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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.

Previous work identified Pt or Pd on Zn/Mn/Zr co-precipitated metal oxides as promising catalysts for the conversion of a 10/1 methanol/ethanol blend to higher oxygenates.¹⁻³ A series of catalysts have been prepared to determine the effects of metal oxide support composition and noble metal loading on the performance of these catalysts. The three components of the metal oxide have been systematically varied from 10% to 60%. These supports have been tested in the pilot plant with 2% Pt and 2% Pd added. Support composition has shown a surprisingly minor affect on both catalyst activity and selectivity. Supports with high Zn (>45%) and low Zr (<33%) have afforded the best selectivities for the desired branched C₄ products. The Zn/Mn/Zr (60/20/20) support from this series has been impregnated with 0.5, 1, 2 and 5% Pt to evaluate the affect of noble metal loading. The best selectivities to the desired C₄ oxygenates has been observed with the 2% Pt loading. However, the other catalysts showed higher activities as well as lower selectivities in the standard test. Therefore, a more detailed testing protocol will be employed to establish a selectivity versus conversion relationship in order to properly compare these materials.

Evaluation of the 2% Pt on Zn/Mn/Zr (60/20/20) oxide catalyst at high space velocities has indicated that this material may have some activity for C₁-C₁ condensation needed for methanol only conversion to higher alcohols. This material and others will be tested for methanol only conversion.

Two commercial MnO₂ supports have been tested with 2% Pt and 2% Pd. These samples afford substantially higher methanol and ethanol conversions than the non-noble metal containing supports, but higher selectivity to CO_x (primarily CO). Selectivities to isobutanol are very low.

1

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EXPERIMENTAL

Catalysts

Noble Metal/Metal Oxide Catalysts. The bifunctional noble metal/mixed metal oxide catalysts described in this report have been prepared using a common procedure involving co-precipitation of a mixed metal oxide support, drying and calcination, impregnation with an aqueous noble metal solution and a second drying and calcination. Specifically, an aqueous, mixed metal nitrate solution containing all of the support components was co-precipitated by the simultaneous addition of the metal solution and an aqueous KOH solution to a stirred bucket while maintain pH at 11 and temperature at 50 °C. Using this procedure, the following new materials (with the molar compositions) have been prepared:

Zn/Mn/Zr oxide	(33/33/33) ³
Zn/Mn/Zr oxide	(45/45/10) ³
Zn/Mn/Zr oxide	(45/10/45)
Zn/Mn/Zr oxide	(10/45/45)
Zn/Mn/Zr oxide	(60/20/20)
Zn/Mn/Zr oxide	(20/60/20)
Zn/Mn/Zr oxide	(20/20/60)

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. Each of the metal oxide samples were impregnated with 2% Pt or 2% Pd using aqueous metal chloride solutions. After impregnation the materials were re-calcined at 450 °C for 6 hours to afford the final catalysts. In addition, Zn/Mn/Zr oxide supports with 10/45/45 and 20/60/20 ratios calcined at 450 °C for 6 hours (instead of 327 °C for 3 hours) prior to noble metal impregnation.

MnO₂ Based Catalysts. Two commercial samples of MnO₂ from Chemetals (CIR-189 and ODC-924) were impregnated with 2% Pt or 2% Pd by the same procedure used above for the Zn/Mn/Zr oxide catalysts.

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

Noble Metal on Mixed Metal Oxide Catalysts

Noble metal on basic mixed metal oxide supports have been identified as promising catalysts for the synthesis of higher branched alcohols from methanol and methanol/ethanol in previous work in this program.¹⁻³ The highest selectivity and productivity for isobutanol and total C₄₊ products has been obtained with 2 wt.% Pt or Pd on Zn/Mn/Zr oxide. This report describes work done under Task 2.0 of the program directed at the optimization of the catalyst formulation. Key compositional variables that have been investigated are metal oxide support composition and noble metal loading. In addition, the best catalyst from this series has been tested in the pilot plant over a range of space velocities to determine the reaction pathway during methanol/ethanol conversion.

Effect of Support Composition. The mixed metal oxide support presumably provides the solid base functionality that catalyzes the condensation of lower aldehydes (formaldehyde and acetaldehyde) formed by alcohol dehydrogenation to higher oxygenates. The basicity of the support might be expected to have a large impact on the activity and selectivity the catalyst for this condensation. Varying the composition of the mixed metal support is one approach for modifying this catalyst property. The standard pilot plant test using a methanol/ethanol blend feed has been used to determine the whether these changes have an affect on performance for alcohol condensation.

A series of 2% Pt or 2% Pd on Zn/Mn/Zr oxide catalysts have been prepared using the co-precipitation and noble metal impregnation techniques developed in previous work.² The ratios of the three major support components have been varied systematically between 10-60% to sample the compositional space of the ternary material. Table 2 summarizes the pilot plant testing results for the Pt containing catalysts. The key results are also shown in Figures 1 and 2 related to the metal oxide support composition. Figure 1 indicates methanol and ethanol conversion as well as selectivities and productivities to the desired oxygenate products. Figure 2 shows the selectivities of some of the key by-products, methyl formate and methyl

acetate which are presumably formed by Canizzarro reaction of the formaldehyde and acetaldehyde intermediates and CO_x . These results show that wide variation of the composition of the ternary metal oxide has only a small affect on catalyst performance. However, all three components appear to be important since single and dual oxide supports all have inferior performance to the ternary supports. A performance trend toward higher selectivity to isobutanol and isobutyraldehyde with increasing Zn and decreasing Zr contents can be seen in Figure 1. In addition, the lowest Zn content support gives the highest amount of Canizzarro by-products and CO. Based on these results a support composition with $>33\%$ Zn and $<33\%$ Zr appears to most preferable for higher alcohol production. Further characterization of these materials is planned to determine what key physical properties, including surface area and basicity, correlate with the observed performance.

Table 3 and Figure 3 summarize the results for Pd containing catalysts prepared on the same ternary Zn/Mn/Zr oxide supports used above. All of these materials show lower selectivities to isobutanol and isobutyraldehyde products than the Pt catalysts described above. Overall selectivities and productivities to total higher products are comparable with the Pt containing catalysts, but selectivities to the specifically desired C_4 oxygenates are substantially lower.

Effect of Pt Loading. The noble metal loading on the alcohol condensation catalyst will have a major impact on the cost of the catalyst and, therefore, the economic viability of the process. In addition, independence of the catalytic performance on the noble metal loading would suggest that alcohol condensation, rather than dehydrogenation to aldehydes, is the rate determining step in this process. If this is the case, the development of an improved catalyst needs to focus on the basic mixed metal support rather than the noble metal function.

Table 4 summarizes the pilot plant results obtained by impregnation of the Zn/Mn/Zr (60/20/20) oxide support from the support composition series with 0.5%, 1%, 2% and 5% Pt using the standard aqueous impregnation procedure. It can be seen that the highest selectivities to the desired C_4 oxygenates are obtained with the 2% Pt catalyst. However, all of the other catalysts gave higher alcohol conversion, as well as lower selectivities. Therefore, the selectivity differences could be due to activity rather than intrinsic catalytic performance. In order to properly compare these materials, a more through testing procedure, using varied space velocities to determine selectivity versus conversion relationships, is required. In contrast with the C_4 oxygenates, other by-products show clear trends with changing noble metal loadings. Increasing Pt decreases the levels of DME and CO, but increases the amount of Canizzarro products (methyl formate and methyl acetate). The latter observation suggests that more light aldehydes, particularly methyl formate, that can be condensed over the basic metal oxide via the Canizzarro reaction are produced with higher Pt catalysts.

WHSV Testing of 2%Pt on Zn/Mn/Zr Oxide. 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 alcohols² while a 2% Pd on Zn/Mn/Zr oxide catalyst shows evidence for methanol conversion to higher oxygenates at high ethanol conversion levels³. Figures 4 and 5 summarize the results obtained with these catalysts in terms of methanol and ethanol converted and isobutanol, total C₄₊ products, CO and CO₂ produced on a % of total carbon basis.

The best 2% Pt on Zn/Mn/Zr oxide catalyst (8265-76 with a 60/20/20 metal oxide support ratio) has also been evaluated at varying space velocities to determine if evidence supporting C₁-C₁ condensation can be observed. Figures 6-8 summarize the results of these runs. This data shows that the yields of C₄₊ oxygenates, particularly isobutanol and isobutyraldehyde, continue to increase as contact time is increased past the point of complete ethanol conversion (space times greater than 0.3 hr). Figure 7 shows that all three of the major C₄ oxygenate products (iBuOH, isobutyraldehyde and isobutyl methyl ether) have increasing yields in this region. The major by-products that can be produced from methanol only, methyl formate and DME, are also increasing. These results suggest that the additional higher alcohol product may be arising from methanol only. However, other side-reactions involving methanol or formaldehyde only also appear to become more important. Further tests with a methanol only feedstock are planned to further characterize the ability of these catalysts to condense methanol only to higher products.

Screening of Other Potential Catalysts for Higher Alcohol Synthesis

Two commercial MnO₂ samples obtained from Chemetals (CIR 189 and ODC 924) have been tested with 2% Pt and 2% Pd added by the standard aqueous metal chloride impregnation technique. These MnO₂ supports have shown negligible formation of higher oxygenates from methanol/ethanol without noble metal³. Table 5 summarizes the results obtained with the Pt and Pd impregnated catalysts. These catalysts show substantially higher methanol and ethanol conversions, but also higher selectivity to CO_x (primarily CO). Selectivities to isobutanol are very low. Thus, alcohol decomposition appears to be the primary reaction over these materials.

CONCLUSIONS

A series of Pt or Pd on Zn/Mn/Zr co-precipitated metal oxide catalysts have been prepared to determine the effects of metal oxide support composition and noble metal loading on the performance of these catalysts. The three components of the metal oxide have been systematically varied from 10% to 60%. These supports have been tested in the pilot plant with 2% Pt and 2% Pd added. Support composition has shown a surprisingly minor affect on both catalyst activity and selectivity. Supports with high Zn (>45%) and low Zr (<33%) have afforded the best selectivities for the desired branched C₄ products. The Zn/Mn/Zr (60/20/20) support from this series has been impregnated with 0.5, 1, 2 and 5% Pt to evaluate the affect of noble metal loading. The best selectivities to the desired C₄ oxygenates has been observed with the 2% Pt loading. However, the other catalysts showed higher activities as well as lower selectivities in the standard test. Therefore, a more detailed testing protocol will be employed to establish a selectivity versus conversion relationship in order to properly compare these materials.

Evaluation of the 2% Pt on Zn/Mn/Zr (60/20/20) oxide catalyst at high space velocities has indicated that this material may have some activity for C₁-C₁ condensation needed for methanol only conversion to higher alcohols. By-products arising from other methanol/formaldehyde only reactions (DME and methyl formate) also increase at low ethanol conditions. This material and others will be tested for methanol only conversion.

Two commercial MnO₂ supports have been tested with 2% Pt and 2% Pd. These samples afford substantially higher methanol and ethanol conversions than the non-noble metal containing supports, but higher selectivity to CO_x (primarily CO). Selectivities to isobutanol are very low.

REFERENCES

- 1) P. T. Barger, DOE Quarterly Report No. 12, (1994).
- 2) P. T. Barger, DOE Quarterly Report No. 13, (1994).
- 3) P. T. Barger and P. R. Kurek, DOE Quarterly Report No. 14, (1994).

Table 1. Run List

RUN	CATALYST		CATALYST DESCRIPTION	CATALYST B	LOADING	TEMP (C)	CONDITIONS		FEED RATIO
	A	B					TOTAL	MeOH	
	Book #	Book #			g	INLET	PSIG	WHSV	MeOH/EOH/N ₂ (H ₂)
263	8265-56		2.0%Pd / Zn/Mn/Zr (45/10/45) Oxide		5	350	30	2	1/0.1/2 N ₂
264	8265-60		2.0%Pd / MnO ₂ (Chemicals CIR 189)		5	350	30	2	1/0.1/2 N ₂
265	8265-61		2.0%Pt / MnO ₂ (Chemicals CIR 189)		5	350	30	2	1/0.1/2 N ₂
266	8265-64		2.0%Pd / Zn/Mn/Zr (10/45/45) Oxide (450C calc)		5	350	30	2	1/0.1/2 N ₂
267	8265-63		2.0%Pt / MnO ₂ (Chemicals ODC 924)		5	350	30	2	1/0.1/2 N ₂
268	8265-66		2.0%Pd / MnO ₂ (Chemicals ODC 924)		5	350	30	2	1/0.1/2 N ₂
269	8265-66		777%Pt / Zn/Mn/Zr (10/45/45) Oxide (450C calc)		5	350	30	2	1/0.1/2 N ₂
270	8265-69		2.0%Pd / Zn/Mn/Zr (20/60/20) Oxide (450C calc)		5	350	30	2	1/0.1/2 N ₂
271	8265-70		777%Pt / Zn/Mn/Zr (20/60/20) Oxide (450C calc)		5	350	30	2	1/0.1/2 N ₂
272	8265-76		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide		5	350	30	2	1/0.1/2 N ₂
273	8265-77		2.0%Pt / Zn/Mn/Zr (45/10/45) Oxide		5	350	30	2	1/0.1/2 N ₂
274	8265-76		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide		4	350	30	2.5	1/0.1/2 N ₂
275	8265-76		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide		3	350	30	3.3	1/0.1/2 N ₂
276	8265-76		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide		2	350	30	5	1/0.1/2 N ₂
277	8265-76		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide		1	350	30	10	1/0.1/2 N ₂
278	8265-82		2.0%Pt / Zn/Mn/Zr (10/45/45) Oxide		5	350	30	2	1/0.1/2 N ₂
279	8265-80		2.0%Pt / Zn/Mn/Zr (20/20/60) Oxide		5	350	30	2	1/0.1/2 N ₂
280	8265-83		2.0%Pd / Zn/Mn/Zr (10/45/45) Oxide		5	350	30	2	1/0.1/2 N ₂
281	8265-84		2.0%Pt / Zn/Mn/Zr (20/60/20) Oxide		5	350	30	2	1/0.1/2 N ₂
282	8265-85		2.0%Pd / Zn/Mn/Zr (20/60/20) Oxide		5	350	30	2	1/0.1/2 N ₂
283	8265-81		2.0%Pd / Zn/Mn/Zr (20/20/60) Oxide		5	350	30	2	1/0.1/2 N ₂
284	8265-86		0.5%Pt / Zn/Mn/Zr (60/20/20) Oxide		5	350	30	2	1/0.1/2 N ₂
285	8265-87		1.0%Pt / Zn/Mn/Zr (60/20/20) Oxide		5	350	30	2	1/0.1/2 N ₂
286	8265-86		5.0%Pt / Zn/Mn/Zr (60/20/20) Oxide		5	350	30	2	1/0.1/2 N ₂
287	8265-89		2.0%Pt / Zn/Mn/Zr (10/45/45) Oxide	Calched @ 450C before Impregnation	5	350	30	2	1/0.1/2 N ₂
288	8265-90		2.0%Pt / Zn/Mn/Zr (20/20/60) Oxide	Calched @ 450C before Impregnation	5	350	30	2	1/0.1/2 N ₂

**Table 2. Effect of Support Composition -
2% Pt on Zn/Mn/Zr Oxide Supports**

Catalyst Number	8265-76	8265-36	8265-77	8265-50	8265-80	8265-90	8265-82
Description	2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)	2.0% Pt on Zn/Mn/Zr Oxide (45/45/10)	2.0% Pt on Zn/Mn/Zr Oxide (45/10/45)	2.0% Pt on Zn/Mn/Zr Oxide (33/33/33)	2.0% Pt on Zn/Mn/Zr Oxide (20/20/60)	2.0% Pt on Zn/Mn/Zr Oxide (20/60/20)	2.0% Pt on Zn/Mn/Zr Oxide (10/45/45)
Run	272	260	273	258	279	288	278
Conditions	350 C, 30 psig, 2 hr-1 MeOH WHSV, 1/0.1/2 MeOH/EtOH/N ₂ (molar)						
Conversion (%)							
MeOH	58.7	63.6	68.3	57.3	59.0	69.9	73.3
EtOH	100.0	100.0	100.0	99.8	99.4	100.0	100.0
Selectivity (C%)							
nC3OH	0.0	0.0	0.0	0.2	0.3	0.0	0.0
nC4OH	0.0	0.0	0.0	0.0	0.1	0.1	0.0
iC4OH	11.1	10.4	8.0	10.8	8.9	8.2	8.9
iC4 Aldehyde	17.7	16.5	11.3	15.6	11.7	12.1	12.0
Me iButyrate	5.3	3.6	6.8	4.9	4.8	6.3	7.3
MeiBu Ether	0.0	0.1	0.3	0.0	0.0	0.0	0.1
C5+OH	0.9	0.9	0.9	1.1	1.5	1.3	1.0
Other Ald/Ketone	0.8	0.9	0.7	0.9	1.2	0.8	0.8
Other Esters	0.3	0.8	1.4	0.4	0.5	0.5	0.9
Others	5.3	7.6	5.2	9.8	18.8	13.1	4.9
DiME Ether	1.1	0.6	3.6	1.3	2.4	1.4	1.0
MeEt Ether	0.0	0.0	0.0	0.0	0.1	0.0	0.0
Me Formate	2.5	4.2	3.3	2.7	1.5	1.7	0.6
Me Acetate	1.8	1.6	2.6	2.2	2.2	1.2	0.2
C1	0.8	1.4	2.2	0.9	0.8	1.3	0.6
C2+s	1.1	2.8	1.5	2.1	2.4	1.6	0.8
CO	25.4	22.5	24.2	21.0	15.5	24.5	38.6
CO ₂	26.0	27.4	26.4	26.2	27.0	25.9	22.3

**Table 3. Effect of Support Composition -
2% Pd on Zn/Mn/Zr Oxide Supports**

Catalyst Number	8265-34	8265-56	8265-22	8265-81	8265-85	8265-83
Description	2.0% Pd on Zn/Mn/Zr Oxide (45/45/10)	2.0% Pd on Zn/Mn/Zr Oxide (45/10/45)	2.0% Pd on Zn/Mn/Zr Oxide (33/33/33)	2.0% Pd on Zn/Mn/Zr Oxide (20/20/60)	2.0% Pd on Zn/Mn/Zr Oxide (20/60/20)	2.0% Pd on Zn/Mn/Zr Oxide (10/45/45)
Run	251	263	247	283	282	280
Conditions	350 C, 30 psig, 2 hr ⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N ₂ (molar)					
Conversion (%)						
MeOH	44.4	70.0	45.0	53.5	33.2	50.9
EtOH	96.4	98.7	97.3	97.0	66.5	96.4
Selectivity (C%)						
nC3OH	1.3	0.3	1.2	1.5	2.7	1.5
nC4OH	0.3	0.1	0.2	0.3	0.1	0.1
iC4OH	5.9	7.0	7.3	5.1	1.0	7.4
iC4 Aldehyde	12.1	8.7	11.8	7.3	4.1	9.6
Me iButyrate	1.8	3.5	2.2	1.5	1.3	2.9
MeiBu Ether	0.1	0.1	0.0	0.1	0.0	0.0
C5+OH	1.2	1.0	1.1	0.4	0.7	1.0
Other Ald/Ketone	4.1	1.2	3.2	3.8	11.7	4.0
Other Esters	0.3	1.2	0.4	0.5	0.2	0.3
Others	14.4	23.1	12.0	25.5	18.9	19.7
DiME Ether	0.5	2.2	1.6	2.6	0.4	0.7
MeEt Ether	0.0	0.1	0.0	0.1	0.0	0.0
Me Formate	7.0	3.6	2.1	2.0	0.3	0.9
Me Acetate	4.1	3.2	3.0	2.9	0.9	1.7
C1	1.1	0.9	1.2	1.1	0.7	0.5
C2+s	5.4	4.3	5.2	6.0	1.4	2.8
CO	13.6	13.5	21.7	14.4	40.4	21.7
CO ₂	27.0	25.9	26.0	24.8	15.1	25.2

Table 4. Effect of Noble Metal Loading - Pt on Zn/Mn/Zr Oxide Supports

Catalyst Number	8265-86	8265-87	8265-76	8265-88
Description	0.5% Pt on Zn/Mn/Zr Oxide (60/20/20)	1.0% Pt on Zn/Mn/Zr Oxide (60/20/20)	2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)	5.0% Pt on Zn/Mn/Zr Oxide (60/20/20)
Run	284	285	272	286
Conditions	350 C, 30 psig, 2 hr-1 MeOH WHSV, 1/0.1/2 MeOH/EtOH/N2 (molar)			
Conversion (%)				
MeOH	68.5	71.6	58.7	67.6
EtOH	100.0	100.0	100.0	99.8
Selectivity (C%)				
nC3OH	0.0	0.0	0.0	0.1
nC4OH	0.1	0.0	0.0	0.1
iC4OH	8.5	9.2	11.1	8.2
iC4 Aldehyde	12.1	12.1	17.7	10.9
Me iButyrate	6.5	6.2	5.3	3.0
MeiBu Ether	0.1	0.1	0.0	0.1
C5+OH	1.3	1.1	0.9	0.9
Other Ald/Ketone	0.8	0.7	0.8	0.8
Other Esters	0.6	0.4	0.3	0.7
Others	6.2	8.5	5.3	15.3
DiME Ether	2.1	1.3	1.1	0.6
MeEt Ether	0.0	0.0	0.0	0.1
Me Formate	1.0	1.2	2.5	3.3
Me Acetate	0.9	0.5	1.8	1.8
C1	1.0	1.2	0.8	1.3
C2+s	1.0	1.1	1.5	3.2
CO	32.9	31.6	25.4	22.6
CO2	24.8	24.7	26.0	27.2

Table 5. Screening of Other Potential Higher Alcohols Catalysts

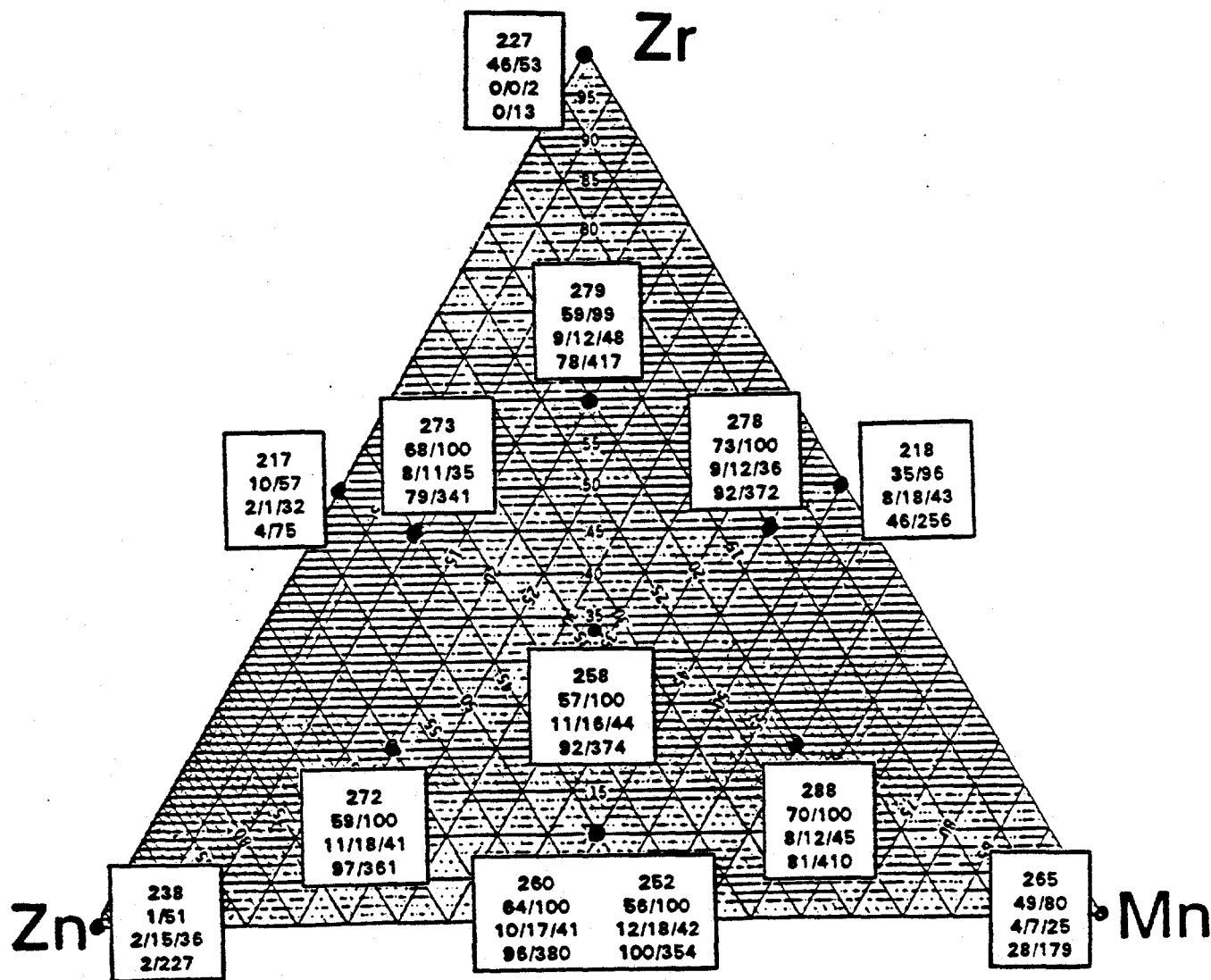
Catalyst Catalyst Number	Run	Conversion (%)		Selectivity (mole%)		Productivity (g/kg cat/hr)
		MeOH	EtOH	iC ₄ OH	CO _x	
Commercial MnO ₂						
Chemetals CIR-189						
None	254	7	6	3	8	2
2% Pt	265	49	80	4	64	28
2% Pd	264	42	81	3	48	20
Chemetals ODC-924						
None	255	7	-6	4	14	2
2% Pt	267	57	79	1	78	11
2% Pd	268	16	36	2	50	6

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

Figure 1.

2% Pt on Zn/Mn/Zr Oxide Catalysts Effect of Support Composition

Testing Conditions: 350 °C, 30 psig, 2 hr⁻¹ MeOH WHSV,
1/0.1/2 MeOH/EtOH/N₂ (molar)

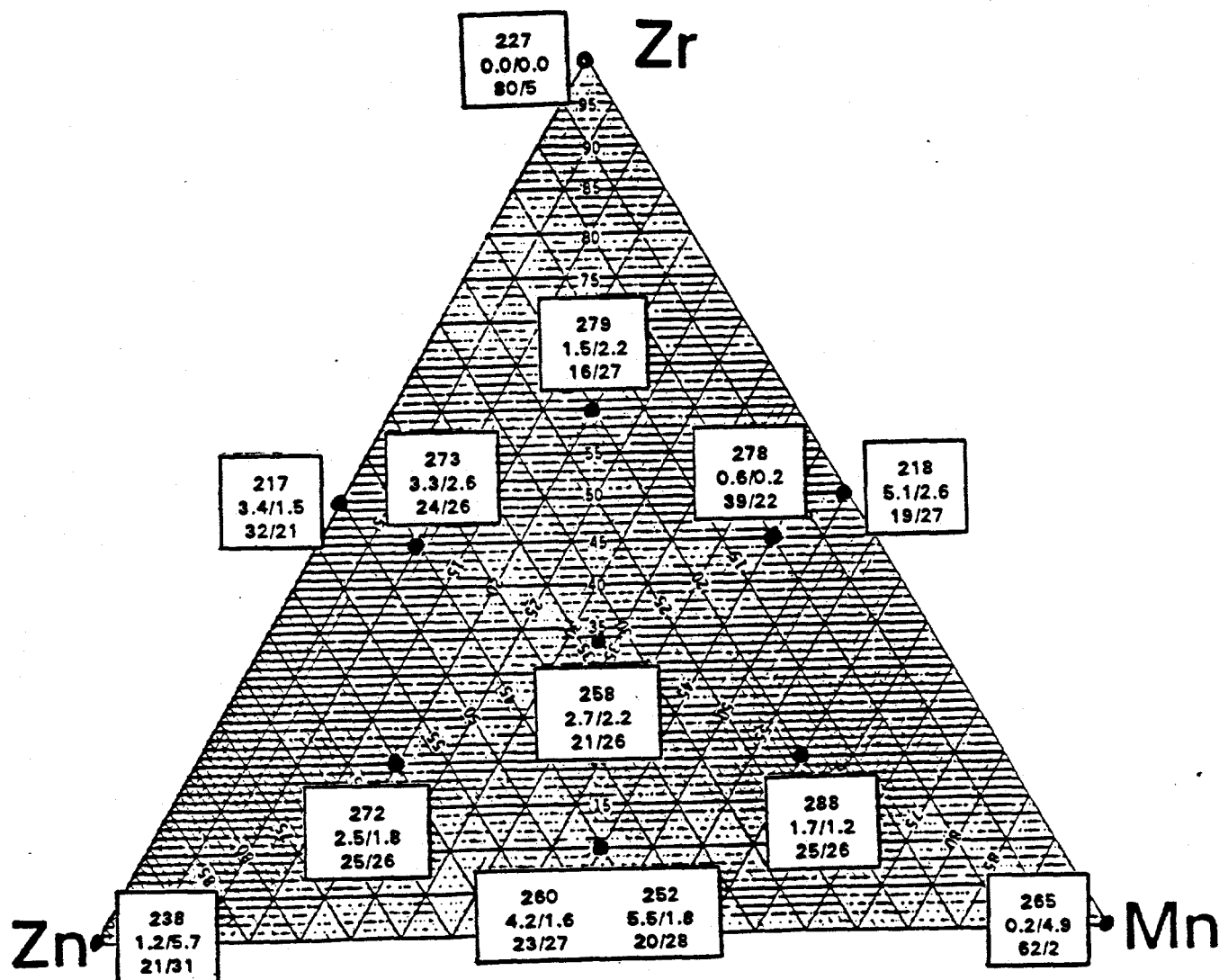


Run Number
MeOH/EtOH Conversions (%)
iC ₄ OH/iC ₄ Ald/Sum C ₄₊ Selectivities (mole %)
iC ₄ OH/Sum C ₄₊ Productivities (g/kg cat/hr)

Figure 2.

2% Pt on Zn/Mn/Zr Oxide Catalysts Effect of Support Composition

Testing Conditions: 350 °C, 30 psig, 2 hr⁻¹ MeOH WHSV,
1/0.1/2 MeOH/EtOH/N₂ (molar)

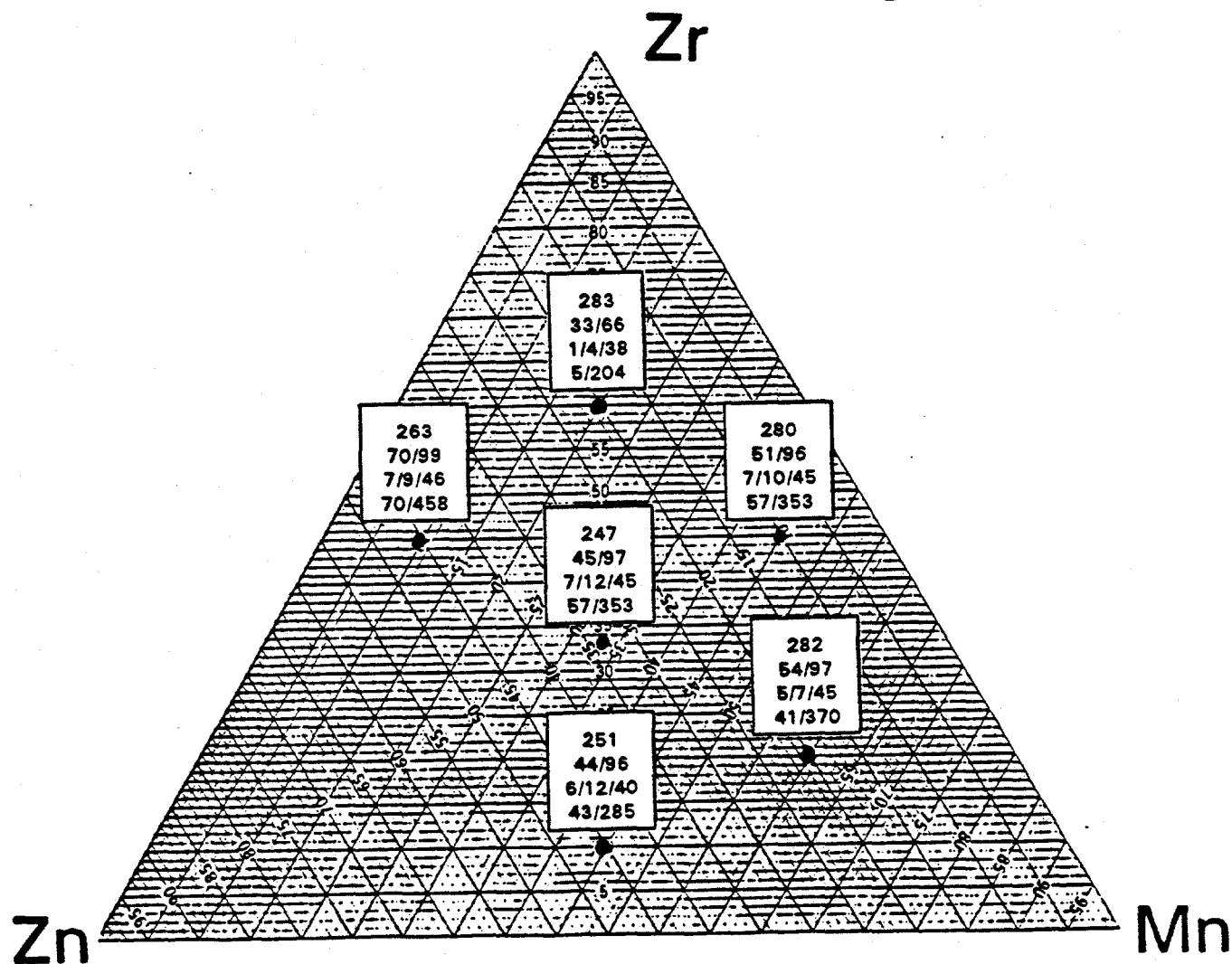


Run Number
Me Formate/Me Acetate Selectivities (mole %)
CO/CO₂ Selectivities (mole %)

Figure 3.

2% Pd on Zn/Mn/Zr Oxide Catalysts Effect of Support Composition

Testing Conditions: 350 °C, 30 psig, 2 hr⁻¹ MeOH WHSV,
1/0.1/2 MeOH/EtOH/N₂ (molar)



Run Number
MeOH/EtOH Conversions (%)
iC ₄ OH/iC ₄ Ald/Sum C ₄₊ Selectivities (mole %)
iC ₄ OH/Sum C ₄₊ Productivities (g/kg cat/hr)

Figure 4.

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

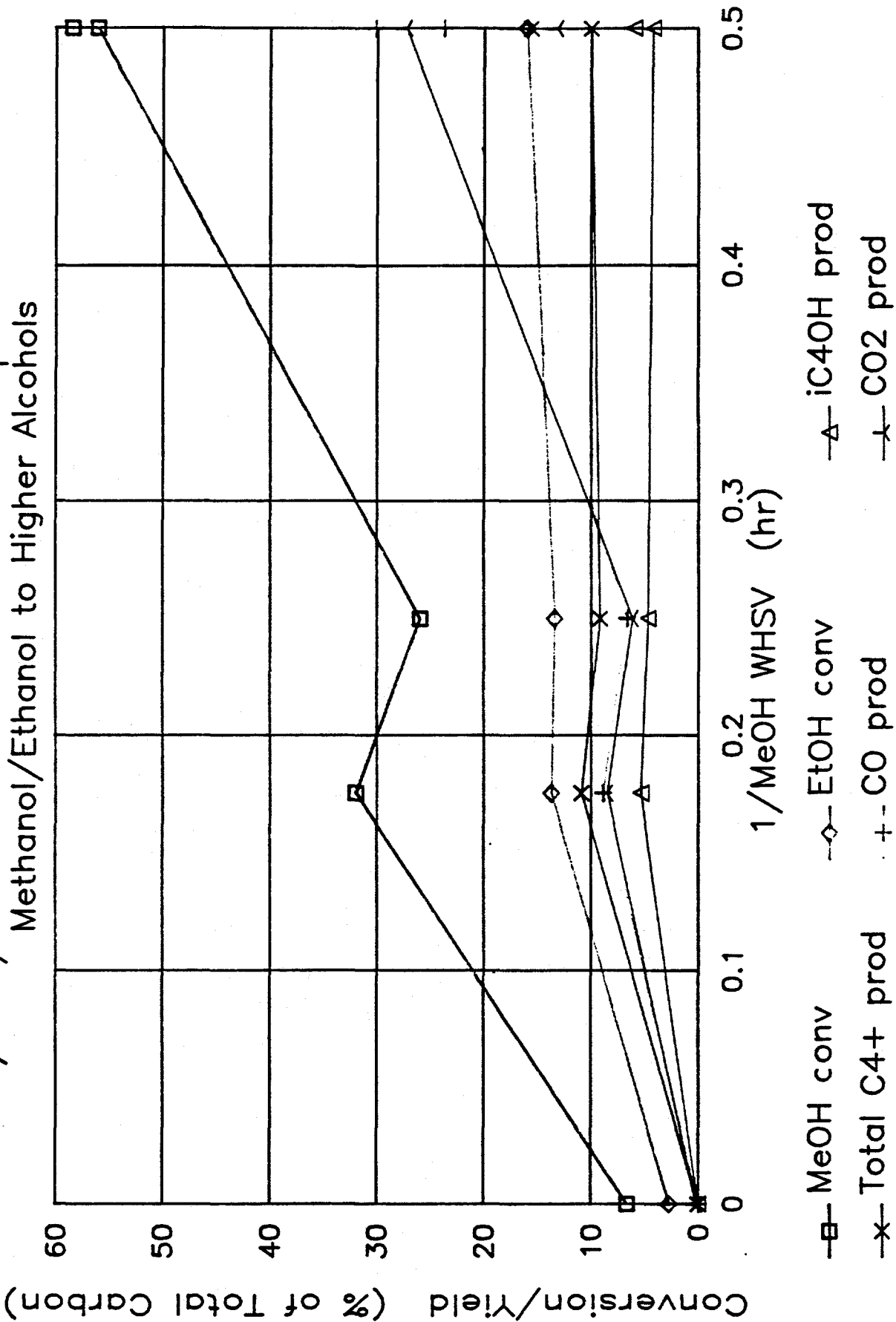


Figure 5.

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

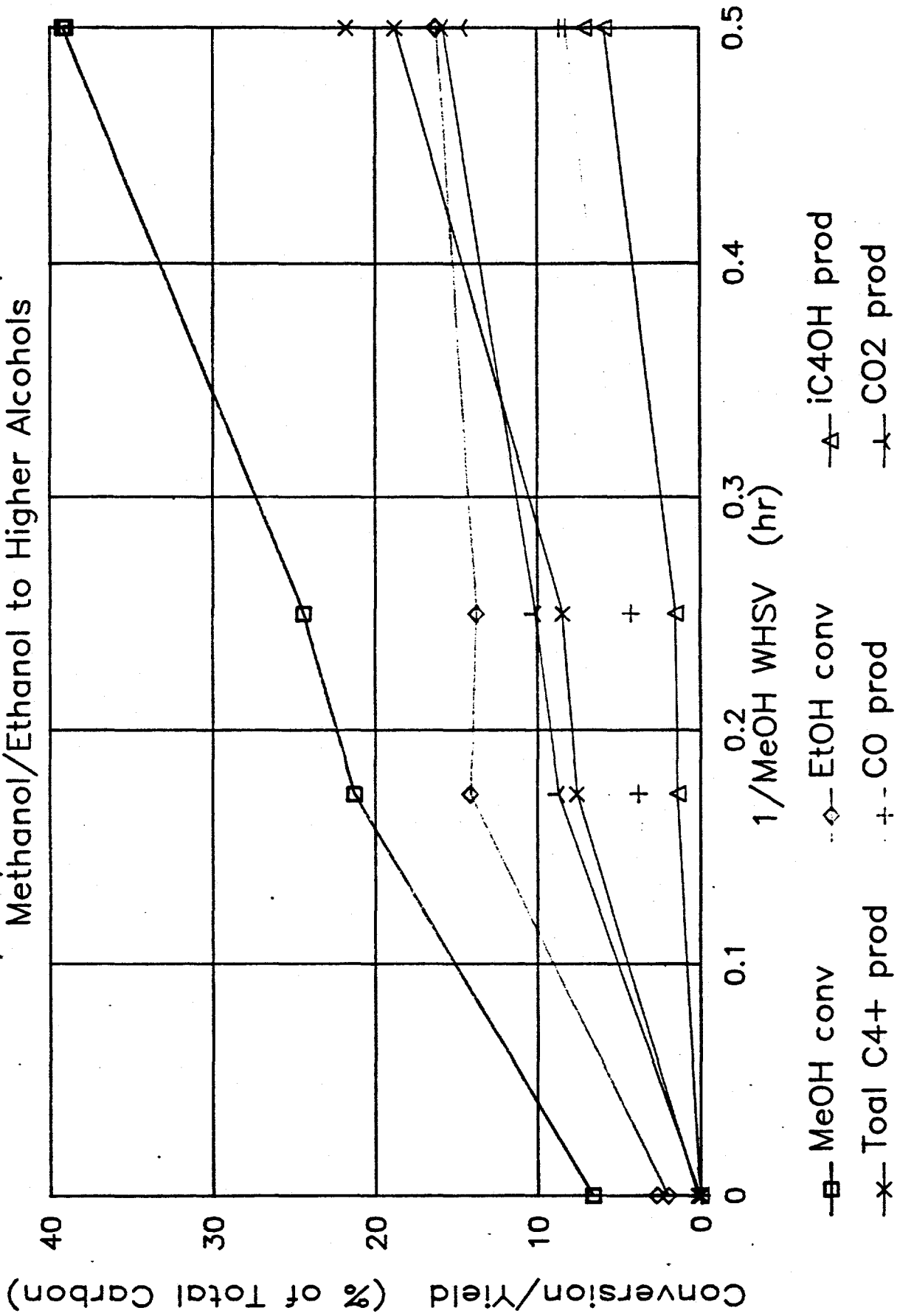


Figure 6.

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

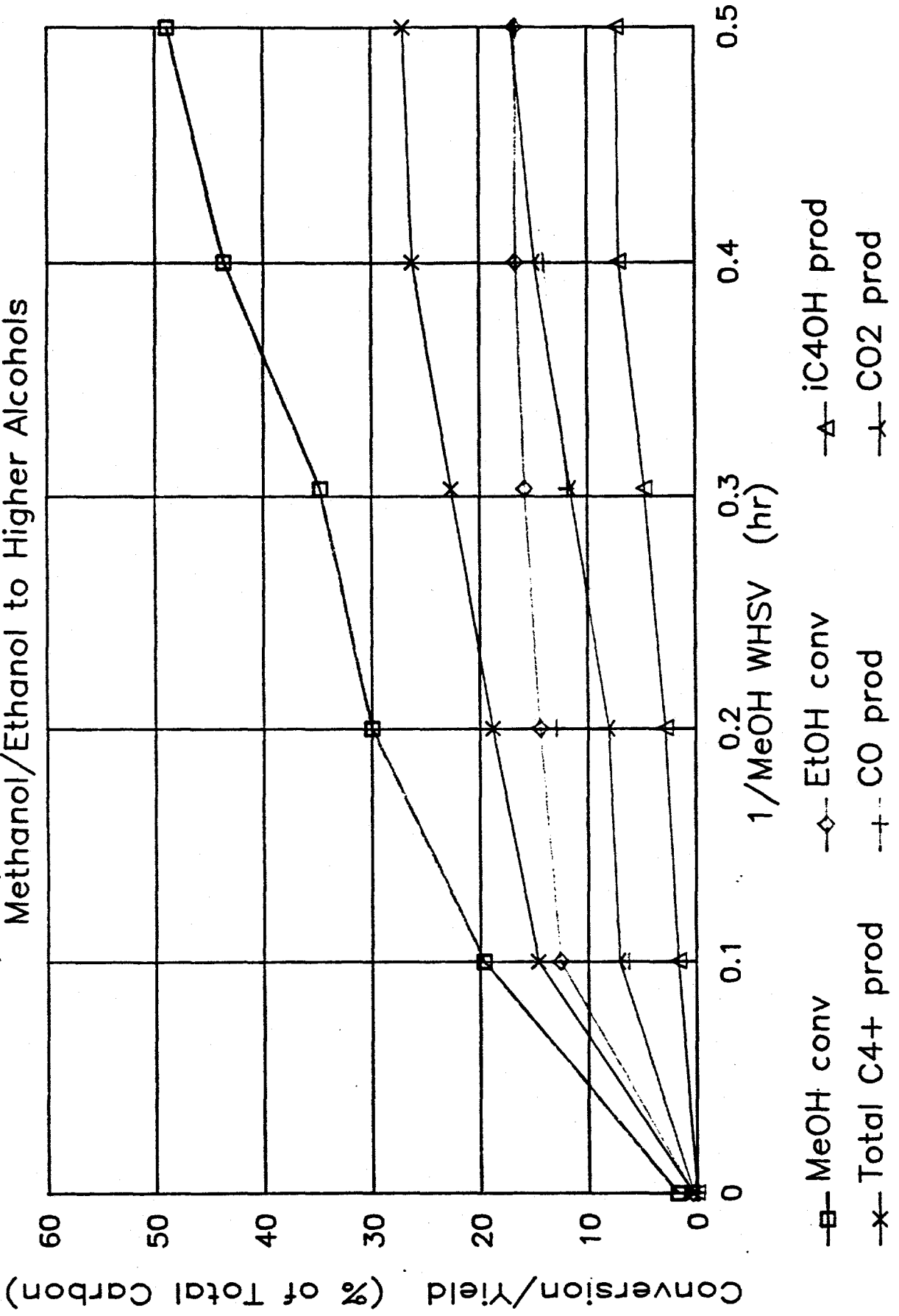


Figure 7.

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

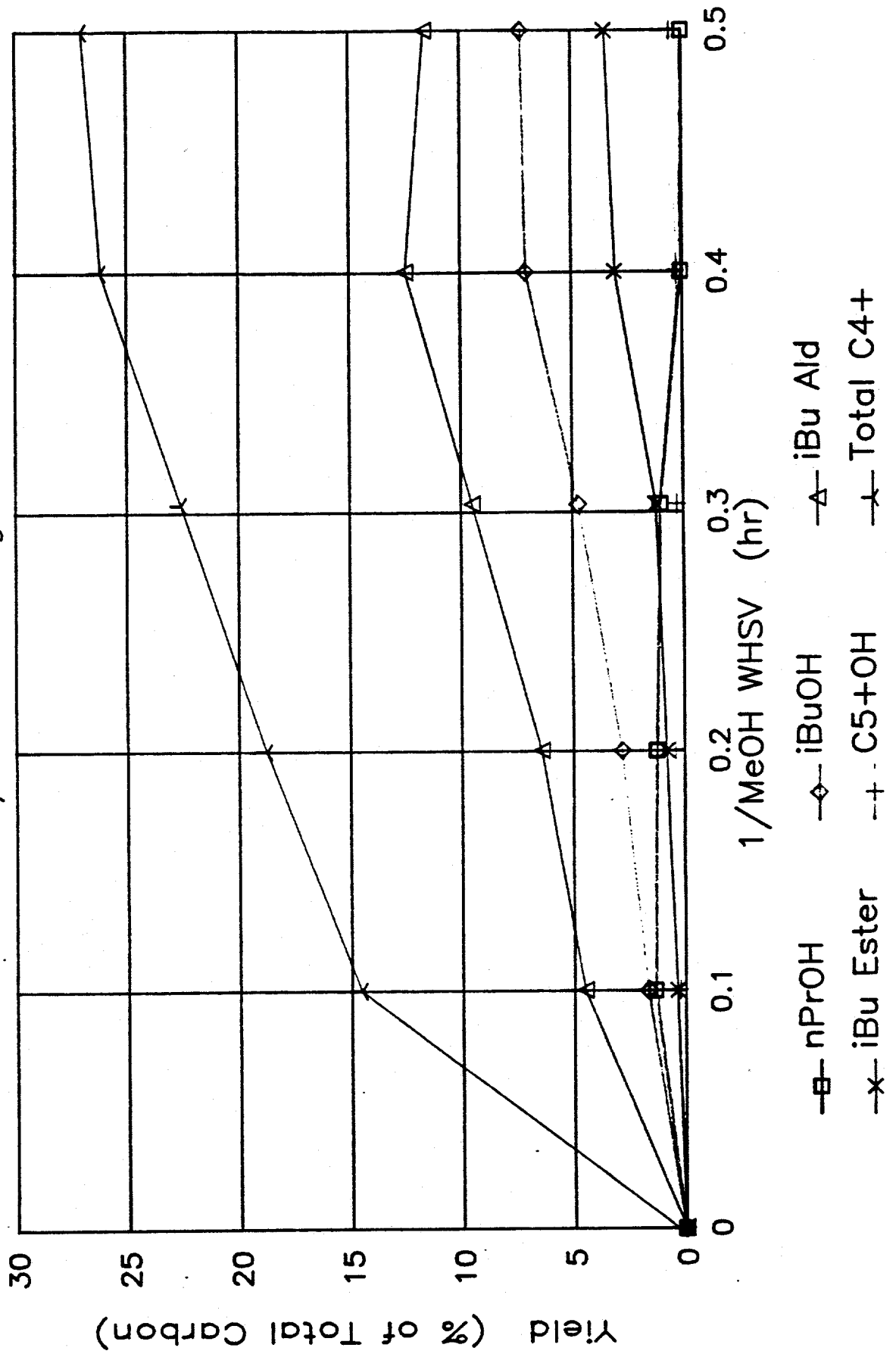


Figure 8.

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

