DOE/PC/90042--T13

CONTRACT TITLE AND NUMBER:
Development of a Catalyst for Conversion
of Syngas-Derived Materials to Isobutylene
DE-AC22-91PC90042

Date:
Quarterly Report No. 14
Reporting Period:
7/1/94-9/30/94

Contractor:
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Contract Period: March 15, 1991 to September 14, 1995

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 had identified Pt and Pd on Zn/Mn/Zr oxide and Pd on Zn/Mn/Cr oxide as promising catalysts for the conversion of a 10/1 methanol/ethanol blend to higher oxygenates.[1,2] The reproducibility of these catalyst preparations has been found to be generally good, although some variations in performance have been observed between the Pd containing samples. Further characterization of the catalysts showing performance differences is in progress to determine whether compositional variations can account for the discrepancies.

Several new 2% Pt on metal oxide catalysts have been prepared and tested. None of these materials performed better than the original 2% Pt on Zn/Mn/Zr (34/34/32 molar) oxide catalyst. However, a lower Zr content support (45/45/10 Zn/Mn/Zr oxide) gave similar results.

Evaluation of the 2% Pd on Zn/Mn/Cr oxide at high space velocities has indicated that this material may be substantially less active for the C_1-C_1 condensation step necessary for methanol only conversion to higher alcohols. In view of this finding, subsequent research will focus on the development of the Zn/Mn/Zr oxide support.

A variety of alternative catalyst formulations have also been prepared and tested, but have failed to match the performance of noble metal on mixed metal oxide catalysts. These materials have include Cu and Mo on TiO_2, Mg/Al MOSS and polyvinylpyridine and commercial and laboratory prepared Mn oxide samples.

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EXPERIMENTAL

Catalysts

Noble Metal/Metal Oxide Catalysts. The bifunctional noble metal/mixed metal oxide catalyst 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	(34/34/32, repeat of previous preparation)
Zn/Mn/Zr oxide	(45/45/10)
Zn/Mn/Cr oxide	(34/33/33, repeat of previous preparation)
Zn/Mn/La oxide	(34/32/34)
Zr oxide	
Zn oxide	
Zn/Mg oxide	(50/50)

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. The ZnO and Zn/Mg oxide supports did not have sufficient physical strength to maintain 20-40 mesh granules. Therefore, these two materials were bound with 50% SiO_2 by making a paste with an aqueous colloidal silica solution (Ludox AS-40) and evaporating the excess water at 90 °C. A high potassium content (6 wt.%) Zn/Mn/Zr (34/34/32) oxide support was prepared by reducing the post-precipitation water washing from about 50 liters to 4 liters. Single metal oxide samples were also obtained from commercial sources: MnO_2 from Chemetals (CIR-189) and MgO from Marine Magnesium Company (Maglite D). Each of the metal oxide samples were impregnated with Pd or Pd using aqueous metal chloride solutions. After impregnation the materials were re-calcined at 450 °C for 6 hours to afford the final catalysts.

Supported Cu and Mo Catalysts. A series of copper and molybdenum containing catalysts have been prepared on a variety of supports, including TiO_2 (Engelhard, TI-0720T), Mg/Al MOSS (Alcoa, Sorbplus) and a polyvinylpyridine resin (Reilly, PVP425). Each of these materials was impregnated with aqueous solutions of either ammonium molybdate or copper acetate to give 2 wt.% metal on the support. After drying at 110 °C, each catalyst was treated with an ethanolic solution of sodium borohydride for 30-45 minutes to reduce the impregnated metal to the zero valent state. The catalyst was recovered by filtration and dried at 115 °C for 16 hr. In addition, the polyvinylpyridine support was impregnated with Pd using the same procedure used for the mixed metal oxide catalysts.

MnO_2 Based Catalysts. Several samples of MnO_2 have been evaluated with no additional noble metal. These have included two commercial MnO_2 materials obtained from Chemetals (CIR-189 and ODC-924) which were used as received. In addition two experimental manganese oxide samples with the cryptomelane and pharmacosiderite structures have been prepared in-house. The CIR-189 commercial MnO_2 support was also impregnated with a methanolic solution of cobalt phthalocyanine to afford a catalyst with 250ppm Co after calcination at 327 °C in air.

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 N_2 at 250 °C, 10 psig, 0.5 scf/hr for 1 hour then pressure tested with N_2 at 250 °C, 500 psig for 1 hour. After restarting the N_2 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 CO_2) 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.[1,2] The highest selectivity and productivity for isobutanol and total C_{4+} products has been obtained with 2 wt.% Pt or Pd on Zn/Mn/Zr oxide and 2 wt.% Pd on Zn/Mn/Cr oxide catalysts. This report describes testing on the reproducibility of these catalyst formulations as well as testing on other experimental catalyst formulations.

New samples of Zn/Mn/Zr and Zn/Mn/Cr oxide supports have been prepared following the same procedures used previously.[2] Table 2 summarizes the pilot plant results obtained with catalysts prepared by the impregnation of these supports with Pd for the conversion of a 10/1 methanol/ethanol blend to higher oxygenates and compares them with earlier catalyst samples. In the case of the Zn/Mn/Zr support, a first reproduction shows very comparable performance to the earlier sample. However, another sample prepared by a separate Pd impregnation on this second Zn/Mn/Zr oxide support showed substantially lower activity and selectivity to isobutanol. Differences in performance between two Pd impregnations on the same support are also seen with the original Zn/Mn/Cr oxide support. In this case, activities were similar but selectivities to isobutanol and total C_{4+} products were different. A second co-precipitation of the Zn/Mn/Cr oxide support afforded a very poor catalyst with low activity and selectivity to isobutanol. Elemental analyses of these samples are in progress to determine whether the lack of reproducibility is due to catalyst composition variations.

Better catalyst preparation reproduciblity has been obtained with two Pt containing catalysts made on Zn/Mn/Zr and Zn/Mn/Cr oxide supports. Table 3 compares the pilot plant results of these catalysts with earlier samples. The Pt on Zn/Mn/Zr oxide sample shows good reproducibility with the previous material, while the Pt on Zn/Mn/Cr catalyst shows lower activity and higher selectivity to total C_{4+} products than the original sample. It should be noted that the poor performances of these Zn/Mn/Cr catalysts is similar to that of the Pd catalyst prepared using the second Zn/Mn/Cr oxide support. Table 3 also shows the results of two pilot plant runs of a single catalyst (Pt on 45/45/10 Zn/Mn/Zr oxide) that gave very similar conversions and selectivities. Therefore, the differences in performance appear to be due to catalyst variations rather than changes in plant operation.

Tables 3 and 4 also show the results of additional Pt containing catalysts for this process. None of these materials give performances that exceed that of the Pt on Zn/Mn/Zr (34/34/32 molar) oxide catalyst. Reduction of the Zr content of the Zn/Mn/Zr support to a 45/45/10 molar ratio shows little effect on performance. In contrast, the presence of a high level of K on the catalyst, by reducing the washing of the wet support after the KOH precipitation, has a deleterious effect on activity and selectivity. Two formulations where the Zr component is replaced with either Ce or La are also listed in Table 3. Both of these materials have activities comparable to the Zn/Mn/Zr oxide catalyst. The Ce sample gives selectivities that are only slightly lower than the Zn/Mn/Zr oxide, while the La sample is significantly poorer. Table 4 shows the results of Pt catalysts prepared on pure metal oxide supports. In the case of ZnO, the oxide powder was bound with 50% SiO_2 to obtain a material with a particle size sufficient for use in the pilot plant. While the ZnO sample shows some activity and selectivity for isobutanol formation, the MnO_2 and ZrO_2 samples have virtually no activity. Finally, a Zn/Mg oxide support, also made with a SiO_2 binder, shows high activity but low selectivity to isobutanol and total higher products.

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

One of the primary mechanistic questions in the production of branched C_4 oxygenates from methanol is the relative rates of the C_1-C_1 and C_1-$C_{2,3}$ condensation steps. While the latter condensation is sufficient for the production of higher alcohols from a methanol/ethanol feed blend, the C_1-C_1 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 C_1-C_1 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 alcohols[1] while a 2% Pd on Zn/Mn/Zr oxide catalyst shows evidence for methanol conversion to higher oxygenates at high ethanol conversion levels. Figures 1 and 2 summarize the results obtained with these catalysts in terms of methanol and ethanol converted and isobutanol, total C_{4+} products, CO and CO_2 produced on a % of total carbon basis.

The 2% Pd on Zn/Mn/Cr oxide catalyst (7887-90) has also been evaluated at varying space velocities to determine if C_1-C_1 condensation is occurring with this material. Figure 3 summarizes the results of these runs. This data shows that at space velocities where ethanol conversion is complete (space times greater than 0.2 hr), the yield of isobutanol and total C_{4+} products is flat. This indicates that the additional methanol converted is going to other products, mainly CO and CO_2. Therefore, the Zn/Mn/Cr support appears less active for methanol conversion than the Zn/Mn/Zr oxide. In addition, comparison of the CO yields in Figures 2 and 3 shows that the Zn/Mn/Cr support is much more active for the decomposition of the light alcohols. Based on these findings, subsequent research will focus on the Zn/Mn/Zr support. The effect of support composition and noble metal concentration will be evaluated.

Screening of Other Potential Catalysts for Higher Alcohol Synthesis

Pd and Pt on MgO catalysts have shown no activity for the formation of higher oxygenates from methanol/ethanol (Table 5). Rather, virtually complete decomposition of the light alcohols to CO is observed. The only other products are light hydrocarbons.

A series of Cu and Mo containing catalyst have been prepared on TiO2, Mg/Al MOSS, polyvinylpyridine polymer supports. The performances of these material are summarized in Table 5. The Cu on metal oxide samples give isobutanol and total C_{4+} product selectivities that are comparable with those obtained with the best Pt catalysts, but activity is substantially lower. The Mo containing catalysts have higher

[redacted]

alcohols conversions, but poorer selectivities to the desired products. The polyvinylpyridine supported catalysts all show very low conversion and no production of either isobutanol or CO_x.

A variety of commercial and lab prepared MnO_2 catalysts with no noble metal addition have been evaluated in the standard methanol/ethanol pilot plant test. These catalysts all show very low activity and selectivity for isobutanol (Table 6). The negative selectivities observed for ethanol suggest that some methanol is being converted to ethanol over these catalysts, but the levels are very low.

CONCLUSIONS

The reproducibility of Pt and Pd on Zn/Mn/Zr oxide and Pd on Zn/Mn/Cr oxide catalyst preparations has been found to be generally good, although some variations in performance have been observed between the Pd containing samples. Further characterization of the catalysts showing performance differences is in progress to determine whether compositional variations can account for the discrepancies. The reaction pathway for methanol/ethanol conversion over the 2% Pd on Zn/Mn/Cr oxide has been investigated using high space velocity testing. This work has indicated that this material may be substantially less active for the C_1-C_1 condensation step necessary for methanol only conversion to higher alcohols. In view of this finding, subsequent research will focus on the development of the Zn/Mn/Zr oxide support.

Several new 2% Pt on metal oxide catalysts have been prepared and tested. None of these materials performed better than the original 2% Pt on Zn/Mn/Zr (34/34/32 molar) oxide catalyst. However, a lower Zr support (45/45/10 Zn/Mn/Zr oxide) gave similar results. A variety of alternative catalyst formulations have also been prepared and tested, but have failed to match the performance of noble metal on mixed metal oxide catalysts.

Catalyst development will now be shifted to the development of a noble metal on Zn/Mn/Zr catalyst. Initial work will focus on optimizing the catalyst formulation (support composition, level of noble metal and preparation procedure). Pilot plant work will also be directed at key process variable concerns. These include the conditions required to obtain satisfactory conversion of methanol alone and the effect of co-feeds, such as CO and CO_2, to suppress undesired by-products.

REFERENCES

[redacted]

1) P. T. Barger, DOE Quarterly Report No. 12, (1994).

2) P. T. Barger, DOE Quarterly Report No. 13, (1994).

Table 1. Run List

RUN	CATALYST A Book #	CATALYST B Book #	CATALYST DESCRIPTION CATALYST A	CATALYST DESCRIPTION CATALYST B	SIZE	LOADING g	CONDITIONS TEMP (C) INLET	CONDITIONS TEMP (C) MAX	CONDITIONS TOTAL PSIG	CONDITIONS MeOH WHSV	CONDITIONS FEED RATIO MeOH/EtOH/N2(H2)
224	7887-82		2.0%Pt / Zn/Mn/La (34/32/34) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
225	7887-84		2.0%Pt / Zn/Mn/Zr/K (34/34/32/6%) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
226	7887-62		2.0%Pt / Zn/Mn/Cr (34/33/33) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
227	7887-86		2.0%Pt / Zr (100) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
228	7887-90		2.0%Pd / Zn/Mn/Cr (34/33/33) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
229	7887-90		2.0%Pd / Zn/Mn/Cr (34/33/33) Oxide		20-40M	4		350	30	2.5	1 / 0.1 / 2 N2
230	7887-90		2.0%Pd / Zn/Mn/Cr (34/33/33) Oxide		20-40M	3		350	30	3.3	1 / 0.1 / 2 N2
231	7887-90		2.0%Pd / Zn/Mn/Cr (34/33/33) Oxide		20-40M	2		350	30	5	1 / 0.1 / 2 N2
232	7887-90		2.0%Pd / Zn/Mn/Cr (34/33/33) Oxide		20-40M	1		350	30	10	1 / 0.1 / 2 N2
233	7887-94		2.0%Pt / ZnO + SiO2 (1/1)		20-40M	5		300	30	2	1 / 0.1 / 2 N2
234	7887-89		2.0%Pt / Zn/Mg (50/50) Oxide + SiO2 (1/1)		20-40M	5		300	30	2	1 / 0.1 / 2 N2
235	7887-96		2.0%Pt / MgO		20-40M	5		300	30	2	1 / 0.1 / 2 N2
236	7887-96		2.0%Pt / MgO		20-40M	5		350	30	2	1 / 0 1 / 2 N2
237	7887-98		2.0%Pd / MgO		20-40M	5		350	30	2	1 / 0.1 / 2 N2
238	7887-94		2.0%Pt / ZnO + SiO2 (1/1)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
239	7887-89		2.0%Pt / Zn/Mg (50/50) Oxide + SiO2 (1/1)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
240	8125-8		2.0%Cu / TiO2		20-40M	5		350	30	2	1 / 0.1 / 2 N2
241	8125-10		2.0%Mo / TiO2		20-40M	5		350	30	2	1 / 0.1 / 2 N2
242	8265-12		2.0%Mo / Polyvinylpyridine (PVP425)		20-40M	5		350	30	2	1 / 0 1 / 2 N2
243	8265-13		2.0%Cu / Polyvinylpyridine (PVP425)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
244	8265-16		2.0%Mo / Mg/Al MOSS (Alcoa)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
245	8265-18		2.0%Cu / Mg/Al MOSS (Alcoa)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
246	8265-14		2.0%Pd / Polyvinylpyridine (PVP425)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
247	8265-22		2.0%Pd / Zn/Mn/Zr (33/33/33) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
248	8265-24		2.0%Pd / Zn/Mn/Cr (33/33/33) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
249	8265-26		2.0%Pt / Zn/Mn/Cr (33/33/33) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
250	8265-32		2.0%Pd / Zn/Mn/Zr (33/33/33) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
251	8265-34		2.0%Pd / Zn/Mn/Zr (45/45/10) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
252	8265-36		2.0%Pt / Zn/Mn/Zr (45/45/10) Oxide		20-40M	5		350	30	2	1 / 0 1 / 2 N2
253	8265-38		2.0%Pd / NH2-Terminated Polysiloxane		20-40M	5		350	30	2	1 / 0.1 / 2 N2
254	8265-42		100% MnO2		20-40M	5		350	30	2	1 ' 0 1 / 2 N2
255	8265-44		100% MnO2		20-40M	5		350	30	2	1 ' 0 1 / 2 N2
256	8265-46		100% MnO2		20-40M	5		350	30	2	1 ' 0 1 / 2 N2
257	8265-48		100% MnO2		20-40M	5		350	30	2	1 ' 0 1 / 2 N2
258	8265-50		2.0%Pt / Zn/Mn/Zr (33/33/33) Oxide		20-40M	5		350	30	2	1 ' 0 1 / 2 N2
259	8265-52		250ppm Co / MnO2		20-40M	5		350	30	2	1 ' 0 1 / 2 N2
260	8265-36		2.0%Pt / Zn/Mn/Zr (45/45/10) Oxide		20-40M	5		350	30	2	1 0 1 / 2 N2

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_4OH	Sum C_{4+}	CO_x	iC_4OH	Sum C_{4+}
Zn/Mn/Zr (34/34/32)								
Precipitation 1 7923-64	198	51	99	8	41	37	62	328
Precipitation 2								
Impregnation 1 8265-22	247	45	97	7	38	48	52	273
Impregnation 2 8265-32	250	25	80	1	49	33	6	214
Zn/Mn/Cr (34/33/33)								
Precipitation 1								
Impregnation 1 7887-52	212	79	100	9	36	57	99	399
Impregnation 2 7887-90	228	87	100	5	26	67	65	305
Precipitation 2 8265-25	248	19	76	1	42	45	4	144

Conditions: 30 psig, 2 hr^{-1} MeOH WHSV, 1/0.1/2 MeOH/EtOH/N_2

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

Support Catalyst Number	Run	Conversion (%)		Selectivity (mole%)			Productivity (g/kg cat/hr)	
		MeOH	EtOH	iC_4OH	Sum C_{4+}	CO_x	iC_4OH	Sum C_{4+}
Zn/Mn/Zr (34/34/32)								
Precipitation 1 7887-48	211	47	99	14	49	44	102	373
Precipitation 2 8265-50	258	57	100	11	54	47	92	356
Zn/Mn/Zr (45/45/10) 8265-36	252	56	100	12	42	48	100	353
	260	64	100	10	41	50	96	379
Zn/Mn/Zr/K (34/34/32/6%) 7887-84	225	12	49	1	33	56	4	80
Zn/Mn/Cr (34/33/33)								
Precipitation 1 7887-62	216	51	90	2	18	75	17	102
Precipitation 2 8265-26	249	31	72	2	33	58	9	161
Zn/Mn/Ce (33/33/33) 7887-68	219	50	100	12	46	48	91	349
Zn/Mn/La (34/32/34) 7887-82	224	58	99	8	33	64	68	278

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Conditions: 30 psig, 2 hr^{-1} MeOH WHSV, 1/0.1/2 MeOH/EtOH/N_2

Table 4. Screening of 2% Pt on Single/Double Metal Oxide Catalysts

Support Catalyst Number	Run	Conversion (%)		Selectivity (mole%)			Productivity (g/kg cat/hr)	
		MeOH	EtOH	iC_4OH	Sum C_{4+}	CO_x	iC_4OH	Sum C_{4+}
ZnO / 10% SiO_2 Binder 7887-94	238	37	95	7	36	52	44	224
MnO_2 7887-80	222	36	83	2	14	77	9	63
ZrO_2 7887-86	227	46	53	0	2	85	0	13
Zn/Mg (50/50)/10% SiO_2 7887-89	239	71	100	6	25	70	65	250

Conditions: 30 psig, 2 hr^{-1} MeOH WHSV, 1/0.1/2 $MeOH/EtOH/N_2$

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Table 5. Screening of Other Potential Higher Alcohols Catalysts

Support	Catalyst Number	Run	Conversion (%)		Selectivity (mole%)			Productivity (g/kg cat/hr)	
			MeOH	EtOH	iC_4OH	Sum C_{4+}	CO_x	iC_4OH	Sum C_{4+}
MgO									
2% Pt	7887-96	236	100	100	0	0	91	0	0
2% Pd	7887-98	237			0	0	93	0	0
TiO_2									
2% Cu	8125-8	240	11	31	14	53	11	28	106
2% Mo	8125-10	241	38	77	2	27	11	9	121
Mg/Al MOSS									
2% Cu	8265-18	245	7	31	12	50	4	17	72
2% Mo	8265-16	244	14	34	8	24	11	19	56
Polyvinylpyridine									
2% Cu	8265-12	242	-1	11	0		0	0	
2% Mo	8254-13	243	3	-7	0		0	0	
2% Pd	8265-14	246	10	-3	0		0	0	

Conditions: 30 psig, 2 hr^{-1} MeOH WHSV, 1/0.1/2 MeOH/EtOH/N_2

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Table 6. Screening of Other Potential Higher Alcohols Catalysts

Catalyst Catalyst Number	Run	Conversion (%)		Selectivity (mole%)			Productivity (g/kg cat/hr)	
		MeOH	EtOH	iC_4OH	Sum C_{4+}	CO_x	iC_4OH	Sum C_{4+}
Commercial MnO_2								
Chemetals CIR-189 8265-42	254	7	6	3		8	2	
250ppm Co 8265-52	259	5	9	4		13	4	
Chemetals ODC-924 8265-44	255	7	-6	4		14	2	
Lab Prepared Mn Oxides								
Cryptomelane 8265-46	256	7	-7	3		21	2	
Pharmacosiderite 8265-48	257	6	-15	0		4	0	

[redacted]

Conditions: 30 psig, 2 hr^{-1} MeOH WHSV, 1/0.1/2 MeOH/EtOH/N_2

Figure 1.

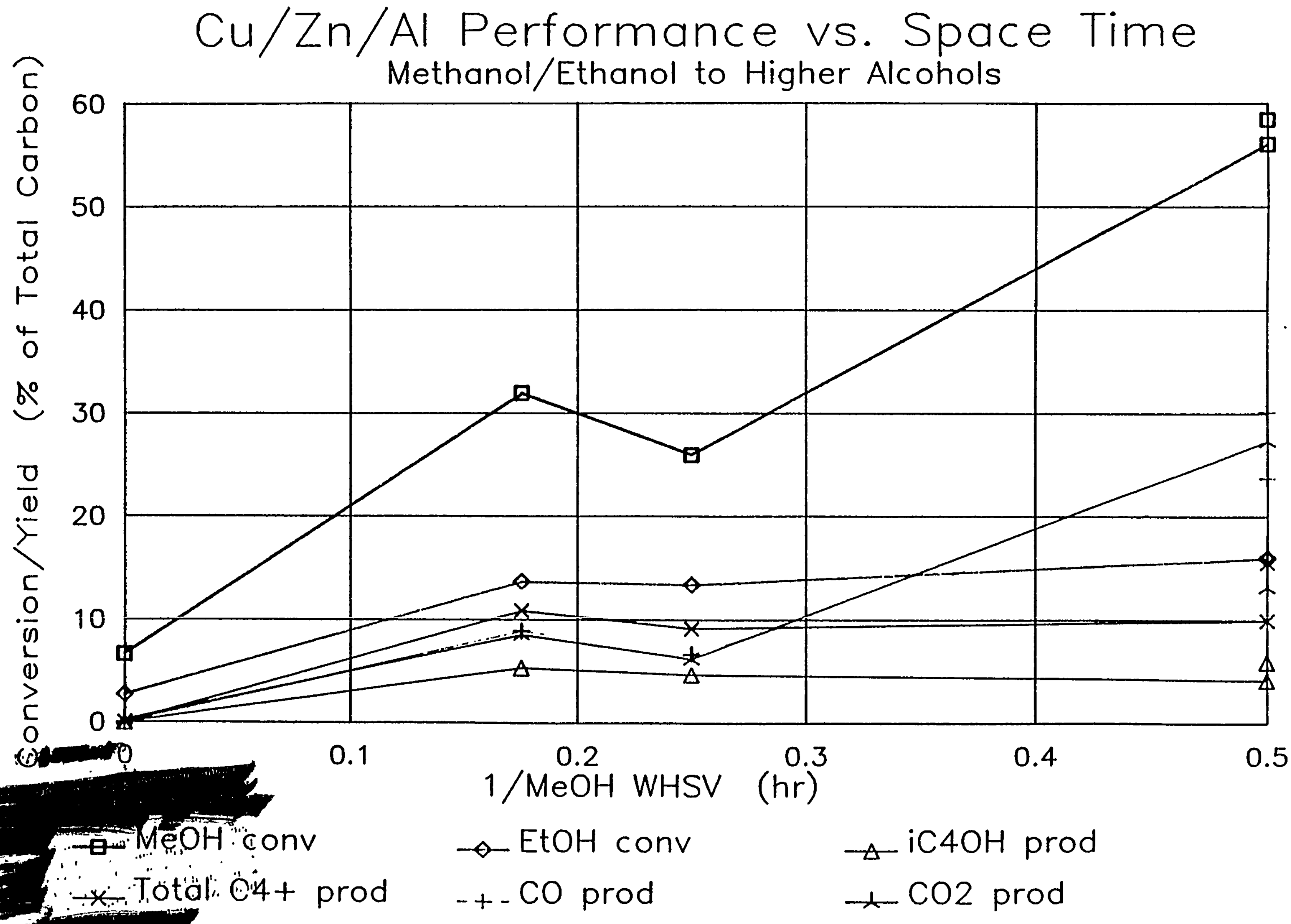
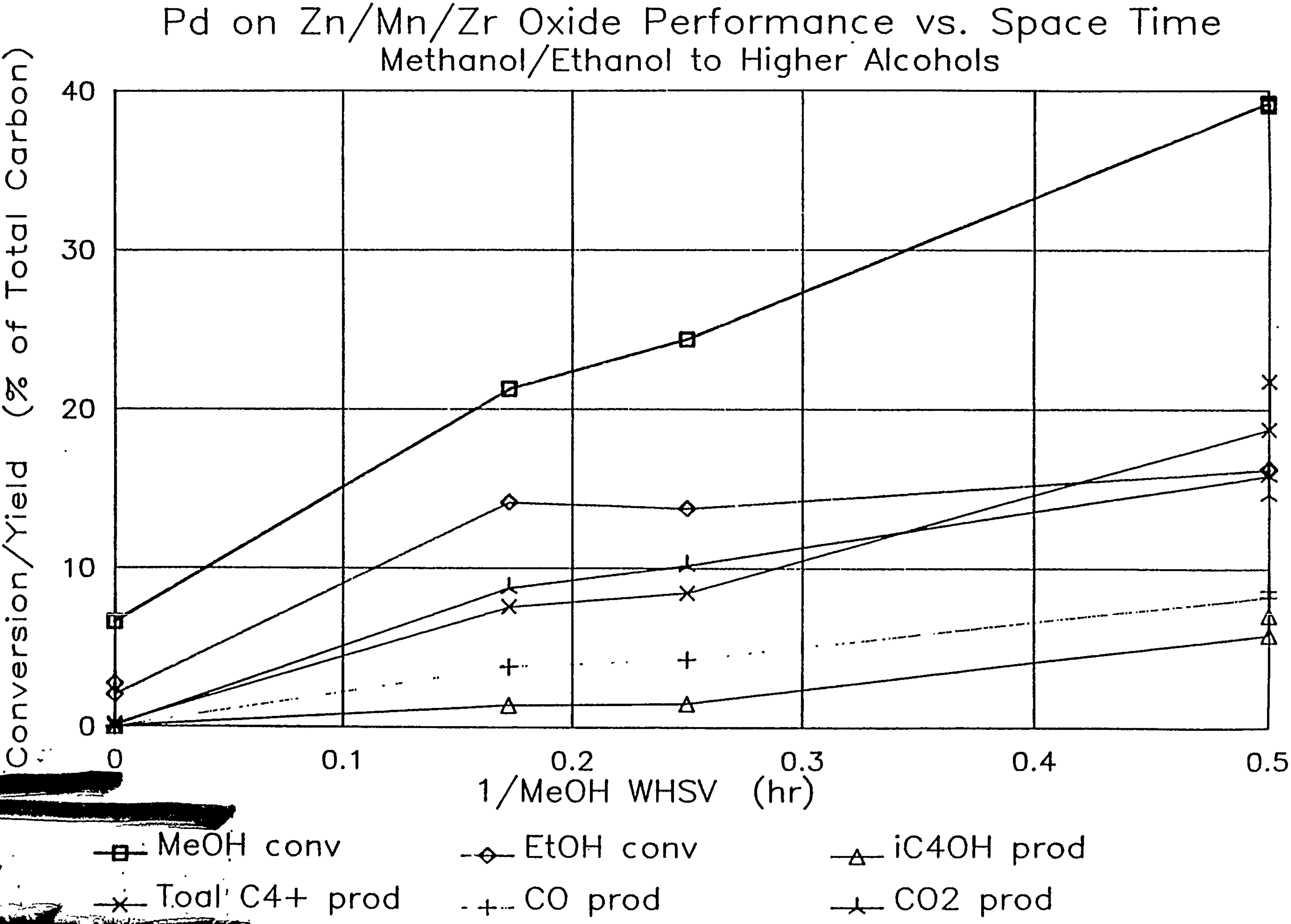
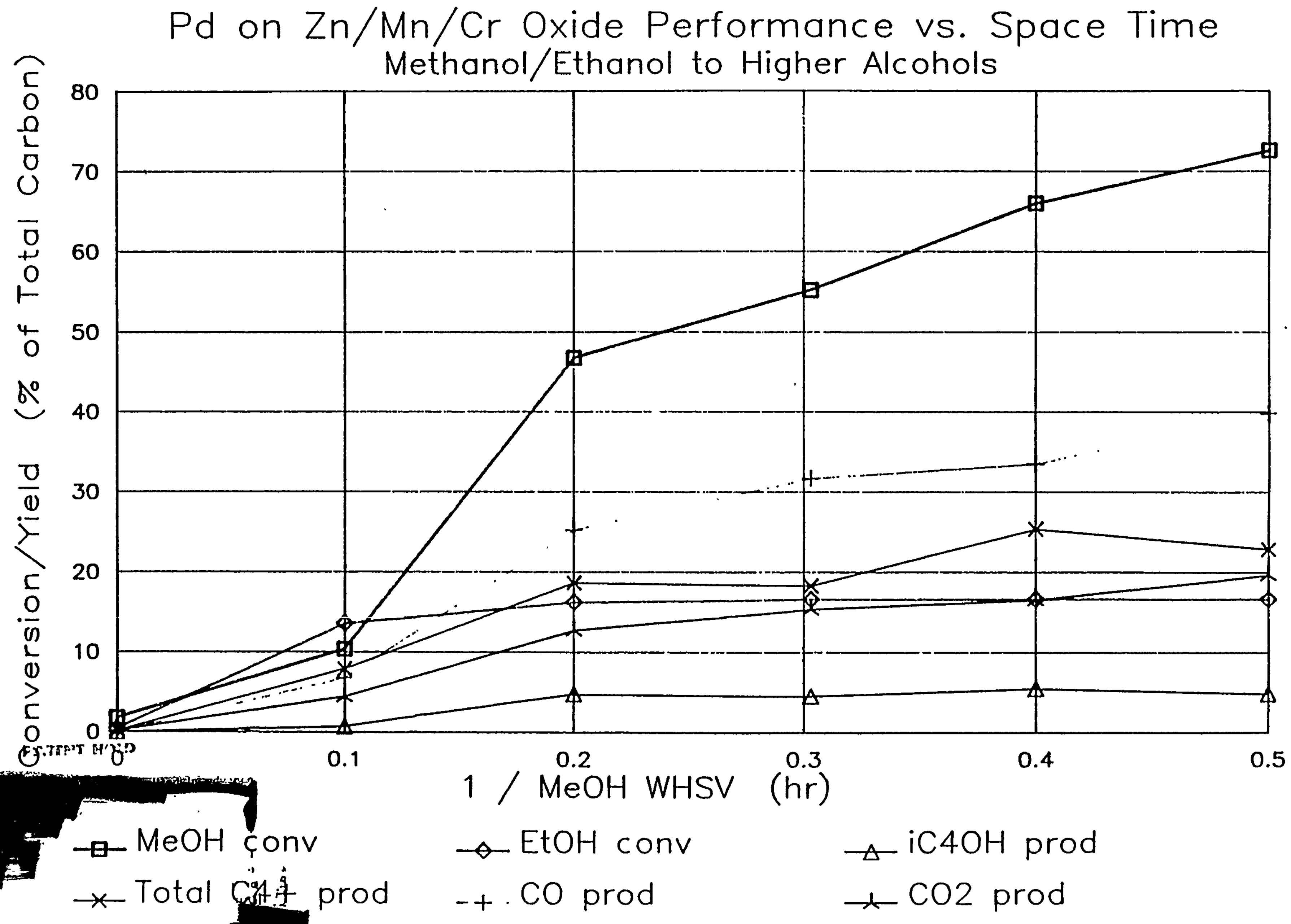

Cu/Zn/Al Performance vs. Space Time
Methanol/Ethanol to Higher Alcohols
Conversion/Yield (% of Total Carbon)
60
50
40
30
20
10
0
0
0.1
0.2
0.3
0.4
0.5
1/MeOH WHSV (hr)
MeOH conv
EtOH conv
iC4OH prod
Total C4+ prod
CO prod
CO2 prod

Figure 2.



[redacted]

Figure 3.


Pd on Zn/Mn/Cr Oxide Performance vs. Space Time
Methanol/Ethanol to Higher Alcohols
Conversion/Yield (% of Total Carbon)
80
70
60
50
40
30
20
10
0
0
0.1
0.2
0.3
0.4
0.5
1 / MeOH WHSV (hr)
MeOH conv
EtOH conv
iC4OH prod
Total C4+ prod
CO prod
CO2 prod