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Development of a Catalyst for Conversion
of Syngas-Derived Materials to Isobutylene
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QUARTERLY TECHNICAL REPORT

The goals of this project are to develop a catalyst and process for the conversion of syngas to isobutanol. The research will identify and optimize key catalyst and process characteristics. In addition, the commercial potential of the new process will be evaluated by an economic analysis.

This report describes the preparation and testing of a variety of potential higher alcohols synthesis catalysts based on a bifunctional formulation consisting of a noble metal dehydrogenation function on a basic mixed metal oxide support. A pilot plant catalyst screening test using a 10/1 methanol/ethanol feed blend has been used to identify a new class of catalysts that afford higher selectivities and productivities of the desired isobutanol and other C₄₊ products than the Cu/Zn/Al oxide methanol synthesis catalyst that is being used as a baseline for this work¹. 2% Pd or Pt on a Zn/Mn/Zr oxide support and 2% Pd on a Zn/Mn/Cr support have given the best performances to date. In addition to isobutanol, these catalysts afford significant quantities of isobutyraldehyde and methyl isobutyrate. In order to elucidate the reaction pathway occurring with this class of catalyst, the 2%Pd on Zn/Mn/Zr oxide catalyst has been evaluated over a range of space velocities. It has been found that isobutanol and higher oxygenates yields increase with decreasing space velocity at ethanol conversions greater than 90%. This suggests that this catalyst is capable of converting methanol alone to higher alcohols. This is different from the result obtained with the Cu/Zn/Al oxide baseline catalyst, which showed no change in product yields at high ethanol conversions¹. Therefore, further effort will be focussed on the development of these noble metal/basic metal oxide catalysts for this application.

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EXPERIMENTAL

Catalysts

Two co-precipitation procedures have been used to prepare the mixed metal oxide supports described in this report. Aqueous metal nitrate solutions containing all of the metals were used in both methods. In the first method the co-precipitation was accomplished by simultaneous addition of the metal solution and an aqueous KOH solution to a stirred bucket while maintaining pH at 11 and temperature at 50 °C. The following materials have been prepared by this procedure:

Zn/Mn/Zr oxide	(34/34/32 molar)
Zn/Mn/Cr oxide	(34/33/33)
Zn/Mn/Ce oxide	(33/33/33)
Zn/Mn oxide	(50/50)
Zn/Zr oxide	(50/50)

The second co-precipitation procedure was similar, except that a Na₂CO₃ solution and pH 7 were used. The materials that have been prepared using this method are:

Zn/Mn/Cu oxide	(34/33/33 molar)
Zn/Al oxide	(74/26)
Zn/Cr oxide	(74/26)

After the precipitation the solids were recovered by filtration, washed extensively with deionized water, dried at 127 °C for 15 hours, sized to 20-40 mesh and calcined at 327 °C in air for 3 hours. An additional metal oxide sample, of MnO₂, was obtained from Chem Metals of Baltimore, MD.

Portions of the metal oxides described above were impregnated with Pd, Pt or Ag using aqueous metal chloride (Pt and Pd) or metal nitrate (Ag) solutions. After impregnation the materials were re-calcined at 400 °C to afford the final catalysts. A mixed Ag metal / Zn/Mn/Zr oxide catalyst was also prepared by physically mixing the mixed metal oxide with 60 mesh Ag granules obtained from Aldrich.

Catalytic Testing Procedure

The pilot plant testing of catalysts for the conversion of a methanol/ethanol blend to isoalcohols was accomplished as follows. The catalyst, as 20-40 mesh granules, was loaded into a 1/2" I.D. stainless steel reactor. The reactor was purged N₂ at 250 °C, 10 psig, 0.5 scf/hr for 1 hour then pressure tested with N₂ at 250 °C, 500 psig for 1 hour. After restarting the N₂ purge, temperature and pressure were adjusted to the desired conditions. After 2 hours, the methanol/ethanol blend (10/1 molar) was cut into the plant at the desired rate and continued for 16 hours. Product analyses were obtained using two on-line GCs to analyze the total hydrocarbon/oxygenate product and the overhead gas. Conversions, selectivities and productivities (including CO and

CO₂) are based on moles of carbon. For all of the tests described in this report, the averages of results obtained between 8 and 16 hours on stream are reported. A listing of the pilot plant runs included in this report is given in Table 1.

RESULTS AND DISCUSSION

Catalyst Screening of Noble Metal on Mixed Metal Oxides

This report describes catalyst preparation and testing directed at identifying a promising noble metal and basic metal support for further development. Previous work in this project found that a 2 wt.% Pd on Zn/Mn/Zr oxide catalyst gave the highest isobutanol selectivity and productivity of any catalyst that had been tested to date in this program for the conversion of a methanol/ethanol blend to higher alcohols¹. This material is similar to the catalysts described by Keim, et al. to give high isobutanol selectivity from syngas, albeit at very severe conditions (high temperature and pressure)².

The ability of bifunctional materials to catalyze the conversion of light alcohols to higher branched alcohols can be rationalized in the following way. The aldol coupling reaction, that presumably affords the C-C bond forming in this system, likely requires the presence of aldehyde as a target for nucleophilic attack. This suggests that the rate of condensation can be increased if the concentration of aldehyde species in the feed can be raised. Noble metal catalysts are well known to catalyze this dehydrogenation. For example, silver metal is used commercially for the conversion of methanol to formaldehyde. Therefore, the addition of a noble metal function to a catalyst support capable of promoting the aldol condensation reaction should lead to a superior catalyst.

A series of mixed metal oxide supports have been prepared by the co-precipitation of a metal nitrate solution with KOH at constant pH. These supports, after drying and calcining, have been impregnated with both 2 wt.% Pd and 2 wt.% Pt and tested in the standard pilot plant screening test for the conversion of a 10/1 (molar) methanol/ethanol blend. Table 2 summarizes the testing results of the Pd containing catalysts, while Table 3 summarizes results with Pt containing materials.

In the case of Pd, the Zn/Mn/Cr (33/33/33 molar) support affords the highest isobutanol selectivity and productivity. The Zn/Mn/Zr (33/33/33) support gives comparable selectivity, but at a slightly lower activity level. This material also shows lower CO_x selectivity due to reduced CO. Other supports tested, Zn/Mn/Ce, Cu/Zn/Al and Zn/Mn, all show lower selectivity to the desired isobutanol product than the best catalysts.

The Zn/Mn/Zr (33/33/33) support gives the best Pt containing catalyst, with the Zn/Mn/Ce (33/33/33) catalyst a close second. On contrast to the Pd findings, Pt on the Zn/Mn/Cr support gave poor selectivity to isobutanol and total C₄₊ products and high selectivity to CO_x. The preparations of Pd and Pt catalysts on this support will be repeated to determine if this difference is reproducible. The Cu/Zn/Al support, as well as several bimetallic oxide supports, gave lower isobutanol selectivity than the best samples.

Table 4 summarizes the results with the best two supports, Zn/Mn/Zr and Zn/Mn/Cr, as a function of the noble metal functionality. The Pd or Pt metal addition clearly increases the activity of these catalysts for methanol/ethanol conversion. Catalyst with either no metal or Ag as the metal (either impregnated or physically mixed), show much lower conversion levels. This suggests that the dehydrogenation of alcohol to aldehyde is an important, and perhaps rate limiting, step in the condensation process. In the case of Zn/Mn/Zr, it appears that isobutanol selectivity is relatively independent of the identity or presence of the noble metal. This suggests that oxygenate selectivity may be primarily a function of the basic metal oxide support. Therefore, variations of this support composition would be a reasonable approach for improving isobutanol selectivity. Table 5 shows an overall summary of the selectivities to all identified products observed with the Pt and Pd containing catalysts on a CO_x included basis. All of these catalyst show higher selectivity to isobutyraldehyde than to isobutanol. This may be due to the low pressure (30 psig) used in this testing, where equilibrium favors the dehydrogenated product. The presence of substantial amounts of methyl isobutyrate, the ester derived from methanol and butyric acid, suggests that either further oxidation to the carboxylic acid or condensation of iC₄ aldehyde and methanol is also occurring. Acid catalyzed etherification of methanol to DME appears to be minimal, except for the Pd on Zn/Mn/Zr oxide catalyst, but light ester formation, presumably by the reaction of methanol with formaldehyde and acetaldehyde intermediates, occurs at about 3% selectivity. The Pd containing catalysts show twice as much CO formation as the Pt samples, which is highly undesirable since it represents that reverse of the methanol synthesis process.

WHSV Testing of Pd on Zn/Mn/Zr Oxide to Determine the Reaction Pathway

One of the primary mechanistic questions in the production of branched C₄ oxygenates from methanol is the relative rates of the C₁-C₁ and C₁-C_{2,3} condensation steps. While the latter condensation is sufficient for the production of higher alcohols from a methanol/ethanol feed blend, the C₁-C₁ coupling step is necessary for the primary goal of this project which is the condensation of methanol only to higher alcohols. In order to evaluate the extent of C₁-C₁ coupling occurring over the experimental catalysts, tests have been conducted to determine the dependence of product yields on space velocity. In particular, at conditions where ethanol conversion is high, an increase in the yields of isobutanol and other higher oxygenates as WHSV

is decreased suggests that methanol alone is being converted to the desired products. Previous testing has shown that the baseline Cu/Zn/Al methanol synthesis catalyst is poor for converting methanol alone to higher alcohols¹. Figures 1 and 2 show conversions and yields as a function of space time for this catalyst.

The 2% Pd on Zn/Mn/Zr oxide catalyst (7887-64) has also been evaluated at varying space velocities to determine if C₁-C₁ condensation is occurring with this material. Figure 3 shows methanol, ethanol and total carbon conversions as a function of space time. This data shows that ethanol conversion exceeds 80% at space time greater than 0.15 hr and reach 95% at 0.50 hr. Figure 4 shows that over this range of space times the yields for the desired products, isobutanol and total C₄₊ oxygenates, increase 2-3 fold. This suggests that this catalyst may be capable of condensing methanol alone to higher alcohols. Further testing with a methanol only feedstock will be conducted to confirm this conclusion.

CONCLUSIONS

A pilot plant catalyst screening test using a 10/1 methanol/ethanol feed blend has been used to identify a new class of catalysts that afford higher selectivities and productivities of the desired isobutanol and other C₄₊ products than the Cu/Zn/Al oxide methanol synthesis catalyst that is being used as a baseline for this work¹. 2% Pd or Pt on a Zn/Mn/Zr oxide support and 2% Pd on a Zn/Mn/Cr support have given the best performances to date. In addition to isobutanol, these catalysts afford significant quantities of isobutyraldehyde and methyl isobutyrate. In order to elucidate the reaction pathway occurring with this class of catalyst, the 2%Pd on Zn/Mn/Zr oxide catalyst has been evaluated over a range of space velocities. It has been found that isobutanol and higher oxygenates yields increase with decreasing space velocity at ethanol conversions greater than 90%. This suggests that this catalyst is capable of converting methanol alone to higher alcohols.

REFERENCES

- 1) P. T. Barger, DOE Quarterly Report No. 12, (1994).
- 2) W. Keim and W. Falter, Catalysis Letters 3, 59, (1989);
M. Roper, W. Keim and J. Seibring, Eur. Pat. Appl. 208,012, (1986);
W. Falter and W. Keim, Eur. Pat. Appl. 335,092, (1989).

Table 1. Run List

RUN	CATALYST		CATALYST DESCRIPTION	CATALYST B	LOADING g	SIZE	TEMP (C) INLET	CONDITIONS			FEED RATIO MeOH/EtOH/N2(H2)
	A Book #	B Book #						MAX	PSIG	MeOH WHSV	
193	7923	-72	2.0%Pd/ZnMn (50/50) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
194	7923	-88	2.0%Pd/ZnMn/Ce (33/33/33) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
195	7887	-42	Cu/Zn/Al (33/39/28) Oxide (Lab PPT)		5	20-40M	300	30	2	1/0.1/2 N2	
196	7923	-64	2.1%Pd/ZnMn/Zr (34/34/32) Oxide		2.5	20-40M	350	30	4	1/0.1/2 N2	
197	7923	-64	2.1%Pd/ZnMn/Zr (34/34/32) Oxide		1.75	20-40M	350	30	5.8	1/0.1/2 N2	
198	7923	-64	2.1%Pd/ZnMn/Zr (34/34/32) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
199			None (Quartz Chips/a - Alumina)				300	30	(2)	1/0.1/2 N2	
200			None (Glass Beads)				300	30	(2)	1/0.1/2 N2	
201	7923	-64	2.1%Pd/ZnMn/Zr (34/34/32) Oxide		5	20-40M	300	30	2	1/0.1/2 N2	
202	7887	-56	2.1%Ag metal / ZnMn/Zr (34/34/32) Oxide		5	20-40M	300	30	2	1/0.1/2 N2	
203	7887	-50	2.0%Ag / ZnMn/Zr (34/34/32) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
204	7887	-52	2.0%Pd / ZnMn/Cr (34/33/33) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
205	7887	-48	2.0%Pt / ZnMn/Zr (34/34/32) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
206			None (Glass Beads)				350	30	(2)	1/0.1/2 N2	
207			None (Quartz Chips/a - Alumina)				350	30	(2)	1/0.1/2 N2	
208	7887	-48	2.0%Pt / ZnMn/Zr (34/34/32) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
209	7887	-50	2.0%Ag / ZnMn/Zr (34/34/32) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
210	7887	-56	2.1%Ag metal / ZnMn/Zr (34/34/32) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
211	7887	-48	2.0%Pt / ZnMn/Zr (34/34/32) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
212	7887	-52	2.0%Pd / ZnMn/Cr (34/33/33) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
213	7887	-56	2.0%Pd / Cu/Zn/Al (33/39/28) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
214	7887	-52	2.0%Pd / ZnMn/Cr (34/33/33) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
215	7923	-95	ZnMn/Cr (34/33/33) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
216	7887	-62	2.0%Pt / ZnMn/Cr (34/33/33) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
217	7887	-64	2.0%Pt / Zr/Zn (50/50) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
218	7887	-66	2.0%Pt / Zr/Mn (50/50) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
219	7887	-66	2.0%Pt / ZnMn/Ce (33/33/33) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
220	7887	-72	2.0%Pt / Zn/Al (74/26) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
221	7887	-70	2.0%Pt / Zn/Cr (74/26) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
222	7887	-80	2.0%Pt / Mn (100) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	
223	7887	-76	2.0%Pt / ZnMn/Cu (34/33/33) Oxide		5	20-40M	350	30	2	1/0.1/2 N2	

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Table 2. Screening of 2% Pd on Mixed Metal Oxide Catalysts

Support Catalyst Number	Run	Conversion (%)		Selectivity (mole %)			Productivity (g/kg cat/hr)	
		MeOH	EtOH	iC ₄ OH	Sum C ₄₊	CO _x	iC ₄ OH	Sum C ₄₊
Zn/Mn/Zr (34/34/32)	198	51	99	10	41	37	80	328
Zn/Mn/Cr (34/33/33)	212	79	100	10	36	57	110	399
Zn/Mn/Ce (33/33/33)	194	35	92	5	44	33	33	290
Cu/Zn/Al (33/39/28)	213	89	100	7	28	56	87	348
Zn/Mn (50/50)	193	42	95	7	21	40	50	150

Conditions: 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 3. Screening of 2% Pt on Mixed Metal Oxide Catalysts

Support Catalyst Number	Run	Conversion (%)		Selectivity (mole %)		Productivity (g/kg cat/hr) iC ₄ OH Sum C ₄ ⁺
		MeOH	EtOH	iC ₄ OH	Sum C ₄ ⁺ CO _x	
Zn/Mn/Zr (34/34/32)	211	49	99	16	49	122 373
Zn/Mn/Cr (34/33/33)	216	51	90	2	12	17 102
Zn/Mn/Ce (33/33/33)	219	50	100	12	46	91 349
Zn/Mn/Cu (34/33/33)	223	32	95	7	37	37 196
Zn/Al (75/25)	220	74	100	7	30	74 317
Zn/Cr (75/25)	221	66	100	9	34	83 316
Zn/Zr (50/50)	217	10	57	2	32	4 64
Mn/Zr (50/50)	218	35	96	8	42	46 242
Mn (100)	222	36	83	2	14	9 63

Conditions: 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 4. Screening of Metals on Zr/Mn/Zr and Zn/Mn/Cr Oxides

Support Catalyst Number	Run	Conversion (%)		Selectivity (mole %)		Productivity (g/kg cat/hr)	
		MeOH	EtOH	iC ₄ OH	Sum C ₄₊	iC ₄ OH	Sum C ₄₊
Zn/Mn/Zr (34/33/32)							
7887-48 (2% Pt)	211	49	99	16	49	122	374
7923-64 (2% Pd)	198	51	99	10	41	80	328
7887-50 (2% Ag)	209	11	67	13	45	37	128
7887-56 (2% Ag metal)	210	6	63	14	47	30	101
7923-55 (no metal)	188	9	50	13	18	13	18
Zn/Mn/Cr (34/33/33)							
7887-62 (2% Pt)	216	51	90	2	12	17	102
7887-52 (2% Pd)	212	79	100	10	36	110	399
7923-95 (no metal)	215	5	43	1	36	2	72

Conditions: 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 5. Overall Selectivities of Most Promising Catalysts

Run	198	212	211	216
Catalyst	7923-64 2%Pd on Zn/Mn/Zr Oxide	7887-52 2% Pd on Zn/Mn/Cr Oxide	7887-48 2%Pd on Zn/Mn/Zr Oxide	7887-62 2%Pd on Zn/Mn/Cr Oxide
nC ₃ OH	0.7	0.1	0.6	2.0
nC ₄ OHs	0.2	1.1	0.4	0.1
iC ₄ OH	9.9	10.2	16.4	2.1
C ₅₊ OHs	0.8	1.1	0.9	0.5
iC ₄ Aldehyde	14.8	11.9	17.7	6.2
iC ₄ Methyl Ester	3.6	3.5	2.9	0.7
Other Oxygenates	2.2	3.3	1.0	1.1
C ₁₋₂ Aldehydes	0.0	0.0	0.6	0.0
C ₃ Aldehyde	0.8	0.3	0.7	6.6
DME	10.5	0.3	0.9	0.1
Methyl Formate	0.6	0.7	1.7	0.4
Methyl Acetate	2.4	2.0	1.3	2.7
C ₁₋₅ Hydrocarbons	6.0	3.5	1.6	1.6
CO	14.2	40.7	18.0	61.6
CO ₂	22.8	16.3	25.6	13.6
Others	10.5	5.0	9.7	0.7

Conditions: 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Figure 1.

Cu/Zn/Al Performance vs. Space Time Methanol/Ethanol to Higher Alcohols

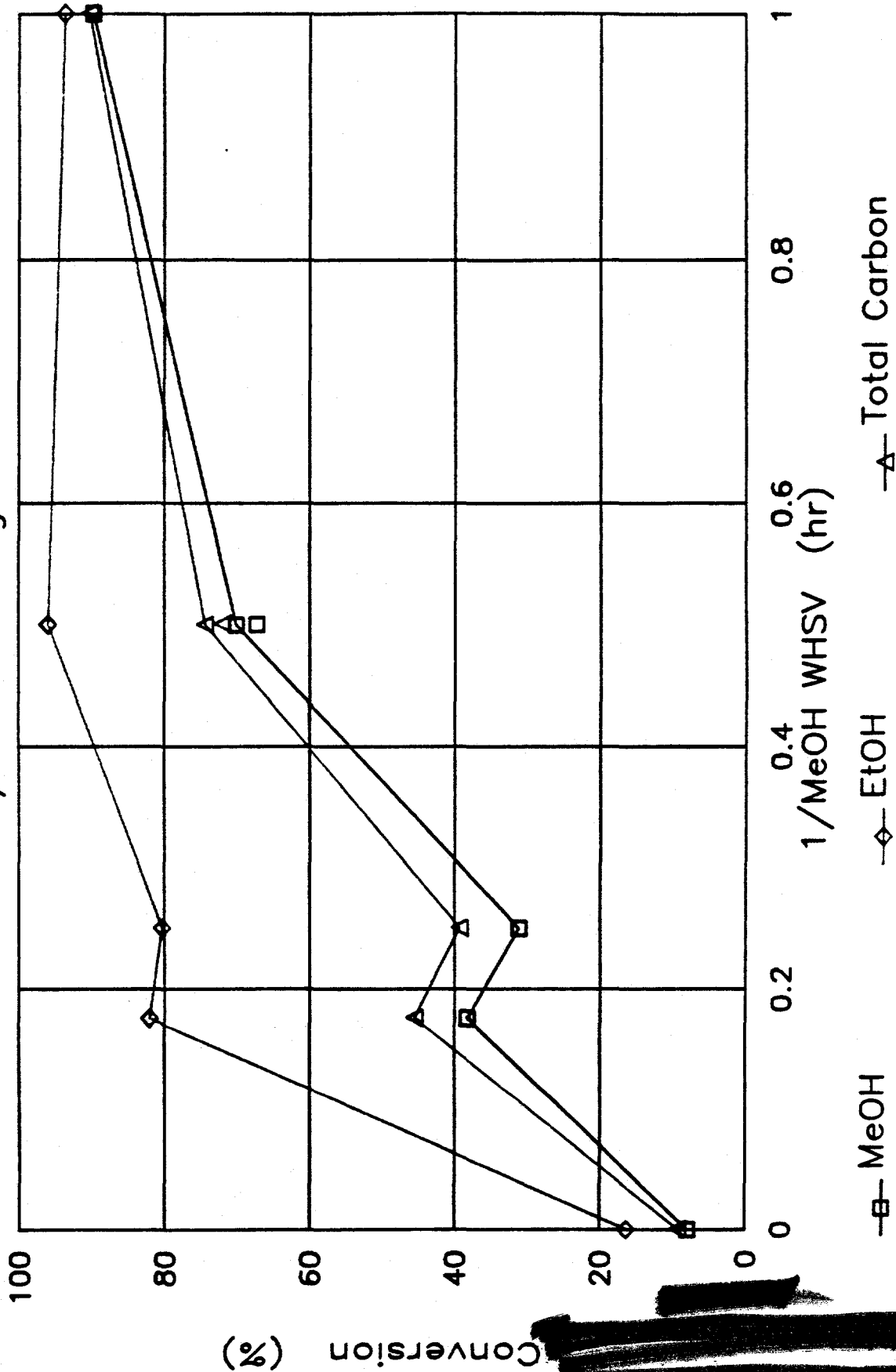


Figure 2.

Cu/Zn/Al Performance vs. Space Time Methanol/Ethanol to Higher Alcohols

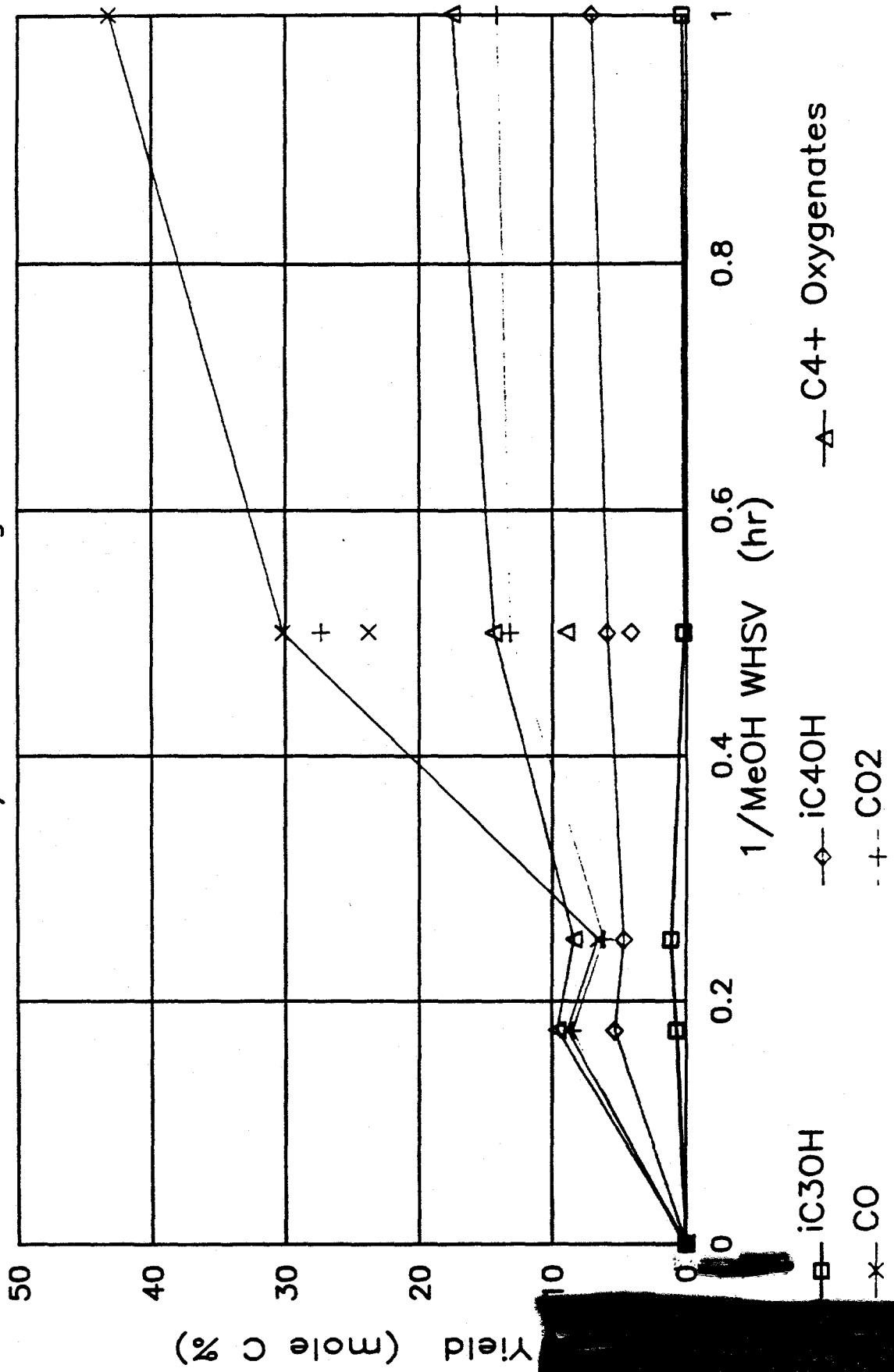


Figure 3.

Pd on Zn/Mn/Zr Oxide Performance vs. Space Time
Methanol/Ethanol to Higher Alcohols

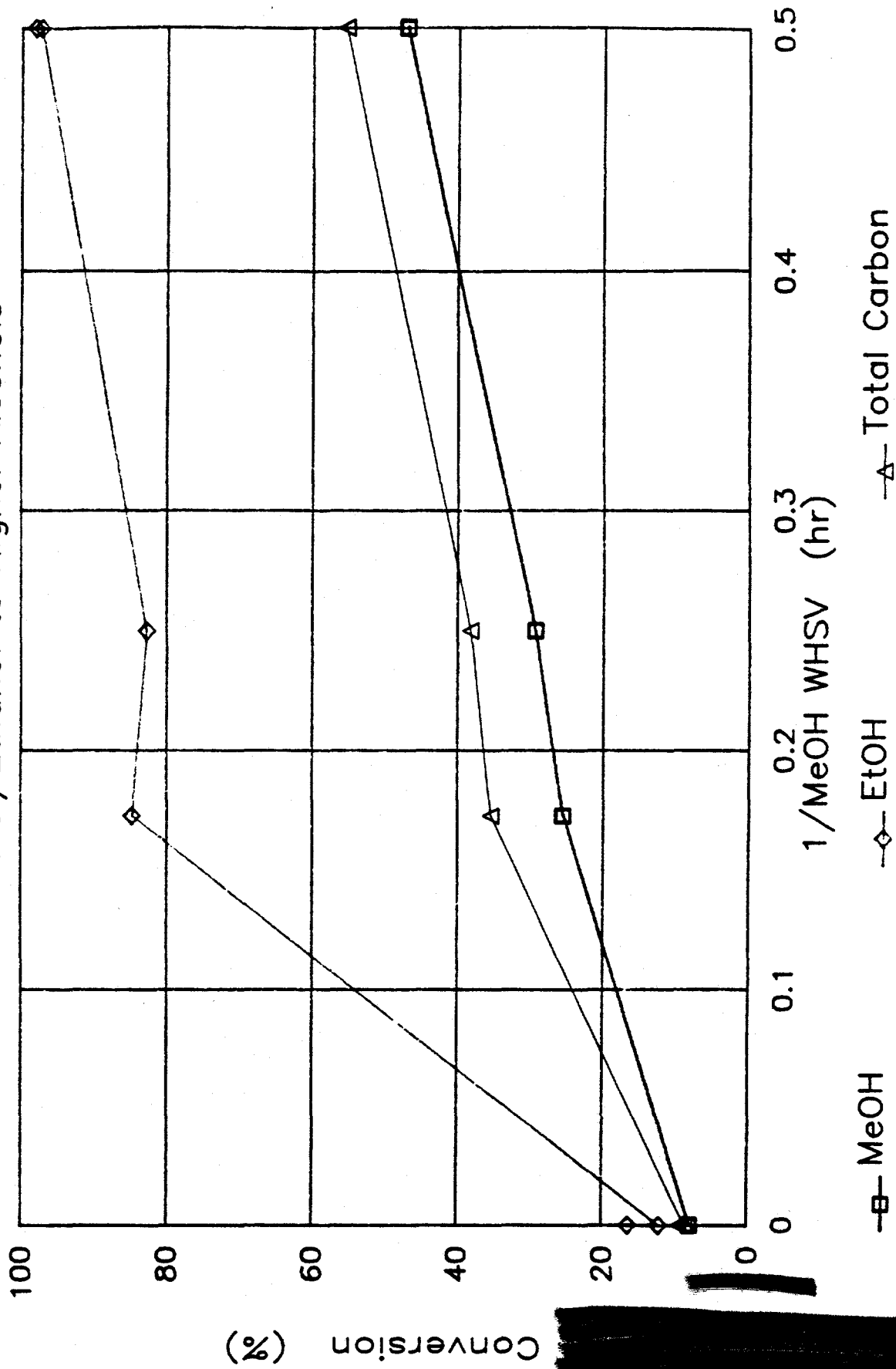


Figure 4.

Pd on Zn/Mn/Zr Oxide Performance vs. Space Time
Methanol/Ethanol to Higher Alcohols

