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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 pilot plant testing using a 10/1 methanol/ethanol feed blend to identify potential catalysts for the conversion of lower alcohols derived from synthesis gas to isobutanol and other C_{4+} oxygenates.

The previous work in this project found that a typical Cu/Zn/Al oxide methanol synthesis catalyst is capable of producing isobutanol and isobutryaldehyde from a feed consisting of a blend of methanol and ethanol[1]. Best performance was obtained at moderate temperature (300 °C) and low pressure (30 psig). This report describes the results of space velocity testing with this catalyst to elucidate the reaction pathway. It has been found that at high ethanol conversion levels (low space velocities), yields of isobutanol and other C_{4+} oxygenates do not increase with increasing methanol conversion. This suggests that Cu/Zn/Al oxide is not active for the condensation of methanol alone to higher alcohols. Therefore, new catalyst formulations are being evaluated for this reaction using the Cu/Zn/Al oxide performance as a baseline. Promising materials will also be examined at high ethanol conversion levels and with a methanol only feed to determine their capability to condense methanol.

Catalyst screening has focussed in two directions. Materials related to conventional methanol synthesis catalysts and Pd on a Zn/Mn/Zr oxide have been evaluated. The former materials have included a low Cu-content Cu/Zn/Al oxide, a Cu/Zn/Mn oxide and two Zn/Al oxides. The Cu containing materials are less active than the baseline Cu/Zn/Al catalyst, but give better selectivities and productivities to the desired products. However, comparison of the performances of these materials to that of the baseline catalyst at a lower temperature, where conversion is comparable, show similar productivies. The non-Cu containing samples have substantially lower activity and selectivity to the desired higher oxygenates.

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Catalysts consisting of Pd (0, 0.2, 2%) on a Zn/Mn/Zr oxide support have been found to be active for the conversion of methanol/ethanol to C_4 oxygenates. These catalysts, particularly with 2% Pd, have shown the best selectivities and productivies to date. Future work will pursue the use of this type of catalyst for this process, including effect of catalyst composition (support and metal function) and space velocity tests to probe the reaction pathway.

EXPERIMENTAL

Catalysts

Mixed metal oxide catalysts consisting of Cu/Zn/Al oxides (31/42/27 and 11/63/26 molar) were prepared by co-precipitating aqueous solutions of nitrate salts with sodium carbonate at 50 °C and pH 7. After extensive water washing, the precipitates were dried at 110 °C for 12 hours, sized to 20-40 mesh and calcined at 400 °C in air for 2 hours. Cu/Zn/Mn oxide (34/33/33 molar) and Zn/Al oxide (74/26 and 63/37 molar) catalysts were prepared by a similar co-precipitation method.

A Zr/Zn/Mn oxide (33/33/33 molar) support was prepared by co-precipitating an aqueous solution of nitrate salts with potassium hydroxide at 50 °C and pH 11[2]. The solid was washed with H_2O, dried at 127 °C for 15 hours, sized to 20-40 mesh and calcined at 327 °C in air for 3 hours. Samples of the Zr/Zn/Mn oxide were impregnated with an aqueous $PdCl_2$ solution and re-calcined at 400 °C to afford a final catalysts with 0.2 and 2.1 wt.% Pd.

Catalytic Testing Procedure

The pilot plant testing of catalysts for the conversion of 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 first N_2 purged 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 productitivies (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, as well as the methanol/ethanol runs using methanol synthesis type catalysts descibed in Quarterly Report 11[1], is given in Table 1.

RESULTS AND DISCUSSION

Reaction Pathway for Cu/Zn/Al Oxide Catalyst in the Conversion of Methanol/Ethanol to Isoalcohols

Previous work in this project identified conditions at which a conventional Cu/Zn/Al oxide methanol synthesis catalyst catalyzes the conversion of a methanol/ethanol feed to isobutanol and other C_4 oxygenates[1]. The best performance, in terms of selectivity and productivity, was obtained at 300 °C and 30 psig (Table 2). It was also found, using a different catalyst, that the condensation step is greatly favored by the use of low pressure. This suggests that aldehyde intermediates, formed by the dehydrogenation of the alcohols, may be important in this reaction.

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, C_1-$C_{2,3}$ and C_2-C_2 condensation steps. The aldol condensation between two C_2 species is expected to yield straight chain C_4 products. The fact that the observed C_4 oxygenate products are highly branched, even with ethanol in the feed, suggests that their formation occurs by sequential C_1 aldol condensations to C_2 and C_3 intermediates. This indicates that C_1-$C_{2,3}$ coupling is substantially favored over C_2-C_2 condensation. In view of the dehydrogenation equilibrium constants at 327 °C of 0.03 for methanol $\rightleftarrows$ formaldehyde + H_2 and 1.12 for ethanol $\rightleftarrows$ acetaldehyde + H_2, it appears that branched C_4s compounds are formed by the condensation of methanol with acetaldehyde and propionaldehyde.

In order to determine whether C_1-C_1 coupling occurs over the Cu/Zn/Al oxide catalyst, a series of low space velocity tests with high ethanol conversion have been conducted. The extent of C_1-C_1 coupling can be elucidated by comparing of the yields of isobutanol and total C_{4+} oxygenates at these conditions with the yields at lower ethanol conversions. Figures 1 and 2 show feed conversions and product yields versus 1/space velocity at 300 °C, 30 psig. At space times greater than 0.5 hr, ethanol conversion exceeds 90%, while methanol and total carbon conversions increase from about 70% to near 90%. However, Figure 2 shows that in this space time region isobutanol and total C_{4+} oxygenates yileds are essentially flat. Only CO yield shows an increase comparable to the total carbon conversion rise. This indicates that the additional conversion occurring in this portion of the catalyst bed is due to methanol reforming to CO rather than aldol condensation. Therefore, it appears that Cu/Zn/Al oxide material is a poor catalyst for the C_1-C_1 condensation required for the production of higher oxygenates from methanol alone. Based on these results, the research effort in this project has focussed on identifing alternative catalysts for this reaction. The performance of the Cu/Zn/Al oxide catalyst will be used as a baseline for judging the results obtained with new materials.

Screening of Catalysts for the Conversion of Methanol/Ethanol to Isoalcohols

Several mixed metal oxide compositions that are related to low temperature and high temperature methanol synthesis catalysts have been evaluated in the methanol/ethanol conversion screening test. The results of these runs are summarized in Table 2. Low Cu content Cu/Zn/Al oxide and Cu/Zn/Mn oxide catalysts are less active than the baseline catalyst, but have superior selectivity and productivity to the desired C_4 oxygenates at 350 °C. However, comparison of the performances of these materials with that of the baseline catalyst at 300 °C, where conversions are comparable, show similar productivies. It is also unlikely that these materials would be significantly more active for the C_1-C_1 coupling needed for methanol only conversion than the baseline catalyst. Zn/Cr and Zn/Al mixed metal oxide materials, based on high temperature methanol synthesis catalysts, show substantially lower activity and productivity of the desired higher alcohol products.

Catalysts consisting of Pd impregnated on a Zn/Mn/Zr mixed metal oxide prepared by co-precipitation of metal nitrates with KOH have been described has having high selectivity for isobutanol from synthesis gas[2]. However, severe conditions (high temperatures and very high pressures) are required to achieve attractive conversion levels. One interpretation of these results is that this catalyst is active for the condensation of light alcohols to higher alcohols with high selectivity to isobutanol, but requires severe conditions for CO hydrogenation. If this is the case, these materials would be promising catalysts for a methanol to higher alcohols process. Therefore, we have evaluated a representative material, with and without noble metal, in the methanol/ethanol screening test. Table 3 summarizes the testing results obtained with a Zn/Mn/Zr metal oxide with 0, 0.2 and 2 wt.% Pd added by impregnation with a $PdCl_2$ solution. These materials show lower activity than the baseline catalyst, but significantly higher selectivity to isobutanol, isobutraldehyde and total C_{4+} oxygenates. In spite of the lower conversions, the Pd containing catalyst give higher productivities to the desired products than the baseline catalyst. In fact, the productivities observed with the 2% Pd catalyst are the highest obtained to date in this program. Future work will pursue the use of this type of catalyst for this process, including effect of catalyst composition (support and metal function) and space velocity tests to probe the reaction pathway.

CONCLUSIONS

Space velocity testing has been used to show that the reaction pathway for condensation of a methanol/ethanol feed blend to higher alcohols over typical Cu/Zn/Al oxide methanol synthesis catalyst proceeds primarily through C_1-$C_{2,3}$ coupling with little C_1-C_1 coupling. This suggests that Cu/Zn/Al oxide would not be active for the condensation of methanol alone to higher alcohols. Therefore, new catalyst formulations are being evaluated for this reaction using the Cu/Zn/Al oxide performance as a baseline. Promising materials will also be examined at high ethanol conversion levels and with a methanol only feed to determine their capability to condense methanol.

Materials related to conventional methanol synthesis catalysts and Pd on a Zn/Mn/Zr oxide have been evaluated for the conversion of methanol/ethanol to isobutanol. The former materials have shown performances either comparable or inferior to the baseline Cu/Zn/Al oxide catalyst. Catalysts consisting of Pd (0, 0.2, 2%) on a Zn/Mn/Zr oxide support have been found to be active for the conversion of methanol/ethanol to C_4 oxygenates. The 2% Pd sample has given the best selectivities and productivies to date. Future work will pursue the use of this type of catalyst for this process, including effect of catalyst composition (support and metal function) and space velocity tests to probe the reaction pathway.

REFERENCES

1) P. T. Barger, DOE Quarterly Report No. 11, (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 A Book #	CATALYST B Book #	CATALYST DESCRIPTION CATALYST A	CATALYST DESCRIPTION CATALYST B	SIZE	LOADING g	TEMP (C) INLET	TEMP (C) MAX	CONDITIONS TOTAL PSIG	CONDITIONS MeOH WHSV	FEED RATIO MeOH/EtOH/Inert
176	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
177	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)		20-40M	5		300	30	2	1 / 0.1 / 2 N2
178	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)		20-40M	5		250	30	2	1 / 0.1 / 2 N2
179	7923-16A		Zn/Cr (75/25) Oxide (Lab PPT)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
180	7923-69		Cu/Zn/Mn (34/33/33) Oxide (Lab PPT)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
181	7887-37		Zn/Al (74/26) Oxide (Lab PPT)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
182	7887-39		Cu/Zn/Al (11/63/26) Oxide (Lab PPT)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
183	7887-41		Zn/Al (63/37) Oxide (Lab PPT)		20-40M	5		350	30	2	1 / 0.1 / 2 N2
184	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)		20-40M	10		250	30	1	1 / 0.1 / 2 N2
185	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)		20-40M	5		250	75	2	1 / 0.1 / 2 N2
186	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)		20-40M	2.5		300	30	4	1 / 0.1 / 2 N2
187	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)		20-40M	10		300	30	1	1 / 0.1 / 2 N2
188	7923-55		Zr/Zn/Mn (34/34/32) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
189	7923-62		0.2%Pd / Zn/Mn/Zr (34/34/32) Oxide		20-40M	5		350	30	2	1 / 0.1 / 2 N2
190	7923-64		2.1%Pd / Zn/Mn/Zr (34/34/32) Oxide		20-40M	5		350	30	2	1 / 0 1 / 2 N2
191	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)		20-40M	5		300	30	2	1 / 0.1 / 2 N2
192	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)		20-40M	1.75		300	30	5.7	1 / 0.1 / 2 N2

Table 2. Evaluation of Methanol Synthesis Type Catalysts

Run	176	177	179	182	180	181	183
Catalyst	Cu/Zn/Al Oxide (31/42/27)		Zn/Cr Oxide (75/25)	Cu/Zn/Al Oxide (11/63/26)	Cu/Zn/Mn Oxide (34/33/33)	Zn/Al Oxide (74/26)	Zn/Al Oxide (63/37)
Temperature (°C)	350	300	350	350	350	350	350
Conversion (%)							
MeOH	97.6	67.3	14.9	62.3	50.8	15.5	17.7
EtOH	99.2	95.9	31.5	97.9	88.8	72.8	81.2
Selectivities (mole%)							
iC_4OH	2.0	5.8	2.8	7.5	5.5	1.1	2.0
iC_4 Ald	2.2	2.3	0.4	6.0	7.2	0.2	0.2
Total C_{4+} Oxy	5.9	12.7	6.2	21.4	14.6	9.8	8.9
CO	45.5	33.0	7.5	28.9	19.4	1.8	2.0
CO_2	40.8	37.9	30.4	31.7	42.0	16.2	18.4
Productivities (mole/kg cat/hr)							
iC_4OH	1.4	3.0	0.7	3.7	2.3	0.2	0.4
Total C_{4+} Oxy	4.1	6.6	1.5	8.1	6.0	1.8	1.8

[redacted]

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

Table 3. Evaluation of Pd on Zn/Mn/Zr Oxide Catalysts

Run	176	177	188	189	190
Catalyst	Cu/Zn/Al Oxide (31/42/27)		Zn/Mn/Zr Oxide (34/34/32)	0.2%Pd on Zn/Mn/Zr Oxide (34/34/32)	2.1%Pd on Zn/Mn/Zr Oxide (34/34/32)
Temperature (°C)	350	300	350	350	350
Conversion (%)					
MeOH	97.6	67.3	8.6	30.3	47.9
EtOH	99.2	95.9	49.5	87.5	97.4
Selectivities (mole%)					
iC_4OH	2.0	5.8	12.9	7.6	10.3
iC_4 Ald	2.2	2.3	0.2	7.4	10.4
Total C_{4+} Oxy	5.9	12.7	18.1	20.8	25.0
CO	45.5	33.0	0.0	9.1	14.7
CO_2	40.8	37.9	14.3	26.0	28.2
Productivities (mole/kg cat/hr)					
iC_4OH	1.4	3.0	0.7	2.2	4.3
Total C_{4+} Oxy	4.1	6.6	1.5	6.0	10.4

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

Figure 1.

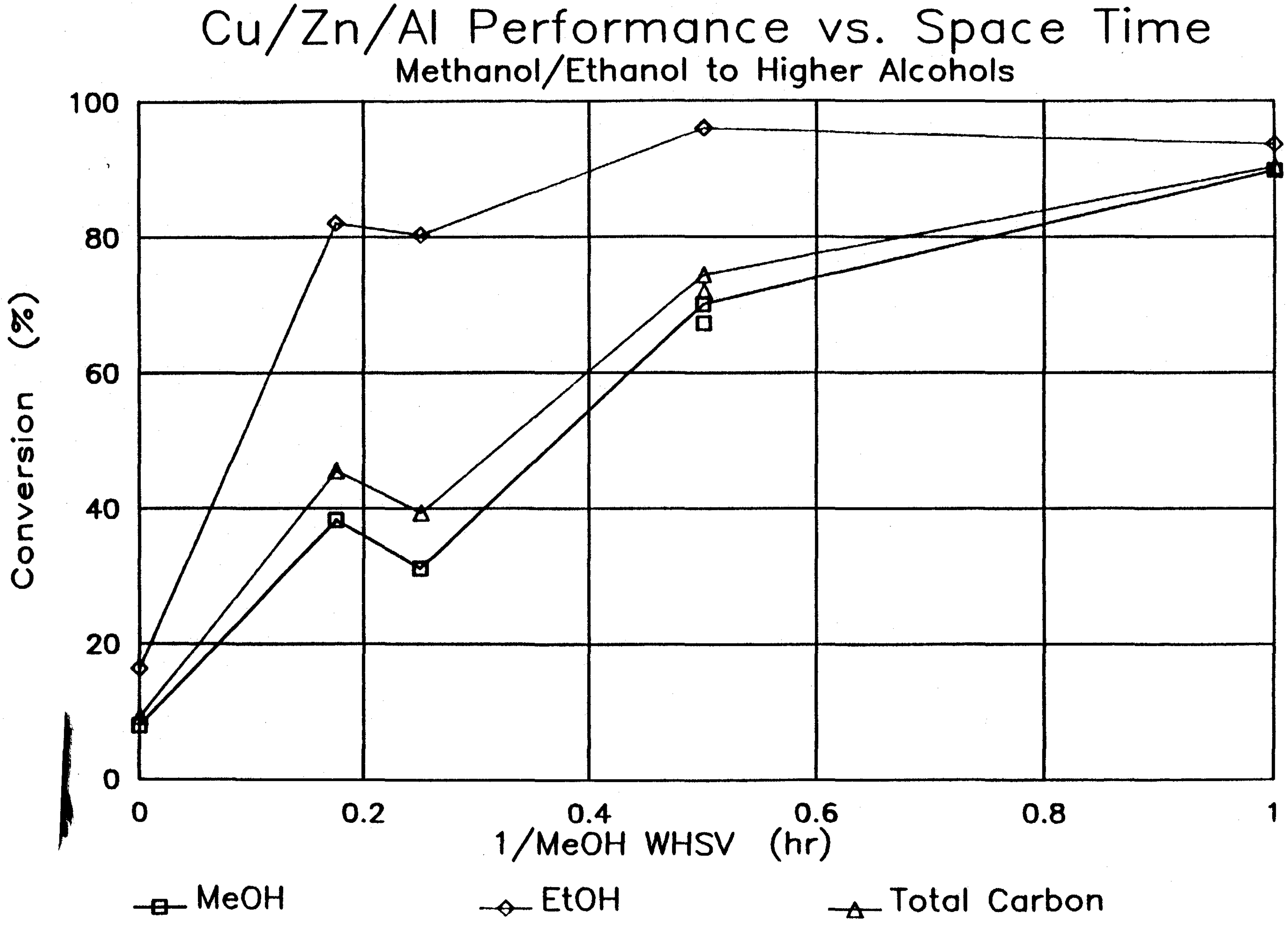
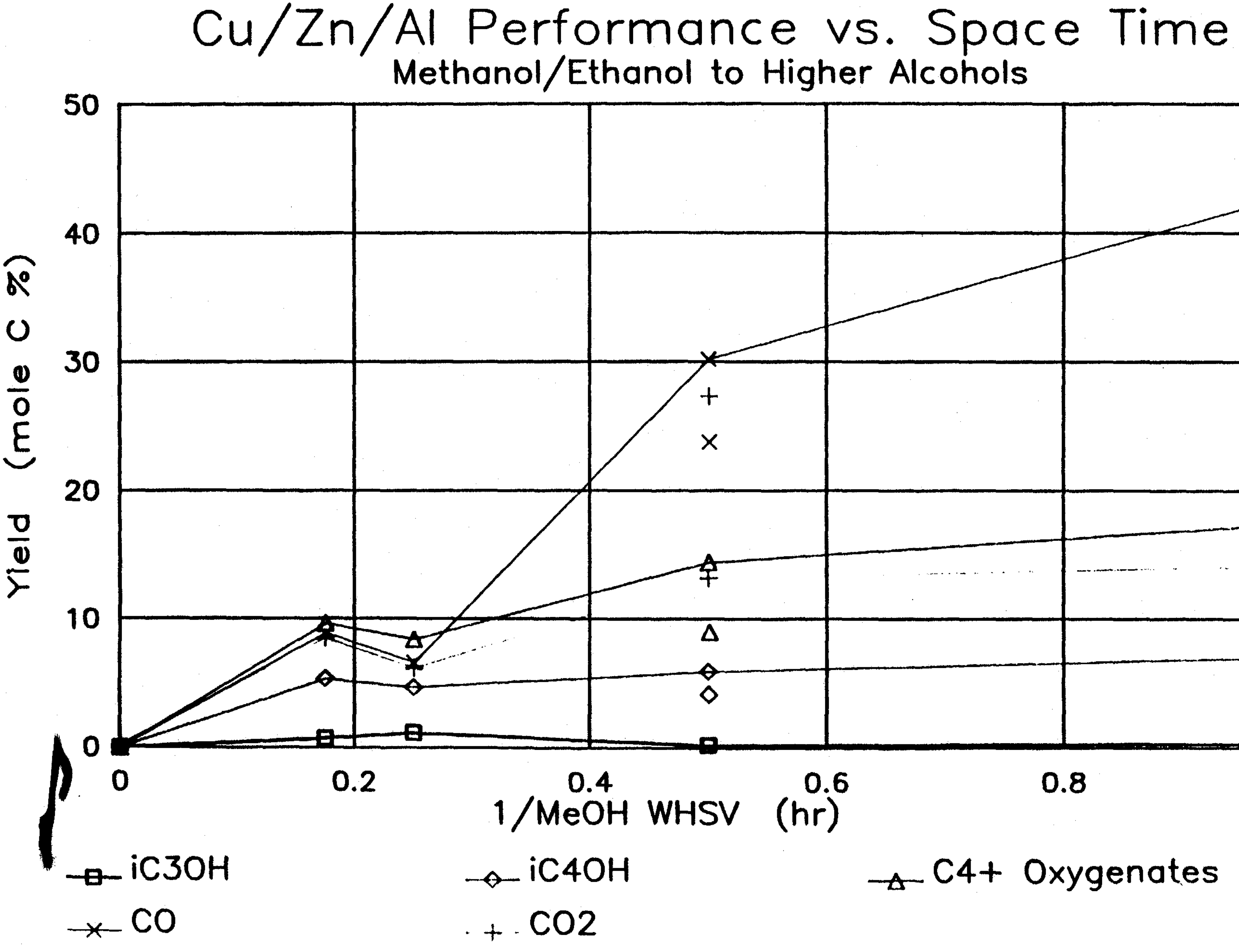

Cu/Zn/Al Performance vs. Space Time
Methanol/Ethanol to Higher Alcohols
Conversion (%)
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1
1/MeOH WHSV (hr)
MeOH
EtOH
Total Carbon

Figure 2.


Cu/Zn/Al Performance vs. Space Time
Methanol/Ethanol to Higher Alcohols
Yield (mole C %)
50
40
30
20
10
0
0
0.2
0.4
0.6
0.8
1
1/MeOH WHSV (hr)
iC3OH
iC4OH
C4+ Oxygenates
CO
CO2