OPTIMUM CATALYTIC PROCESS FOR FUEL ALCOHOLS FROM SYNGAS

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The objective of our research is to discover and evaluate novel catalytic systems for the selective conversion of synthesis gas into a mixture of alcohols useful as a fuel extender or octane enhancer. These systems include both homogeneous and heterogeneous catalysts, and may involve two-stage operation through methanol.

Early contract work included further development of a novel, rhodium-based, low pressure (<1000 psi), methanol homologation process discovered under our previous contract. In addition, homogeneous ruthenium-based catalysts have been studied for synthesis gas conversion to C_1-C_4 alcohols at 3000-5000 psi pressure. Our work has resulted in the development of novel catalyst additives that increase both the activity and selectivity to higher alcohols. Heterogeneous molybdenum sulfide catalysts have been investigated with the objective of discovering new methods of modifying the catalyst to improve performance. Certain additives have been demonstrated to have a beneficial effect, but significant improvements in catalyst performance have not been realized. Our most recent work has been the development of heterogeneous catalysts consisting of one or more transition metals on mixed metal oxide supports with the spinel structure for synthesis gas conversion to normal alcohols. Alcohol yields as great as 13 lbs/ft^3 catalyst/hr have been observed with further improvement expected. Slurry phase reaction studies of both the molybdenum sulfide and transition metal/spinel based catalysts are planned.

NOVEL HOMOLOGATION CATALYST SYSTEM

Objective:	Improve upon known cobalt catalysts for conversion of methanol to acetaldehyde and ethanol.
Question:	Might rhodium be a better homologation catalyst?
Result:	Discovery of diphosphine modified rhodium catalysts that reductively carbonylate methanol at low pressure and temperature with rates that rival the best cobalt catalysts.

Documentation:

Moloy, K. G.; Wegman, R. W. J. Chem. Soc., Chem. Commun. 1988, 820.

Moloy, K. G.; Wegman, R. W. Organometallics, in press.

U.S. Patent 4,727,200 (1988) to Union Carbide.

U. S. Patent Application (preparation of ligands).

NOVEL HOMOLOGATION CATALYST SYSTEM

EXAMPLE

Catalyst Charge:

$Rh(CO)_2(acac)$	1 mmol
$Ph_2P(CH_2)_3PPh_2$	1 mmol
$RuCl_3 \cdot 3H_2O$	4 mmol
CH_3I	40 mmol

Reaction Conditions.

MeOH	40 mL
Pressure	1000 psig $2H_2/CO$
Temperature	140°C
Time	2.5 h

Conversion: 60-70 %

Selectivity: 85 % Total Ethanol
15 % Total Acetic Acid

REACTION SELECTIVITY IS HIGHLY DEPENDENT ON THE DIPHOSPHINE LIGAND

Diphosphine	Selectivity
	80 %
	4 %
	26 %
	4%
	20 %
2 PPh_3	6%

- Significant improvements in rate (>15 mol/L/hr) required.
- Experimental work concluded until further concepts for catalyst improvement developed.

DIRECT SYNGAS CONVERSION BY HOMOGENEOUS CATALYSIS

Objective: Improve upon known ruthenium based homogeneous catalysts discovered by Union Carbide under previous contract for the conversion of synthesis gas to methanol and higher alcohols.

Result: Novel catalyst additives found which improve catalyst activity and selectivity to C_2+ alcohols.

EFFECT OF CATALYST ADDITIVES

Mol/L/hr*		
Total Rate	C_2+ Rate	Additives
1.9	0.8	KI
4.1	1.9	KI, A16, A92
6.7	2.5	LiI, A16, A111

*230°C, 5000 psi, 1:1 H2/CO, NMP or DMI solvent

Documentation:

U. S. Patent Application filed for improved process.

Status: Further improvement in rate required (>15 mol/L/hr).

Experimental work concluded until further concepts for catalyst rate enhancement developed.

DIRECT SYNGAS CONVERSION BY ALKALI PROMOTED MOLYBDENUM SULFIDE

Objective: Explore modifications of the formulation and preparation of alkali promoted MoS2 catalysts in an effort to reduce methane formation while obtaining increased activity (>20 lb/ft^3/hr)

Result: Discovery of novel additive, A116, to increase rate by about 10% without significantly effecting selectivity.

No significant improvements obtained by modifications of the preparation procedure.

No direct correlation between catalyst surface area and activity.

Documentation:

U. S. Patent Application filed for novel additives.

DIRECT SYNGAS CONVERSION BY ALKALI PROMOTED MOLYBDENUM SULFIDE

EFFECT OF ADDITIVE A116

	K-MoS_2	A116-K-MoS_2	Target
Alcohol Yield ($lb/ft^3/hr$)	15-20	18-23	20-25
Wt.% Oxygenates	70-85	70-85	85-100
Wt.% C2+ Oxy.	35-45	35-45	30-50

- Catalyst experimentation work concluded except for:

  1. Identifying the stable form of alkali in the catalyst.

  2. Evaluation of catalyst perfomance in slurry reactor.

- Catalyst leaches sulfur with time on stream resulting in catalyst deactivation. Sulfur content of alcohols is 0.02 to 0.05 wt% as thiols and disulfides.

TRANSITION METALS ON SPINEL OXIDES

Previous work

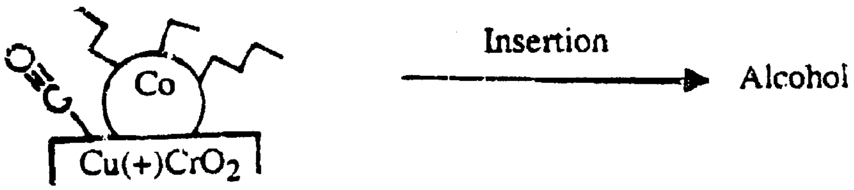
Literature: Insitut Francais du Petrole (IFP)
U.S. Patent 4,122,110 (1978)

Discovery: Co / Cu / Cr or Al / alkali catalysts convert syngas to a Flory distribution of normal alcohols.

Activity = 0.1 to 0.3 g/g cat./hr (6 to 18 lb/ft^3/hr)

Selectivity = 70-99% alcohols (30-75% C_2+)

Postulated mechanism:



TRANSITION METALS ON SPINEL OXIDES

Previous Work
(continued)

Literature: King, T. S. and Sheffer, G. R. Appl. Catal. 1988, 44, 153.
J. Catal. 1989, 116, 95

Performance: Activity = 0.12 g/g cat./hr (8 lb/ft^3/hr)

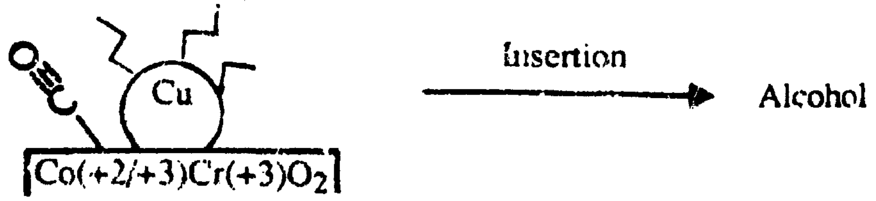
Selectivity = 70% alcohols (50% C_2+)

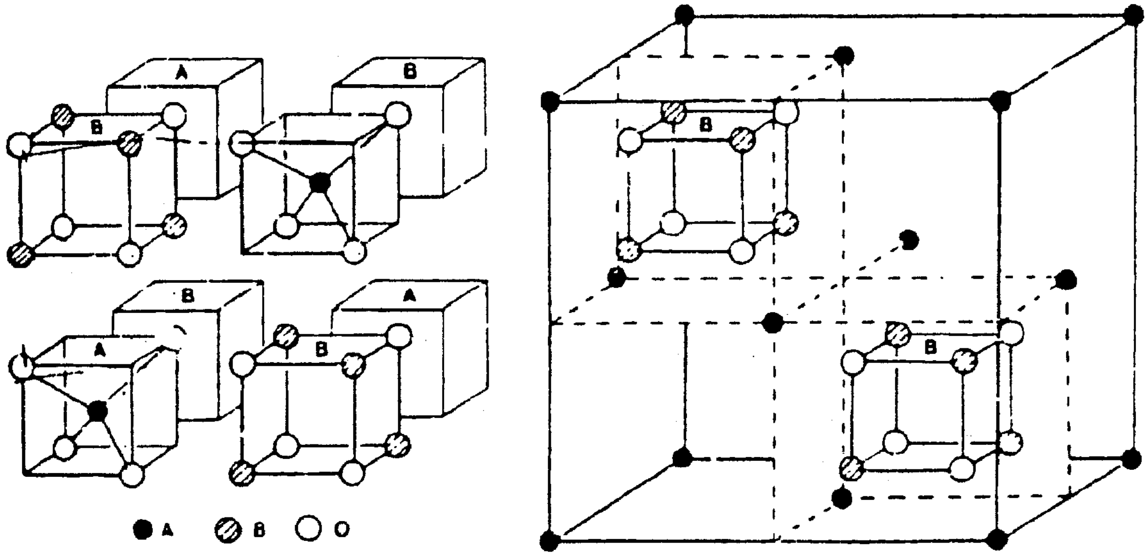
Discovery: Characterization indicated that the catalyst consisted of copper metal supported on a cobalt-chromium spinel.

Activity was sensitive to calcination temperature and correlated with copper metal particle size, especially the circumference.

Lithium promoted unsupported copper catalysts yielded a Flory distribution of alcohols and hydrocarbons.

Postulated mechanism:





'The spinel structure, AB_2O_4. The structure can be thought of as eight octants of alternating AO_4 tetrahedra and B_4O_4 cubes as shown in the left-hand diagram; the O have the same orientation in all eight octants and so build up into a face-centred cubic lattice of 32 ions which coordinate A tetrahedrally and B octahedrally. The four A octants contain four A ions and the four B octants sixteen B ions. The unit cell is completed by an encompassing face-centred cube of A ions (●) as shown in the right-hand diagram, this is shared with adjacent unit cells and comprises the remaining four A ions in the complete unit cell $A_8B_{16}O_{32}$. The location of two of the B_4O_4 cubes is shown for orientation'. (From N. N. Greenwood, *Ionic Crystals, Lattice Defects, and Non-Stoichiometry*, Butterworths, London, 1968)

TRANSITION METALS ON SPINEL OXIDES

Current Work

Objective: To optimize the transition metal(s) on spinel oxide class of higher alcohol catalysts with performance goals:

Activity = 20-25 lb/ft^3/hr (0.3-0.4 g/g cat/hr)

Selectivity = 90+% alcohols (30-40 wt% C_2+)

Initial Questions:

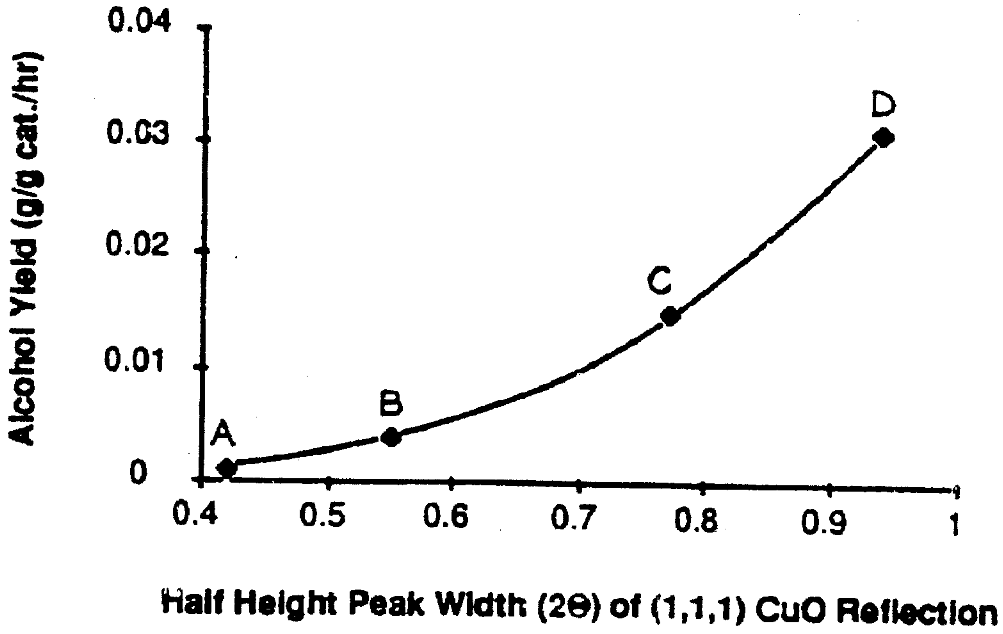
1. What happens when cations in the spinel are changed?
2. Might other transition metals be superior to copper?

Preliminary Research:

1. Decided on coprecipitation of spinels as opposed to citrate complexation methods.
2. Alcohol yield correlated with CuO dispersion.

SPINEL OXIDE SUPPORTED TRANSITION METAL CATALYSTS

Relationship between alcohol yield and copper particle size obtained in preliminary experiments.

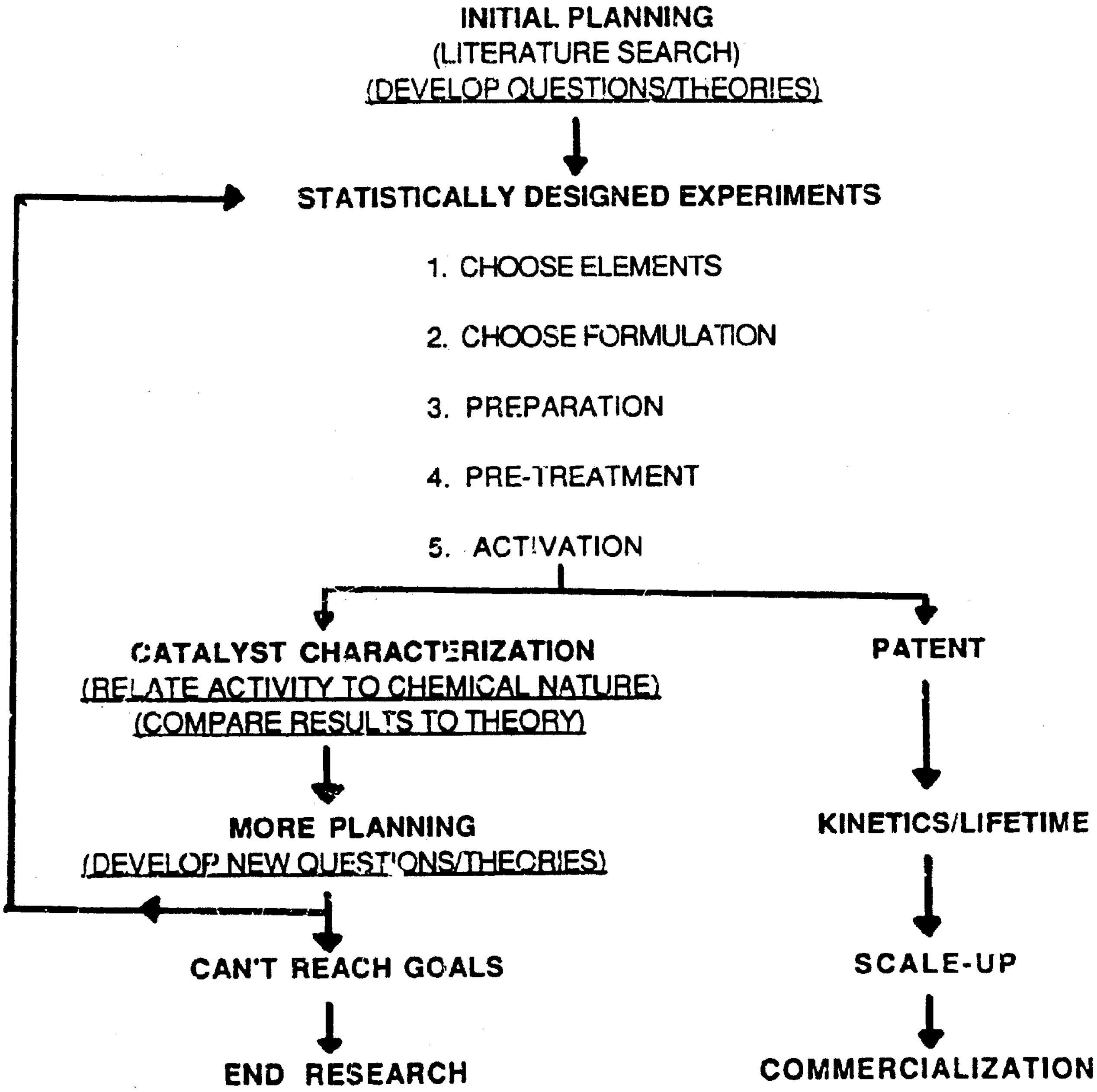


Conditions: 275°C, 750 psig, $H_2/CO = 1$, GHSV = 4000 hr^{-1}

Point identification:

A = Citric acid complexation preparation.
B = Malonic acid complexation preparation.
C = Coprecipitation preparation with alkali impregnation after calcination.
D = Coprecipitation preparation with alkali impregnation before calcination.

CATALYST DEVELOPMENT STRATEGY



SPINEL SUPPORTED TRANSITION METAL CATALYSTS

First Statistical Design Set

5x4 Hyper-Greco-Latin Square

Variable #	Component Type	How Introduced	Level
5	+3 Spinel Cation	Coprecipitated	50 mole%
3	+2 Spinel Cation	Coprecipitated	18 mole%
4	+2/+3 Spinel Cation	Coprecipitated	33 mole%
2	Methanol Syn. Metal	Impregnation	1/8 ML
1	F-T Metal	Impregnation	1/8 ML

Four elements were explored under each component type.

Potassium added to all catalysts by impregnation at a level of 9 mol%.

Reaction Conditions: T = 275°C P = 1000 psig
H_2/CO = 1.0 SV = 65 cc/g cat/min

SPINEL SUPPORTED TRANSITION METAL CATALYSTS

First Statistical Design Set

5x4 Hyper-Greco-Latin Square Responses
Relative to the Grand Average

(each +/- is a set percentage of the grand average for a variable)

Variable	Level	Surface area (m^2/g)	Density (g/ml)	Area/ volume (m^2/ml)	Alcohol selectivity (wt%)	C_2+ alc. selectivity (wt%)
1	none	N/A	N/A	N/A	--	0
1	A128	N/A	N/A	N/A	0	-
1	A129	N/A	N/A	N/A	+++	-
1	A130	N/A	N/A	N/A	-	++
2	A131	N/A	N/A	N/A	++	---
2	A132	N/A	N/A	N/A	0	+++
2	A133	N/A	N/A	N/A	+	+
2	A134	N/A	N/A	N/A	---	0
3	none	---	0	---	0	-
3	A135	+	-	0	0	+
3	A136	0	0	0	++	+
3	A137	++	+	+++	--	-
4	none	--	++	0	--	---
4	A138	0	+	+	+++	-
4	A139	+	---	0	+	++
4	A140	+	-	0	--	++
5	A141	---	---	---	-	+
5	A142	++	---	-	0	0
5	A143	+++	+++	+++	0	+
5	A144	--	+++	-	+	--
Grand Average		46 (+/- = 10%)	0.87 (+/- = 6%)	41 (+/- = 10%)	26 (+/- = 20%)	49 (+/- = 10%)
Maximum Predicted		110	1.49	135	104	104

SPINEL SUPPORTED TRANSITION METAL CATALYSTS

First Statistical Design Set

5x4 Hyper-Greco-Latin Square Responses Relative to the Grand Average

(each +/- is a set percentage of the grand average for a variable)

Variable	Level	Alcohol rate (g/g/hr)	Alcohol rate (g/m^2/hr)	Methanol rate (g/g/hr)	Methanol rate (g/m^2/hr)	C_2+ alc. rate (g/g/hr)	C_2+ alc. rate (g/m^2/hr)
1	none	−	0	−	0	0	−
1	A128	− −	+ +	−	−	−	+ + +
1	A129	−	0	0	0	0	− −
1	A130	+ + +	−	+ + +	+	+	+
2	A131	+ + +	0	+ + +	+ + +	0	− −
2	A132	−	+ + +	−	− −	0	+ + +
2	A133	0	0	0	0	0	−
2	A134	− − −	− − −	− −	− − −	−	− − −
3	none	− −	+ + +	−	+ + +	−	+ + +
3	A135	− −	− −	−	− −	−	− −
3	A136	0	0	−	− −	+ + +	+
3	A137	+ + +	− − −	+ + +	+	0	− −
4	none	− − −	− −	− −	−	− − −	− − −
4	A138	−	+	0	0	−	0
4	A139	0	−	0	− −	+	0
4	A140	+ + +	+ +	+ + +	+ +	+ + +	+ + +
5	A141	−	+	− −	0	0	+
5	A142	0	− −	−	− −	0	− −
5	A143	−	−	−	− −	0	+ +
5	A144	+ + +	0	+ + +	+ + +	0	−
Grand Average		0.006	1.3×10^{-4}	0.003	0.8×10^{-4}	0.003	0.8×10^{-4}
Maximum Predicted		0.031	5.1×10^{-4}	0.026	4.2×10^{-4}	0.009	2.9×10^{-4}

SPINEL SUPPORTED TRANSITION METAL CATALYSTS

First Statistical Design Set Conclusions

1. The inclusion of a F-T type metal is beneficial when compared to the case using none at all.

   A129 and A130 to be further studied.

2. Methanol synthesis metals:

   A132 has effects similar to A128 suggesting interchangeability.

   A131 shows no propensity for higher alcohol formation.

   A132 and A133 to be further studied.

3. +2/+3 cations generally show positive effects primarily wrt selectivity. Consistent with molecular picture derived earlier.

   When compared to case using none, a +2/+3 cation <u>does</u> appear needed.

   A138 and A139 were most effective.

4. Introduction of +2 cations showed only limited positive effects.

5. The +3 cations had the greatest impact on surface areas. Yields were impacted more heavily than selectivities.

   A142 had the least benefit.

   A141 and A144 had some positive attributes wrt selectivity & surface area normalized yields, but there inability to maintain catalyst surface area suggests that perhaps they should be impregnated on a support or mixed with A143.

SPINEL OXIDE SUPPORTED TRANSITION METAL CATALYSTS

Overview of Subsequent Design Sets

SET #	CONCLUSIONS	MAX. ALCOHOL YIELD (LB/FT^3/HR)*
1 (elements)	• +2/+3 element necessary • +2 cations not beneficial • add alkali before calcination	2
2 (elements)	• bimetallics preferred • metals ranking • A146, A147 possible promoters • surface areas low, use A143 as a structural promoter	8
3 (formulation)	• alkali ranking • 2.0 > spinel cation ratio > 0.5 • high C2+ alcohol fraction (>80 wt%), need to reformulate methanol synthesis component back into catalyst.	4
4 (formulation) (& elements)	• A144 / A143 ratio > 3 • alklai combinations not beneficial • methanol / higher alcohol ratio = 1	6
5 (preparation)	• new preparation procedure • A132 better than A133	13

* Conditions: 275°C, 750 psig, $H_2/CO = 1$, GHSV = 4000 hr^{-1}

SPINEL OXIDE SUPPORTED TRANSITION METAL CATALYSTS

CATALYST PERFORMANCE SUMMARY

	Alcohol selectivity (wt%)	C_2+ Alcohol selectivity (wt%)	Yield (lb/ft^3/hr)
Target	90+	30-40	20-25
Literature	70	50	6-8
Best Catalyst (to date)	60	50	15

FUTURE WORK

1. HGL 5x4 design set to further bracket metal, alkali, and other promoter loadings as well as to examine the new preparation procedure.

2. Central composite design set to set final formulation.

3. Slurry reactor evaluation.