 psi, GHSV = 12000, $H_2/CO = 1$.

The 3 wt% Cs, 5.9 wt% Pd catalyst showed improved performance, with a 67% selectivity to total alcohols, a total alcohol rate of 238 g/kg-hr, an isobutanol rate of 161 g/kg-hr and a methanol/isobutanol mole ratio = 1.2 under the same conditions.

The high-Cs catalyst, 5 wt% Cs, 5.9 wt% Pd, showed similar performance to the 3 wt% Cs, 5.9 wt% Pd catalyst with a 81% selectivity to total alcohols, a total alcohol rate = 233 g/kg-hr, an isobutanol rate of 150 g/kg-hr and a methanol/isobutanol mole ratio = 1.2 under the same conditions.

Interestingly, the overall performance at 440°C and only 1000 psi was even better. Recall that the addition of Pd allows operation at lower pressures. Here the high Cs formulation appears to give the best overall performance: isobutanol rate > 150 g/kg-hr with a selectivity to total alcohols of 88% and a methanol/isobutanol mole ratio of 0.58: this represents our best overall performance to date.

4.11.6 Cs Addition to Zn/Cr/Mn Spinel with Excess Zn

This spinel was the support used in the synthesis of 10-DAN-54, our benchmark catalyst. Three catalysts were prepared and tested, containing 1, 3 and 5 wt% cesium on the support.

These catalysts showed a lower overall total alcohol rate than those using the spinel without Mn present — see Tables 4.11-18 – 4.11-20. The optimal Cs loading is also lower — 1 wt% rather than the 3-5 wt% required for the Zn/Cr spinel formulations. This is consistent with Mn substitution for Cr lowering the overall acidity of the spinel. The difference cannot be attributed to the two supports being of different surface areas (thus requiring a different Cs loading) as the surface areas are very close (for the Zn/Cr = 94 m^2/g, for the Zn/Cr/Mn = 85 m^2/g).

4.11.7 Cs and Pd Addition to a Zn/Cr/Mn Spinel with Excess Zn

Three catalysts containing 1, 3 and 5 wt% cesium and 5.9 wt% Pd were prepared and tested — see Tables 4.11-21 – 4.11-23. Once again catalyst activities are lower than for the corresponding formulations on the Zn/Cr spinel. The 5 wt% Cs/5.9 wt% Pd formulation was tested at temperatures above 440°C and the results are shown in Table 4.11-24.

Operation at temperatures above 440°C results in a further increase in the isobutanol rate, a further decrease in the methanol rate, but a marked increase in the hydrocarbon rate suggesting that these formulations may be slightly under promoted in alkali. Promoter optimization may be necessary for successful operation in this higher temperature regime.

4.11.8 Potassium Promotion of Zn/Cr/O and ZnO

We have prepared comparative catalysts based on Zn/Cr spinel oxide support that does not contains excess ZnO and on ZnO by itself, both prepared by controlled pH precipitation. We examined the effect of potassium promotion on (a) a Zn/Cr/O spinel and (b) on ZnO; these two individual components are used together to make our current best support, which is Zn/Cr/O with excess ZnO (1:2 ratio). A potassium traverse (1, 3, 5 wt% K) was conducted on each material and the results are displayed in Tables 4.11-25 – 4.11-32. Comparisons with results previously reported for the spinel with excess ZnO are shown below:

Comparison of (a) Zn/Cr/O, (b) ZnO and (c) Zn/Cr/O with excess ZnO
all promoted with Potassium[1]
440°C, 1500 psi, GHSV = 12000, H_2/CO = 1:1

	Zn/Cr 3 wt% K PR039	ZnO 1 wt% K PR141	Zn/Cr/O w. ex.ZnO 5 wt% K[2] PR195
Sel. Total Alcohols (%)	64	70	71
Total Alcohol Rate (g/kg-hr)	131	85	178
Methanol Rate (g/kg-hr)	39	42	47
Isobutanol Rate (g/kg-hr)	90	38	117
MeOH/i-BuOH mole ratio	1.8	4.5	1.6
Hydrocarbon rate (g/kg-hr)	47	23	14

1 These results are for those potassium levels that showed the highest isobutanol rates.
2 Results previously reported.

All the materials were prepared in the same way, by precipitation at constant pH = 10 from the corresponding nitrate salts by controlled addition of a potassium hydroxide / potassium carbonate solution. The surface area of the Zn/Cr/O spinel is around 80 m^2/g, while that of the ZnO is < 20 m^2/g, which explains why less potassium is needed for ZnO. The combination of the spinel and excess ZnO also has a high surface area (~ 80 m^2/g), suggesting that ZnO may be dispersed over the surface of the spinel and that this "high surface area" ZnO may require more potassium for optimal performance.

The combination of the two components is better than each of the individual parts: the Zn/Cr/O with excess ZnO is as selective and is more active for total alcohols (and more importantly, for isobutanol) than any of the individual components.

4.11.9 Presence and Absence of Excess ZnO

Spinel oxide catalysts promoted with cesium and both cesium and palladium have been prepared without the presence of excess ZnO and have been compared to those prepared with excess ZnO. The presence of the excess ZnO is purported to improve catalyst performance by creating defects in the regular spinel lattice; these defect sites are thought to be active alcohol synthesis sites. Our best catalysts contain excess ZnO.

We have looked at the effect of the presence or absence of excess zinc oxide on the performance of Zn/Cr spinel oxide catalysts (a) promoted with cesium and (b) promoted with both cesium and palladium. Three levels of cesium were examined (1, 3 and 5 wt%); see

Tables 4.11-33 – 4.11-35. The largest isobutanol rates are obtained at high temperatures and pressures (440°C and 1500 psi). Test results for representative catalysts on the two different supports are shown below:

Test conditions: 440°C, 1500 psi, GHSV=12000, $H_2/CO=1$

	Zn/Cr w ex.ZnO with 3 wt% Cs[1] PR490	Zn/Cr only with 3 wt% Cs PR290
Sel. Total Alcohols (%)	77	44
Total Alcohol Rate (g/kg-hr)	248	200
Methanol Rate (g/kg-hr)	58	48
Isobutanol Rate (g/kg-hr)	171	121
MeOH/i-BuOH mole ratio	1.4	1.6
Hydrocarbon rate (g/kg-hr)	18	179

[1] Results previously reported.

Three different Cs/Pd catalysts were examined (1, 3 and 5 wt% Cs with 5.9 wt% Pd) - see Tables 4.11-36 – 4.11-38. The addition of Pd allows the catalysts to operate at lower pressures with good isobutanol rates (> 100 g/kg-hr).

Test conditions: 440°C, 1000 psi, GHSV=12000, $H_2/CO=1$. Test results for representative catalysts on the two supports are shown below:

	Zn/Cr w ex.ZnO with 5 wt% Cs and 6 wt% Pd[1] PR598	Zn/Cr only with 5 wt% Cs and 6 wt% Pd PR498
Sel. Total Alcohols (%)	88	71
Total Alcohol Rate (g/kg-hr)	212	187
Methanol Rate (g/kg-hr)	23	16
Isobutanol Rate (g/kg-hr)	154	126
MeOH/i-BuOH mole ratio	0.58	0.5
Hydrocarbon rate (g/kg-hr)	19	57

[1] Results previously reported.