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HETEROGENEOUS CATALYTIC PROCESS FOR ALCOHOL FUELS FROM SYNGAS

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1. Executive Summary

The principal objectives of this project are to discover and evaluate novel heterogeneous catalysts for conversion of syngas to oxygenates having use as fuel enhancers, to explore novel reactor and process concepts applicable in this process, and to develop the best total process for converting syngas to liquid fuels.

We have tested a number of K/Pd promoted Zn/Mn/Cr spinel oxide catalysts within an experimantal design to determine the effect of K, Pd, temperature and pressure on catalyst performance. Starting test conditions were 400°C, 1000 psi, GHSV = 12000 and syngas ratio (H_2/CO) = 1:1. 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.

The design suggested 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. The effect of the higher Pd loading on catalyst aging has not yet been determined.

The 6 wt% Pd formulation and a 9 wt% Pd formulation were tested with 1:2 syngas in copper-lined tubes. 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 is 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 produces more higher alcohols than methanol on a molar basis at good rates using a syngas mix that could be derived from a Shell gasifier.

2. Project Objectives

- To discover, study, and evaluate novel heterogeneous catalytic systems for the production of oxygenated fuel enhancers from synthesis gas. In particular, novel heterogeneous catalysts will be studied and optimized for the production of: (a) C_1-C_5 alcohols using conventional methanol synthesis conditions, and (b) methanol and isobutanol mixtures which may be used for the downstream synthesis of MTBE or related oxygenates.

- To explore, analytically and on the bench scale, novel reactor and process concepts for use in converting syngas to liquid fuel products.

- To develop on the bench scale the best combination of chemistry, catalyst, reactor, and total process configuration to achieve the minimum product cost for the conversion of syngas to liquid products.

3. Project Organization

This project has been divided into two tasks.

Task 1 is concerned with catalyst identification, preparation, performance evaluation, and characterization. This work is being largely conducted by catalyst chemists and analytical specialists. Chemical studies to support the engineering effort in Task 2 are included in this task, but fundamental aspects of the catalytic chemistry are emphasized in this effort.

Task 2 includes process conceptualization and economics, and bench-scale process evaluation of systems developed in Task 1. This is largely an engineering activity.

4. Technical Progress

4.1. Task 1 – Catalyst Studies

4.1.1. Introduction

It is well known that the addition of alkali promoters to ZnCrO, MnCrO, and ZnMnCrO systems will modify the selectivity of high temperature methanol catalysts towards C_{2+} alcohols. Interest in higher alcohol synthesis (HAS) from syngas has stemmed from the desire to use the alcohol mixtures as high-octane blending stock for gasoline. Currently refining modifications and the use of oxygenated petrochemicals such as methyl-tert-butyl-ether (MTBE) have become favored alternatives. The production of a mixture of methanol and isobutanol is of interest due to its possible use as a feedstock in the production of other oxygenates such as ethers related to MTBE. One could also envision dehydrating the isobutanol to isobutene, followed by reaction with methanol to form MTBE. We have been investigating a series of promoted Zn/Cr/Mn spinel oxide materials as promising catalysts for this process.

Work this quarter has concentrated on increasing laboratory productivity and expanding the scope of our catalyst formulation studies. We had observed differences in performance between our two syngas reactors for several months. The problem has finally been rectified, and we can now examine formulations at twice the speed.

We have also tested a number of K/Pd promoted Zn/Mn/Cr spinel oxide catalysts in a statistically designed set of experiments to determine the effect of K, Pd, temperature and pressure on catalyst performance.

4.1.2. Reactor to Reactor Variability

We had observed differences in performance between our two catalytic reactors for several months and this experimental problem had reduced us to only being able to use one reactor for testing. The problem has finally been traced to differences in reactor sample loops. The loops have been replaced, standardized and calibrated. The comparison, for a standard methanol catalyst, is shown below:

	Reactor #1	Reactor #2
Ref	16DMM97 PR011	16DMM98 PR012
Sel. Total Alcohols (%)	98.7	98.6
Total Alcohol Rate (g/kg-hr)	1016	1060
Methanol Rate (g/kg-hr)	986	1038
Ethanol Rate (g/kg-hr)	12	16
Isopropanol rate (g/kg-hr)	0	0
n-Propanol rate (g/kg-hr)	4	4
Hydrocarbon rate (g/kg-hr)	7	7

Reactor to reactor variation is now 4-5%, well within an acceptable range for catalyst screening tests. We can now examine formulations at twice the speed.

4.1.3. K/Pd Promoted Catalysts

A series of catalysts was synthesized using our "best to date" 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 1-5. 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 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 6 and 7). The effect of the higher Pd loading on catalyst aging has not yet been determined.

4.1.4. Catalyst Tests in Copper-Lined Tubes

The 6 wt% Pd formulation and a 9 wt% Pd formulation were tested with 1:2 syngas in copper-lined tubes, see tables 8 and 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 is 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 produces more higher alcohols than methanol on a molar basis at good rates using a syngas mix that could be derived from a Shell gasifier.

4.1.5. Experimental

4.1.5.1. Catalyst Preparation

The ZnCrMn oxides were prepared by coprecipitating the metal nitrate salts in aqueous medium at a constant pH. An aqueous solution containing the metal nitrate salts and a basic solution were dripped slowly into ~200 mL of the basic solution using two peristaltic pumps. Care is taken to assure that the resulting solution is well stirred during the addition and the pH of the solution is monitored continuously. The flow of the basic solution is adjusted to keep the solution at a constant pH. The resulting mixture is then heated for a given time and then solid precipitate is filtered and washed with at least three liters of water, mixing well during the washing. The solid is dried at 110-120°C overnight and calcined for the desired time at the appropriate temperature. The catalysts were impregnated using the incipient wetness method.

4.1.5.2. Catalyst Testing

The reactor tubes were made from 1/4 inch stainless steel tubing that had been treated overnight with a 50/50 solution of hydrochloric acid and water. The tubes were rinsed with water for 5 minutes followed by an acetone rinse. Newer reaction tubes have been made from 1/4 inch copper tube inserted into 3/8 inch stainless steel tubes. The copper tubing was rinsed well with acetone before use. Reactors were dried under vacuum. One gram of catalyst was mixed with 3 cm^3 of glass beads until the mixture was uniform. The reactors were then loaded while tapping on the sides of reactor tube. Due to the V-like nature of the reactor tubes, each side of the V was loaded with one-half of the catalyst mixture at a time. Glass wool was then put into place on both sides of the reactor. The catalysts were reduced with 5% hydrogen in nitrogen for four hours at the desired temperature.

The reduced catalysts were then loaded into the sand bath and the system was pressurized with nitrogen. Once the reactor reached the correct temperature, the nitrogen was turned off and the syngas feedstream was turned on and adjusted to the correct pressure.

4.1.6. Task 1 Conclusions

Reactor to reactor variability has been reduced by replacement of the reactor sample loops. We can now double laboratory test productivity.

We have shown that stainless steel reactor tubes are not suitable for catalyst screening at a syngas ratio (H_2/CO) of 1:1 at our high temperatures. Copper-lined reactors will be employed from this point on.

High Pd loadings do not improve isobutanol rates or selectivities: the effect of higher Pd loadings on catalyst aging has not yet been determined.

Testing of the 6 wt% Pd formulation show that this catalyst produces more higher alcohols than methanol on a molar basis at good rates using a syngas mix that could be derived from a Shell gasifier.

Among our future plans are to continue formulation screening using K/Pd formulations on other supports, to examine the effect of Cs in place of K as the alkali promoter, and to investigate the use of Rh instead of Pd as a promoter.

Table 1. 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 2. 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 3. 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. 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 5. 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 6. 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 7. 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 8. 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 9. 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	-