DOE/PC/90046--T16

HETEROGENEOUS CATALYTIC PROCESS FOR ALCOHOL FUELS FROM SYNGAS

DOE Contract No. DE-AC22-91PC90046

Pittsburgh Energy Technology Center

Fourteenth
Quarterly Technical Progress Report

April – June 1995

Union Carbide Corporation
South Charleston Technical Center
South Charleston, West Virginia 25303

Contributors to this report: D. M. Minahan

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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.

Our current best catalyst is a formulation that contains 2.25 wt% K, 5.9 wt% Pd on a ZnCrMn spinel oxide prepared via controlled pH precipitation. In order to determine the scope of our potential patent position, we have prepared a comparative Zn/Cr spinel oxide support that contains excess ZnO and have looked at the catalytic performance of (a) the bare support, (b) a potassium traverse on the bare support to determine the effect of alkali addition in the absence of Pd and (c) a potassium traverse on the support impregnated with 6 wt% Pd.

The bare support is an inefficient methanol catalyst. Alkali addition (in the form of potassium at 1, 3, 5 and 7 wt%) results in an increase in selectivity to total alcohols vs. the bare support and a dramatic increase higher alcohol synthesis. For the 7 wt% K formulation, isobutanol can 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 exhibits an isobutanol rate of 7 g/kg-hr, with selectivity to total alcohols of 29% and with a methanol/isobutanol mole ratio of 86!

Pd additions results in further improvements in performance: isobutanol rates of > 130 g/kg-hr are 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 increase with K loading. The 5 wt% K, 5.9 wt% Pd catalyst produces > 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 produces isobutanol at 85 g/kg-hr, with selectivity to total alcohols of 80% and a methanol/isobutanol mole ratio of 1.0.

Further tests will examine alkali (K and Cs) and Pd formulations on spinel supports (Zn/Cr and Zn/Cr/Mn with and without excess Zn) prepared via controlled pH precipitation, a commercial Zn/Cr support and ZnO (off-the-shelf and prepared using controlled pH precipitation).

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.

Our current best catalyst 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 major components/variables involved 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 determine the scope of our potential patent position, we have prepared a comparative Zn/Cr spinel oxide support that contains excess ZnO and have looked at the catalytic performance of (a) the bare support, (b) a potassium traverse on the bare support to determine the effect of alkali addition in the absence of Pd and (c) a potassium traverse on the support impregnated with 6 wt% Pd, determined to be the optimum level on the Zn/Cr/Mn support.

A total of 9 catalysts were examined:

- the bare support
- 4 catalysts with 1, 3, 5 & 7 wt% potassium on the support
- 4 catalysts with 1, 3, 5 & 7 wt% potassium with 6 wt% Pd on the 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

4.1.2. Zn/Cr Spinel With Excess Zn (Bare Support)

The bare support is 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 1. The isobutanol rate is barely detectable at 2 g/kg-hr. Selectivity to total alcohols is only 50%.

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

4.1.3. Addition of K to the Zn/Cr Spinel with Excess Zn

The data appear in Tables 2-5. Alkali addition (in the form of potassium at 1, 3, 5 and 7 wt%) results in an increase in selectivity to total alcohols vs. the bare support and a dramatic increase in higher alcohol synthesis. For the 7 wt% K formulation, isobutanol can 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 exhibits 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 is 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 1-3.

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

The data appear in Tables 6-9. Pd additions result in further improvements in performance: isobutanol rates of > 130 g/kg-hr are 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 increase with K loading. The catalysts are compared at 440°C and 1500 psi in Figures 4-6. The lowest methanol/isobutanol mole ratio is obtained with the 5 wt% K formulation (1.2 at 440°C and 1500 psi).

The 5 wt% K, 5.9 wt% Pd catalyst produces > 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 produces isobutanol at 85 g/kg-hr, with a selectivity to total alcohols of 80% and a methanol/isobutanol mole ratio of 1.0.

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 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

We have prepared a comparative Zn/Cr spinel oxide support that contains excess ZnO and have looked at the catalytic performance of (a) the bare support, (b) a potassium traverse on the bare support to determine the effect of alkali addition in the absence of Pd and (c) a potassium traverse on the support impregnated with 6 wt% Pd.

The bare support is an inefficient methanol catalyst. Alkali addition results in an increase in selectivity to total alcohols vs. the bare support and a dramatic increase higher alcohol synthesis. Pd addition results in further improvements in performance. Selectivities increase with K loading. The 5 wt% K, 5.9 wt% Pd catalyst produces > 100 g/kg-hr of isobutanol at 440°C and 1000 psi, with 85% selectivity to total alcohols and with a methanol/isobutanol mole ratio of < 2.

We intend to continue formulation screening using K/Pd formulations on ZnO and $ZnCr_2O_4$ prepared conventionally and via controlled pH precipitation. We will also examine the effect of Cs in place of K as the alkali promoter and the use of Rh instead of Pd as a promoter.

Table 1. ZnCr support with excess Zn, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR516 T = 400°C P = 1000 psi	PR524 T = 400°C P = 1500 psi	PR540 T = 440°C P=1500 psi	PR548 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	50	61	29	29
Total Alcohol Rate (g/kg-hr)	164	292	170	118
Methanol Rate (g/kg-hr)	160	285	154	101
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	4	2
n-Propanol rate (g/kg-hr)	0	1	5	6
Isobutanol Rate (g/kg-hr)	2	6	7	8
MeOH/i-BuOH mole ratio	269	191	86	48
Hydrocarbon rate (g/kg-hr)	82	91	216	150
Conversion (%)	17	20	21	18

Table 2. ZnCr support with excess Zn and 1% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR017 T = 400°C P = 1000 psi	PR025 T = 400°C P = 1500 psi	PR043 T = 440°C P=1500 psi	PR049 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	70	76	41	41
Total Alcohol Rate (g/kg-hr)	185	327	217	135
Methanol Rate (g/kg-hr)	176	308	158	115
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	2	0
n-Propanol rate (g/kg-hr)	0	0	9	4
Isobutanol Rate (g/kg-hr)	9	18	48	16
MeOH/i-BuOH mole ratio	77	30	13	29
Hydrocarbon rate (g/kg-hr)	38	51	167	101
Conversion (%)	11	15	16	13

Table 3. ZnCr support with excess Zn and 3% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR018 T = 400°C P = 1000 psi	PR026 T = 400°C P = 1500 psi	PR042 T = 440°C P=1500 psi	PR050 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	83	87	49	41
Total Alcohol Rate (g/kg-hr)	168	298	231	151
Methanol Rate (g/kg-hr)	126	229	99	84
Ethanol Rate (g/kg-hr)	0	1	0	3
Isopropanol rate (g/kg-hr)	0	0	7	6
n-Propanol rate (g/kg-hr)	2	8	9	5
Isobutanol rate (g/kg-hr)	40	60	115	51
MeOH/i-BuOH mole ratio	12	15	3.5	6.7
Hydrocarbon rate (g/kg-hr)	18	23	149	149
Conversion (%)	17	19	23	20

Table 4. ZnCr support with excess Zn and 5% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR146 T = 400°C P = 1000 psi	PR171 T = 400°C P = 1500 psi	PR195 T = 440°C P=1500 psi	PR211 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	84	87	71	70
Total Alcohol Rate (g/kg-hr)	134	254	178	106
Methanol Rate (g/kg-hr)	68	157	47	19
Ethanol Rate (g/kg-hr)	0	1	0	1
Isopropanol rate (g/kg-hr)	0	1	5	3
n-Propanol rate (g/kg-hr)	5	11	10	5
Isobutanol Rate (g/kg-hr)	61	84	117	78
MeOH/i-BuOH mole ratio	4.4	7.5	1.6	0.94
Hydrocarbon rate (g/kg-hr)	15	22	48	33
Conversion (%)	15	14	14	15

Table 5. ZnCr support with excess Zn and 7% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR360 T = 400°C P = 1000 psi	PR368 T = 400°C P = 1500 psi	PR384 T = 440°C P=1500 psi	PR392 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	97	96	85	87
Total Alcohol Rate (g/kg-hr)	124	254	189	103
Methanol Rate (g/kg-hr)	72	165	54	20
Ethanol Rate (g/kg-hr)	0	0	1	0
Isopropanol rate (g/kg-hr)	1	2	6	3
n-Propanol rate (g/kg-hr)	14	23	22	10
Isobutanol Rate (g/kg-hr)	37	64	106	69
MeOH/i-BuOH mole ratio	7.8	10.3	2.0	1.2
Hydrocarbon rate (g/kg-hr)	3	6	22	11
Conversion (%)	9	17	18	16

Table 7. ZnCr support with excess Zn, 5.9% Pd and 3% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR444 T = 400°C P = 1000 psi	PR452 T = 400°C P = 1500 psi	PR470 T = 440°C P=1500 psi	PR478 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	70	77	57	55
Total Alcohol Rate (g/kg-hr)	159	294	221	136
Methanol Rate (g/kg-hr)	73	155	54	24
Ethanol Rate (g/kg-hr)	1	4	8	8
Isopropanol rate (g/kg-hr)	1	1	5	6
n-Propanol rate (g/kg-hr)	4	12	18	14
Isobutanol Rate (g/kg-hr)	81	121	136	84
MeOH/i-BuOH mole ratio	3.6	5.1	1.6	1.1
Hydrocarbon rate (g/kg-hr)	43	51	111	78
Conversion (%)	17	21	23	18

Table 8. ZnCr support with excess Zn, 5.9% Pd and 5% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR517 T = 400°C P = 1000 psi	PR525 T = 400°C P = 1500 psi	PR539 T = 440°C P=1500 psi	PR547 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	86	87	73	85
Total Alcohol Rate (g/kg-hr)	137	240	190	161
Methanol Rate (g/kg-hr)	54	129	41	48
Ethanol Rate (g/kg-hr)	0	0	0	0
Isopropanol rate (g/kg-hr)	0	0	0	1
n-Propanol rate (g/kg-hr)	9	17	15	9
Isobutanol Rate (g/kg-hr)	74	94	134	102
MeOH/i-BuOH mole ratio	2.9	5.5	1.2	1.9
Hydrocarbon rate (g/kg-hr)	14	21	50	20
Conversion (%)	12	15	17	15

Table 9. ZnCr support with excess Zn, 5.9% Pd and 7% K, tested in a copper-lined tube with GHSV 12000 and $H_2/CO = 1$

	PR292 T = 400°C P = 1000 psi	PR300 T = 400°C P = 1500 psi	PR316 T = 440°C P=1500 psi	PR324 T = 440°C P = 1000 psi
Sel. Total Alcohols (%)	91	91	78	80
Total Alcohol Rate (g/kg-hr)	171	313	239	158
Methanol Rate (g/kg-hr)	76	180	53	21
Ethanol Rate (g/kg-hr)	0	2	3	0
Isopropanol rate (g/kg-hr)	3	3	10	5
n-Propanol rate (g/kg-hr)	24	36	42	47
Isobutanol Rate (g/kg-hr)	69	93	132	85
MeOH/i-BuOH mole ratio	4.5	7.8	1.6	1.0
Hydrocarbon rate (g/kg-hr)	11	18	45	29
Conversion (%)	14	15	15	16

Figure 1. Selectivity to total alcohols vs. K loading on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

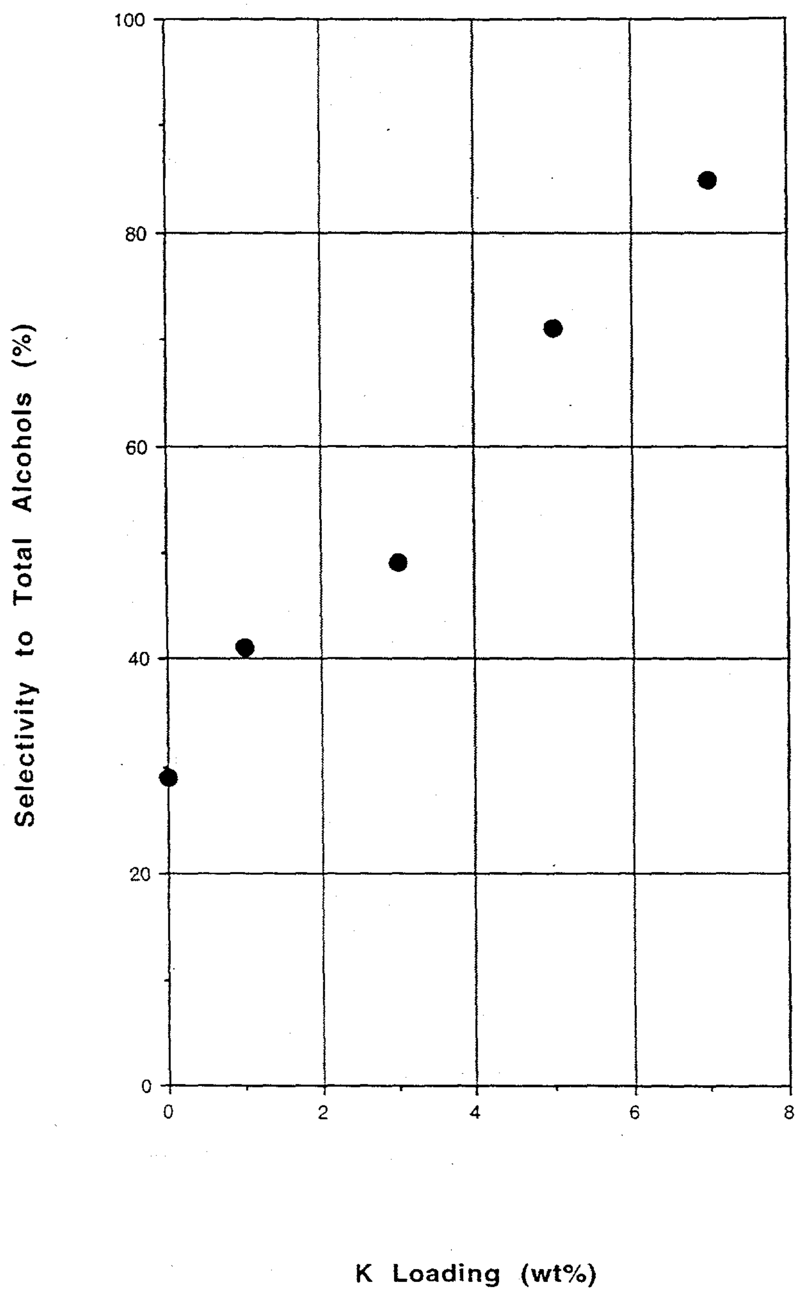

Figure 2. Rate to total alcohols vs. K loading on ZnCr spinel with excess Zn.
Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

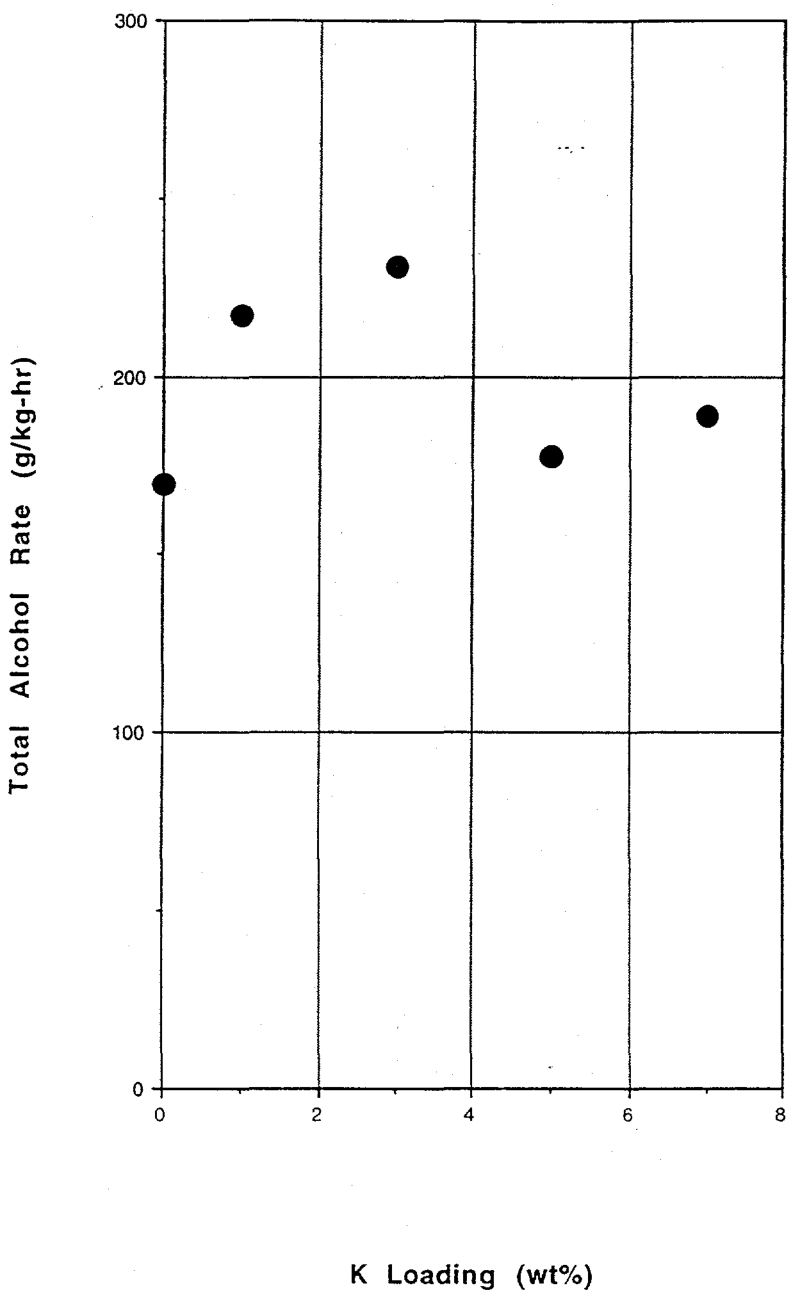

Figure 3. Rates to methanol and isobutanol vs. K loading on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

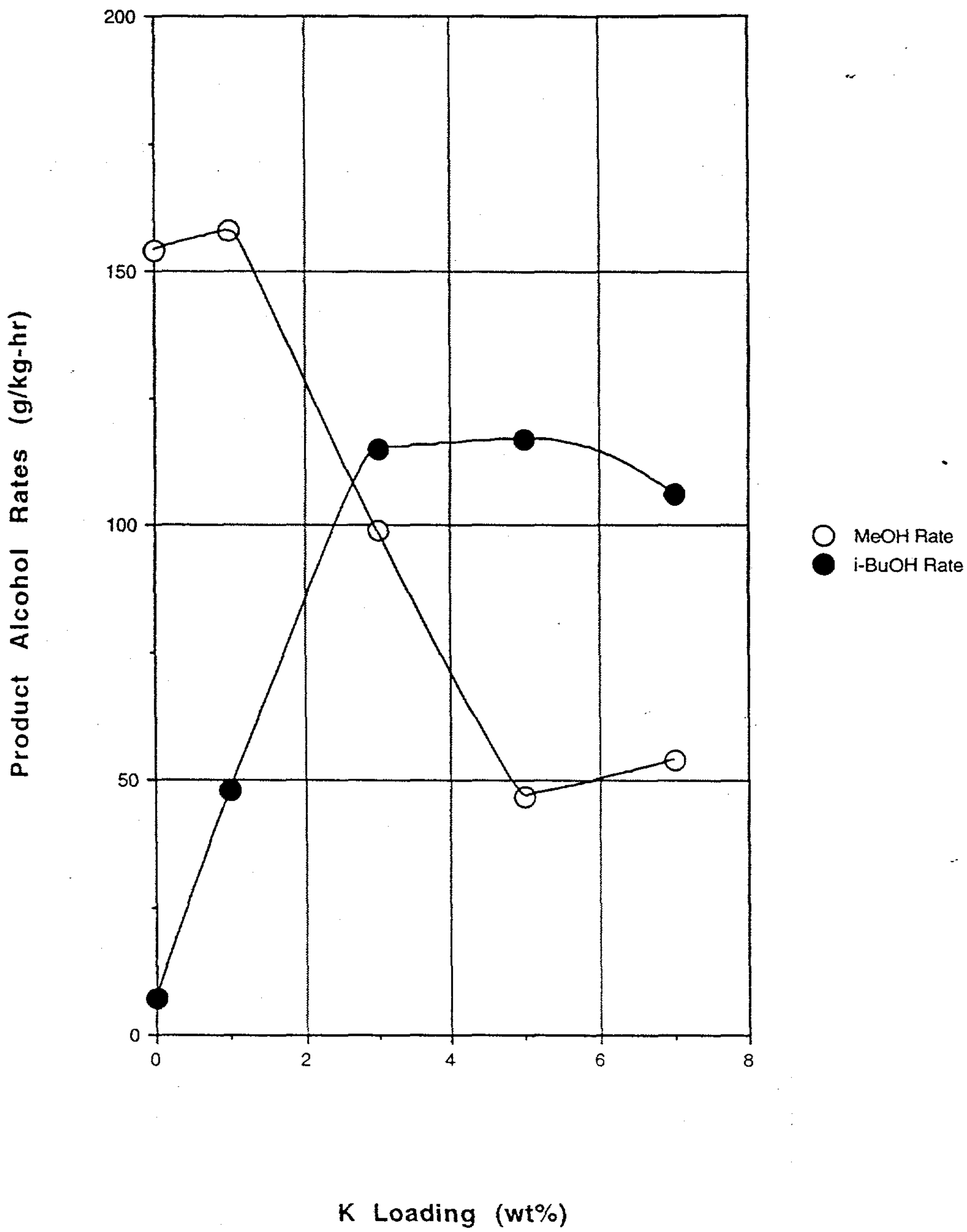

Figure 4. Selectivity to total alcohols vs. K loading for 6 wt% Pd on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

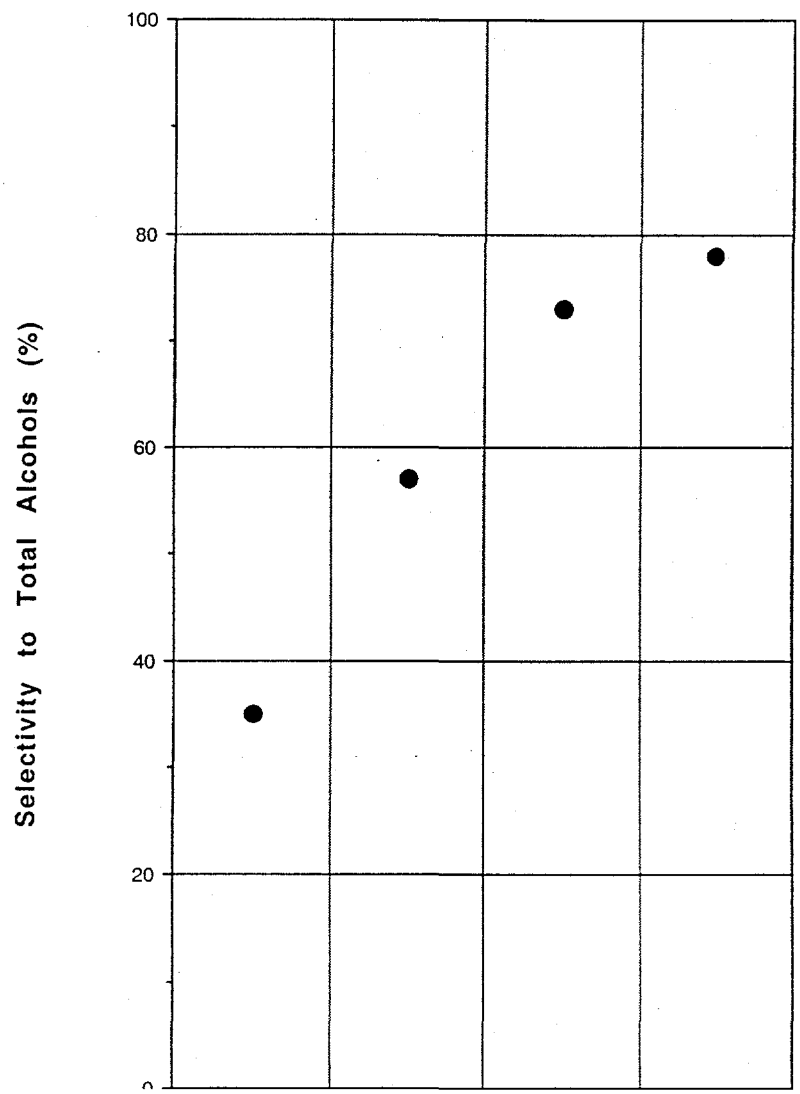

Figure 5. Rate to total alcohols vs. K loading for 6 wt% Pd on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

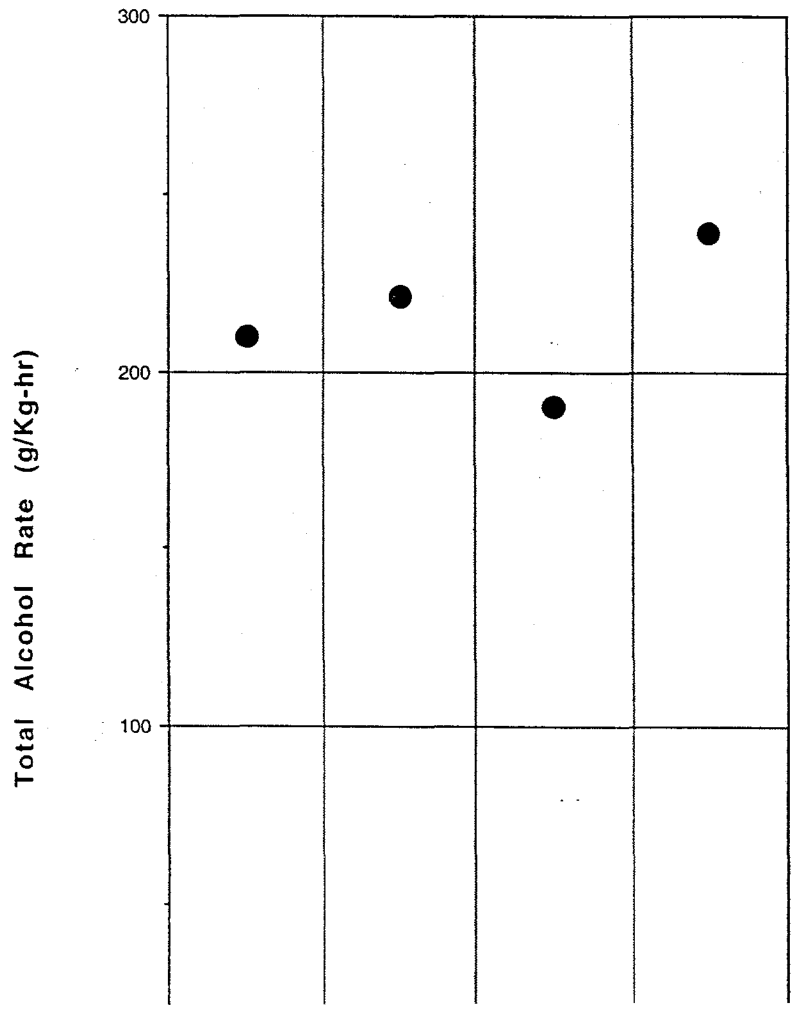

Figure 4. Selectivity to total alcohols vs. K loading for 6 wt% Pd on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

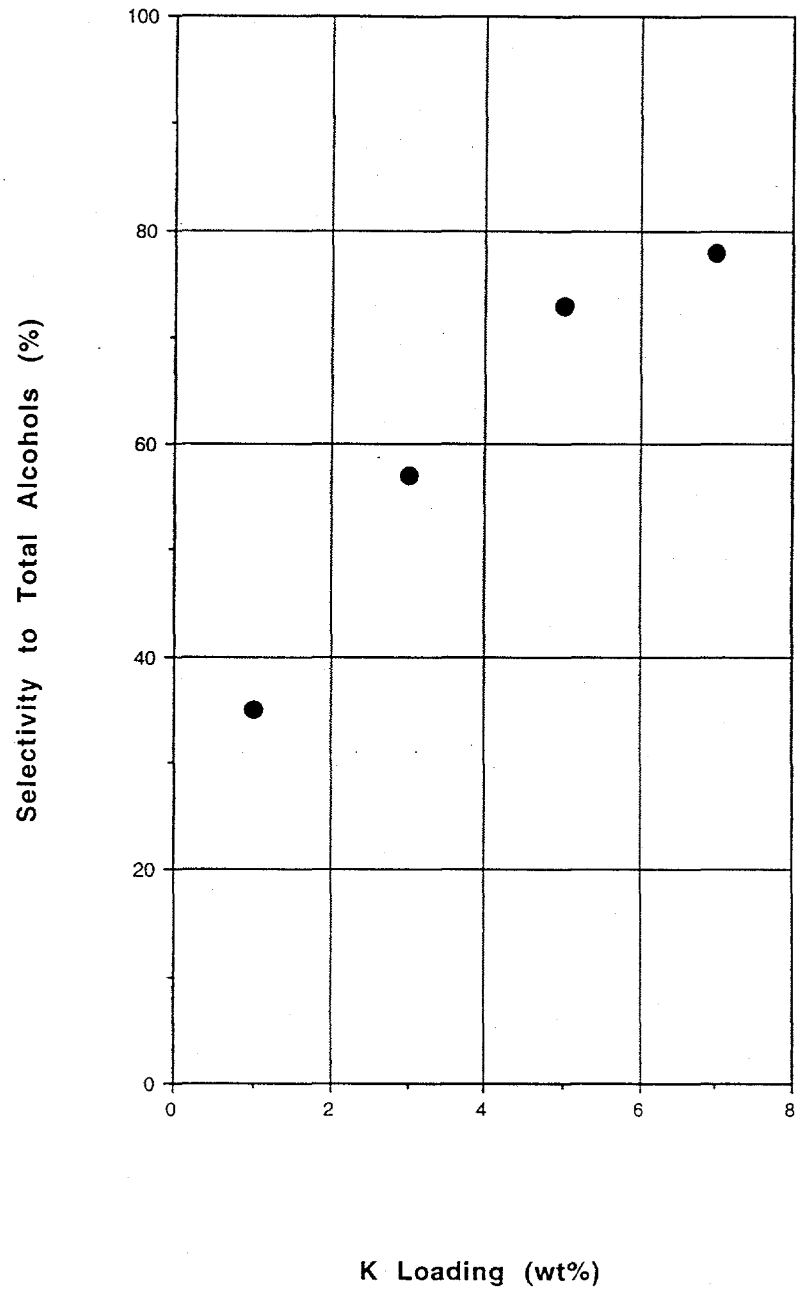

Figure 5. Rate to total alcohols vs. K loading for 6 wt% Pd on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$

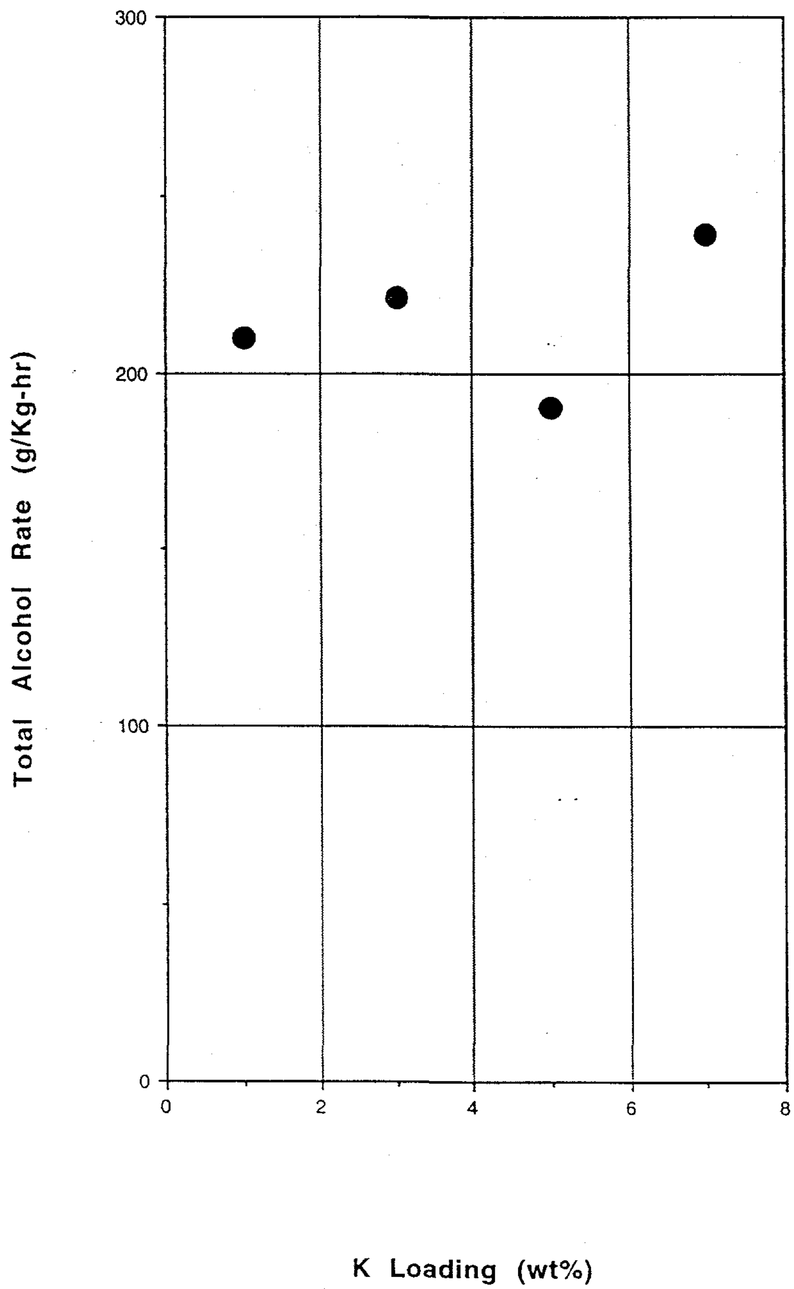

Figure 6. Rates to methanol and isobutanol vs. K loading for 6 wt% Pd on ZnCr spinel with excess Zn. Tested in a copper-lined tube at 440°C, 1500 psi with GHSV 12000 and $H_2/CO = 1$